Tunneling spectroscopy of single electron spin

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The possibility of detection of the electron spin of a single paramagnetic species (an atom, a radical, or an ion) on the surface was discussed. The analysis was based on spin chemistry laws taking into account the statistics of the spin states of both the tunneling electron and paramagnetic center. The equations for the tunneling current as a function of temperature and magnetic fied strength were derived.

Key words: tunneling spectroscopy, electron spin resonance, spin.

A series of recent studies[1–3] promoted the transformation of tunneling microscopy from a "topographic" method used to scan the atom-molecular relief of the surface into the tunneling vibrational spectroscopy of single atoms and molecules. This new method of chemical physics makes it possible to detect the spectroscopical "image" of a single molecule, to identify it, and to trace its "destiny" (including chemical transformations). The last mentioned circumstance is a major breakthrough in modern chemistry, since the possibility of observing chemical transformations of a single reliably identified molecule appears for the first time, whereas the classical chemistry (even in its best version, *viz.*, the method of molecular beams) deals with molecular ensembles.

In fact, a new strategy of studying the physics of chemical processes on the surface arises with the discovery of the spectroscopy of single molecules. It includes the preparation of atoms or atomic clusters at specified points of the surface and/or on specified elements of the crystal lattice (faces, edges, terraces, *etc.*), the "landing" (adsorption) of a particular molecule at a given point, identification of the adsorpted molecule by its spectrum, and, finally, a time (dynamical) monitoring of chemical behavior of the molecule (in this case the term "molecule" implies any chemical species).

In the framework of such a strategy the problem of detecting a single chemical species which carries an electron spin (an atom, a radical, or a paramagnetic ion) can also be posed. Among characteristic indications of such a paramagnetic species are the presence of the electron spin and Zeeman electron levels in the magnetic field, which makes it possible to use the well-known ESR method for its study. In other words, the problem of detecting the ESR signal of a single electron spin or a single paramagnetic species (we will call it the single spin electron spin resonance, or SS ESR) is posed. The solution of this problem is the subject of this work.

Physical background of SS ESR

To observe the SS ESR, it is necessary that the tunneling electron be able to distinguish (discriminate) two spin states of the unpaired electron with $S_z = \pm 1/2$. There are two parameters suitable for performing such a discrimination, *viz.*, energy and spin. The Zeeman frequency of the unpaired electron is equal to $\sim 10^{10}$ Hz (in typical fields $H \approx 3000$ G), and the corresponding energy is $\sim 10^{-4}$ eV, which is 4—5 orders of magnitude less than the energy of the tunneling electron and 3 orders of magnitude less than the resolution of tunneling spectroscopy (~0.05 eV). Hence, it is impossible to use energy as a parameter for discriminating the Zeeman levels of the unpaired electron and, therefore, the other parameter, *viz.*, spin, should be used. This means that the principles of detecting the SS ESR must be based on the spin chemistry laws, since the tunneling probability is dependent on the spin orientation.

Let us consider from this viewpoint the spin states and spin dynamics of two electron spins, the spin of a paramagnetic (probed) center and that of a tunneling (probing) electron. This two-spin system (in the spin chemistry, it is a spin analog of the radical pair) can be in two states, *viz.*, in a singlet state with the total spin $S = 0$ or in a the triplet state with the total spin $S = 1$.

As is known,[4] the amplitude of scattering of the electron by a paramagnetic center (PMC) is strongly dependent on the total spin of the electron+PMC system. This dependence is due to the different magnitude of the exchange interaction between the incident electron and the electronic system of PMC for different spin multiplicities of the combined system. In other words, a change in the tunneling barrier (and, hence, in the "tunneling" exponent) is affected by the multiplicity of the combined system, *i.e.*, the tunneling current is dependent on the spin of this system.

The electron scattering by PMC is an analog of the reaction in a radical pair.[5] However, in contrast to the radical pair, the total spin of the combined system

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electron+PMC did not change in the scattering time. In addition, scattering occurs in both the triplet and singlet states of the combined system (though with different amplitudes), whereas the chemical reaction in the radical pair occurs only between species in singlet states. Hence the detection of the SS ESR must be based on the spin statistics of a two-electron system, *i.e.*, on the ratio of the singlet and triplet states. The microwave radiation affecting the spins of both electrons (which can be achieved owing to different *g*-factors and spin-lattice relaxation times) can change the ratio of singlet and triplet states, thus modulating the tunneling current. In other words, the SS ESR can be detected only by manipulating the spin statistics of the contacts of two electrons (one of them is the tunneling electron) by means of microwave pumping of Zeeman levels of either both electrons simultaneously or each of them, selectively.

An additional argument in favor of this statement is as follows. The combined electron+PMC system has a short lifetime ($\sim 10^{-14}$ s), so the spin dynamics in this state can be neglected. Magnetic interactions (the Zeeman interaction, the spin-orbital interaction, *etc.*) cannot be so strong as to change the direction of the spin in a time of $\sim 10^{-14}$ s. It is possible to change the direction of the spin in this time using the microwave pumping only if $(\gamma H_1)^{-1} \approx 10^{-14}$ s, which corresponds to virtually unattainable amplitude of pumping $H_1 \gg 3 \cdot 10^7$ G. Hence it is possible to detect the SS ESR only by means of the effect of microwave pumping on the populations of the spin states of the two-electron (the tunneling electron and the unpaired (probed) one) system, thus affecting the tunneling current.

