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# ESR study on gold atoms produced in γ-irradiated MTHF and 10 M NaOH aqueous solutions containing $Au^+$ ions at 77 K

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## Abstract

MTHF and 10 M NaOH aqueous solutions containing $Au^+$ ions were γ-irradiated at 77 K. ESR measurements at 73 K revealed the production and trapping of $Au^0$ atoms in the solid solutions. This is the first ESR report of $Au^0$ atoms which are produced radiation–chemically by reducing $Au^+$ ions. The $g_J$ and hyperfine splitting values of $Au^0$ atoms were determined.

## 1. Introduction

The 1B metal atoms ($M^0$) are produced by radiation–chemical conversion from $M^+$ ions in solid solutions by the following reactions:

$$S \rightsquigarrow S^+ + e^- \quad (1)$$

$$e^- + M^+ \rightarrow M^0 \quad (2)$$

where S and $e^-$ stand for solvent molecules and mobile electrons, respectively, the latter being generated by ionization of solvent molecules. The metal atoms thus produced are not free atoms, but are perturbed in some degree by their environments. The nature of the atoms which are produced by this method and trapped in solid solutions is also expected to be different from that in rare-gas matrixes.

In fact, a variety of experimental studies have been carried out for silver ($Ag^0$) atoms, which are produced radiation–chemically by reducing $Ag^+$ ions in aqueous and organic solid solutions at low temperatures, by means of optical absorption [1,2], ESR [3–5] and fluorescence lifetime measurements [6,7]. These studies elucidated the structure of trapping sites of $Ag^0$ atoms and the formation mechanism of complexes between $Ag^+$ ions and ligand molecules in the solid solutions.

ESR studies were previously reported for gold ($Au^0$) atoms trapped in several polar and non-polar solids [8] and solid rare-gas matrixes [9] by simultaneous condensation at 77 K of gold and solvent vapor. It has long been considered that spectroscopic studies of $Au^0$ atoms produced in a variety of aqueous and non-aqueous solid solutions would give further information on the nature in common and peculiar to 1B metal atoms as for the structure of

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trapping sites and interaction with their environments such as ligand molecules and $Au^+$ atoms in solid solutions, if they could be successfully produced by the radiation–chemical method at low temperatures. However, such comparative studies have been unsuccessful because of the instability and the insolubility of $Au^+$ monovalent compounds in many aqueous and non-aqueous solvents.

In this study, we used two sets of solute–solvent combination: $AuClP(C_2H_5)_3$ in 2-methyltetrahydrofuran (MTHF) and AuCN in 10 M NaOH and have successfully produced $Au^0$ atoms radiation–chemically in these solid solutions at 77 K. ESR characteristics of $Au^0$ atoms in the solid solutions are obtained and are compared with those of $Au^0$ atoms which were produced by the condensation method [8]. This pioneer study will initiate a variety of experimental and theoretical studies of $Au^0$ atoms in the solid solutions hereafter.

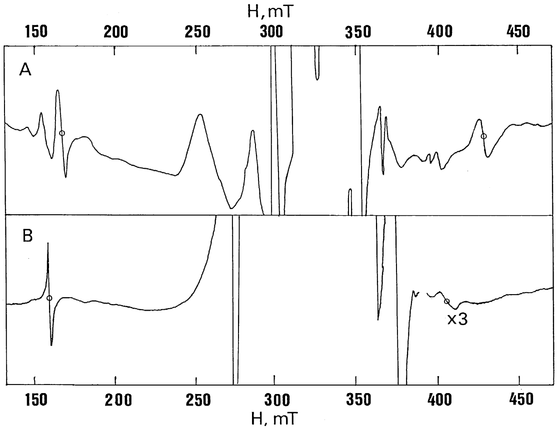

Fig. 1. ESR spectra of $Au^0$ atoms produced radiation–chemically in MTHF (A) and 10 M NaOH aqueous (B) solutions containing $AuClP(C_2H_5)_3$ and AuCN, respectively. The solute concentration was $2\times10^{-2}$ M. The γ-irradiation was carried out at 77 K and the dose was typically 60 kGy. ESR measurements were done at 73 K.

## 2. Experimental

$AuClP(C_2H_5)_3$ of the purity claimed to be more than 97% and the reagent grade AuCN and NaOH were used. Reagent grade MTHF was distilled fractionally and then dried over Na and K alloy. The concentration of both $AuClP(C_2H_5)_3$ in MTHF and AuCN in 10 M NaOH was $2\times10^{-2}$ M. The solutions were first bubbled by $N_2$ gas for a few minutes and transferred into ESR tubes and then cooled to 77 K by immersing them into liquid nitrogen.. The γ-irradiation of the frozen samples was carried out at the dose rate of 30 kGy $h^{-1}$ at 77 K. The total dose was typically 60 kGy for each sample. X-band ESR measurements were carried out at 73 K by bubbling helium gas into liquid nitrogen in an ESR Dewar to avoid bubbling from liquid nitrogen.

## 3. Results and discussion

The ESR spectra of the irradiated MTHF and 10 M NaOH aqueous solutions are shown in Fig. 1(A) and (B), respectively. In each spectrum, two separate lines were observed at low-($H_1$) and high-($H_2$) magnetic fields. The values of ($H_1$, $H_2$) in the units of mT are (165.2, 433.2) for MTHF and (157.9, 406.8) for 10 M NaOH aqueous solutions. The values of the magnetic field, mutual spacing of these lines are similar to those of the corresponding two lines out of four lines due to $Au^0$ atoms which are produced by the condensation method in various matrixes [8,9]. Thus we conclude that $Au^+$ ions are reduced by γ-radiolysis of the solid solutions to be converted to $Au^0$ atoms and trapped in the matrixes at 77 K. The observed lines at $H_1$ and $H_2$ are attributed to the ESR transitions ($F=1,\ m=1 \leftrightarrow F=2,\ m=2$) and ($F=2,\ m=-2 \leftrightarrow F=2,\ m=-1$) of $Au^0$ atoms, respectively, where $m$ is the magnetic quantum number of the total moment of $Au^0$ atoms $\mathbf{F}=\mathbf{J}+\mathbf{I}$ in which $\mathbf{J}$ and $\mathbf{I}$ are, respectively, the electronic and nuclear angular momenta. The alternative interpretation of the spectra is possible, if the hyperfine splitting is larger than the spectrometer frequency [8,9]: The line at $H=H_1$ is the ‘NMR’ transition ($F=1,\ m=-1 \leftrightarrow F=2,\ m=-2$) and the line at $H=H_2$ is the ESR transition ($F=2,\ m=-2 \leftrightarrow F=2,\ m=-1$) [8,9]. However, we ascribe the two lines observed at $H_1$ and $H_2$ to the ESR transitions, since the calculated hyperfine splitting values are always lower than the working frequency (see Table 1). The ESR lines at $H_1$ and $H_2$ are accompanied by satellite lines which are more clearly resolved in MTHF than

Table 1
Comparison of the values of $a$ and $g_J$ of $Au^0$ atoms which are radiation–chemically produced in this study (a) with those for the condensation method reported by Zhitnikov et al. (b). The set of transitions ($F=1,\ m=1 \leftrightarrow F=2,\ m=2$) and ($F=2,\ m=-2 \leftrightarrow F=2,\ m=-1$) was used for the calculation of $a$ and $g_J$ values by using the Breit–Rabi equation in this study.

| Matrix | $a$ (MHz) | $\delta(a)/a_{\mathrm{free}}$ (%) | $g_J$ |
|---|---|---|---|
| MTHF [a] | $5025.3 \pm 6.5$ | $-17.7$ | $2.107 \pm 0.001$ |
| 10 M-NaOH [a] | $5144.7 \pm 4.0$ | $-15.8$ | $2.257 \pm 0.002$ |
| $C_{11}H_{24}$ [b] | $5909.0 \pm 5.7$ | $-3.24$ | $2.00422 \pm 0.00060$ |
| $H_2O$ [b] | $6105.6 \pm 3.2$ | $-0.02$ | $2.00306 \pm 0.00015$ |
| $C_2H_5OH$ [b] | $4146.7 \pm 13.1$ | $-32.1$ | $2.07150 \pm 0.00100$ |
| Free [b] | $6107.1 \pm 1.0$ |  | $2.00412 \pm 0.00012$ |

[a] This work.
[b] Ref. [8].

10 M NaOH aqueous solution. It is plausible that the satellites are due to $Au^0$ atoms trapped in an environment different from that of a majority of $Au^0$ atoms. However, this should be further clarified.

It seems that the line observed at H = 264 mT for MTHF solution includes the third line due to the transition ($F=1,\ m=0 \leftrightarrow F=2,\ m=1$) of $Au^0$ atoms, although its linewidth is more broadened than expected. The corresponding line was not distinguished for 10 M NaOH aqueous solution according to the large signal due to radicals of the solution. The fourth line due to the transition ($F=1,\ m=-1 \leftrightarrow F=2,\ m=0$) is expected to appear at around 340 mT, but the signal due to radicals of the solutions is too intense for the $Au^0$ line in this magnetic field region to be distinguished.

From the Breit–Rabi relation [10], the following equations are derived for the ESR transitions at $H = H_1$ and $H_2$:

$$\nu_1 = a\left\{\tfrac{1}{2}\left(1+x_1+x_1^2\right)^{\frac{1}{2}}+\tfrac{1}{2}\left(1+x_1\right)\right\}+\frac{g_I\beta H_1}{h}, \tag{3}$$

$$\nu_2 = a\left\{\tfrac{1}{2}\left(1-x_2+x_2^2\right)^{\frac{1}{2}}-\tfrac{1}{2}\left(1-x_2\right)\right\}+\frac{g_I\beta H_2}{h}, \tag{4}$$

where $x_i = \dfrac{(g_J - g_I)\beta H_i}{ha}$ for $i = 1, 2$ and $a$ is the hyperfine splitting value. The values of $a$ and $g_J$ are numerically obtained by substituting experimental values of $\nu_i$ and $H_i$ in Eq. (3) and Eq. (4). The least squares fitting calculation was used and the values of $a$ and $g_J$ thus obtained are listed in Table 1 together with the values of Zhitnikov et al. [8] The relative shifts of the values of $a$, i.e. $\delta(a)/a_{\mathrm{free}}$ where $\delta(a) = a - a_{\mathrm{free}}$ are also listed in Table 1.

It is seen from Table 1 that the values of $a$ and $g_J$ derived from the transitions ($F=1,\ m=1 \leftrightarrow F=2,\ m=2$) and ($F=2,\ m=-2 \leftrightarrow F=2,\ m=-1$) in this study are rather closer to those reported for $C_2H_5OH$ than other matrixes. The large negative shifts of $a$ were observed for MTHF and 10 M NaOH aqueous solutions in this study. The present results indicate that the electronic delocalization onto ligand molecules amounts to ca 16% for both solid solutions and that the Van der Waals type interaction between $Au^0$ atoms and ligand molecules is dominant.

As shown in Table 1, the values of $g_J$ for MTHF and 10 M NaOH aqueous solutions are much larger than that of the free $Au^0$ atoms, that is, the sign of the deviation from the $g_J$ value of the free atom, $\Delta g_J$, is positive. The same is true for $Au^0$ atoms condensed in $C_2H_5OH$ matrix in which $\Delta g_J$ of silver atoms is negative on the contrary [8]. When the wavefunction of a $Au^0$ atom in its $^2S_{1/2}$ state is admixed into the $p$ orbitals of the ligand molecules, a strong spin–orbit interaction is caused so that a shift of $g_J$ occurs. In this case $\Delta g_J$ becomes negative [11]. Now it should be kept in mind that the values of $a$ and $g_J$ for $Au^0$ atoms in this study as well as those reported [8,9] were calculated from the

Table 2
Comparison of the values of the linewidths (in mT) of $Au^0$ atoms, which are radiation–chemically produced in this study (a) with those for the condensation method reported by Zhitnikov et al. (b).

| Matrix | Transition | | | |
|---|---|---|---|---|
| | (1, 1 ↔ 2, 2) | (1, 0 ↔ 2, 1) | (1, -1 ↔ 2, 0) | (2, -2 ↔ 2, -1) |
| MTHF [a] | 4.5 | – | – | 6.8 |
| 10 M-NaOH [a] | 2.0 | – | – | 9.1 |
| $C_{11}H_{24}$ [b] | 4.6 | 3.9 | 2.1 | 3.0 |
| $H_2O$ [b] | 2.7 | 2.1 | 1.1 | 1.5 |
| $C_2H_5OH$ [b] | 7.1 | 4.1 | 2.8 | 7.3 |

[a] This work.
[b] Ref. [8].

Breit–Rabi equation that is valid for the case of isotropic forces of interaction of the atom with the surrounding ligand molecules. The applicability of the equation could be tested by comparing the values of $a$ and $g_J$ calculated from various pairs of lines of a given ESR spectrum. In this context, we cannot assess the validity in this study, because each ESR spectrum shows only the single reliable pair of lines. Let it suffice to say that the positive shift of $\Delta g_J$ observed for MTHF and 10 M NaOH aqueous solutions in this study together with the result for $C_2H_5OH$ by Zhitnikov is now not rare and that it may be necessary to add an anisotropic interaction term to the Breit–Rabi equation for such cases as the atoms trapped in some aqueous and non-aqueous, organic solutions.

It is seen in Table 2 that the linewidth at the high field is broader than that at the low field both for MTHF and 10 M NaOH aqueous solutions. This is in a similar fashion to the result for $C_2H_5OH$, but is in the sharp contrast to the observation in $C_{11}H_{24}$ and $H_2O$ matrixes. As inferred by Zhitnikov et al. [8], the linewidth may be determined by the inhomogeneity and anisotropy of the interaction of $Au^0$ atoms with the matrix molecules. However, there is as yet no satisfactory explanation of the discrepancies of line broadening observed between various matrixes.

The line broadening mechanism and the cause of the positive shift of $\Delta g_J$ must be elucidated hereafter for the organic matrixes of different physicochemical properties. In order to shed light also on the solvation and desolvation mechanism of $Au^+$ ions and $Au^0$ atoms and the interaction between the atoms and the ions and/or solvent molecules, further studies are in progress by means of optical absorption and fluorescence spectroscopies as well as ESR measurements.

## 4. Conclusion

The present work provides ESR characteristics of $Au^0$ atoms produced radiation–chemically in MTHF and 10 M NaOH aqueous solutions at 77 K. The hyperfine splittings showed the negative shifts, indicating that the Van der Waals interaction of the atoms with environments is dominant. The positive value of $\Delta g_J$ obtained for the solutions may bring in the necessity of adding anisotropic term to the Breit–Rabi equation for the atoms trapped in specified matrixes. The ESR lines of $Au^0$ atoms in the solid solutions investigated are broadened in the same fashion as that for ethanol, but different from undecane and water. The nature of the inhomogeneity and anisotropy of the interaction of $Au^0$ atoms with the environment must be further investigated.

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