Spin statistics of electron pair

To derive the equations for the tunneling current in different modes of microwave pumping, let us consider the statistics of a spin pair consisting of the spin of the tunneling electron and that of the unpaired electron of a paramagnetic species and changes in this statistics caused by microwave pumping.

Let us define the tunneling current in the absence of pumping. Both electrons can be in α or β states (with $S_z = +1/2$ and $S_z = -1/2$, respectively). The $\alpha\alpha$ and $\beta\beta$ combinations correspond to the $T_{\pm}$ triplet states (with $S_z = +1$ and $S_z = -1$, respectively) and therefore contribute to the I_T tunneling current corresponding to tunneling in the triplet state. The $\alpha\beta$ and $\beta\alpha$ combinations correspond to equal portions of the S singlet and T_0 triplet states (both of them with $S_z = 0$) and make equal contributions to the singlet I_S and triplet I_T tunneling currents. The total tunneling current is proportional to the number of electrons leaving the tip and to the probability of their tunneling in the vicinity of the PMC, which is dependent on the spin multiplicity of the electron+PMC system.

Let us introduce the quantities $\Delta = (N_\beta - N_\alpha)/N$ and $\delta = n_\beta - n_\alpha$, where N_β (N_α) is the number of electrons leaving the tip and having spin β (or α), and n_β (n_α) are the populations of the Zeeman level of the PMC having spin β (or α). Since $N_\alpha + N_\beta = N$ and $n_\alpha + n_\beta = 1$, we get

$$N_\beta = N(1 + \Delta)/2,\ N_\alpha = N(1 - \Delta)/2,$$
$$n_\beta = (1 + \delta)/2,\ n_\alpha = (1 - \delta)/2.$$

Then, the numbers of electrons N_S and N_T incident on the PMC in the singlet or triplet state, respectively, are defined by the following relationships:

$$N_S = (N/4)(1 - \Delta\delta),$$
$$N_T = (N/4)(3 + \Delta\delta). \qquad (1)$$

Taking into account the probabilities of tunneling in the singlet and triplet states (W_S and W_T, respectively), we get the following expression for the total tunneling current:

$$I = W_S N_S + W_T N_T = [(3/4)W_T + (1/4)W_S] + (N/4)\Delta\delta(W_T - W_S) = I_0 + i. \qquad (2)$$

The relative magnitude of the current portion i dependent on the difference in the spin populations of PMC is defined by the following relationship:

$$i/I_0 = \Delta\delta(W_T - W_S)/(3W_T + W_S). \qquad (3)$$

It follows from Eq. (3) that the tunneling current can be dependent on the difference in the spin populations of PMC (δ) only if (1) the tunneling probability is affected by the spin multiplicity, *i.e.*, $W_S \neq W_T$, and (2) the tunneling electrons are polarized, *i.e.*, $\Delta \neq 0$. The tunneling current can be changed by changing the difference in the populations δ (for instance, by saturating the ESR line of PMC); in particular, $\delta = 0$ and $i = 0$ at complete saturation.

Let us estimate the relative amplitude i/I_0 of the change in the current upon saturation of the ESR line of PMC. In the equilibrium state we have

$$n_\alpha/n_\beta = \exp[-\hbar\gamma H/(kT)] = \exp(-\varphi). \qquad (4)$$

Taking into account that $n_\alpha + n_\beta = 1$, we get

$$\delta = [1 - \exp(-\varphi)]/[1 + \exp(-\varphi)] = \mathrm{th}(\varphi/2). \qquad (5)$$

In contrast to the spin populations in PMC, the spin population of the electrons leaving the tip is determined by the $\hbar\gamma H/(2V)$ value (where V is the potential difference between the tip and the surface) rather than by the $\hbar\gamma H/(2kT)$ ratio. This is due to the fact that the difference in the populations arises in the energy region of electron levels near the Fermi surface.[6] Taking into account this fact, we get

$$\Delta \equiv \mathrm{th}[\hbar\gamma H/(2V)]. \qquad (6)$$

Thus, the Δ value is independent of temperature, and in magnetic fields $H \approx 3000$ G typical of ESR and at $V \approx 0.1$ V we get $\Delta \approx 10^{-4}$. At room temperature and in the same magnetic field, the δ value is approximately

equal to $5 \cdot 10^{-4}$ and, according to Eq. (3), the relative change in the tunneling current is negligible ($\sim 10^{-7}$—10^{-8}). Even at helium temperatures this ratio does not exceed 10^{-5}—10^{-6}.

To make the effect observable, it is necessary to strongly increase the polarization of the unpaired PMC electrons (for instance, by the action of high magnetic field) or that of tunneling electrons. The latter can be achieved by using a ferromagnetic tip or a tip coated with another paramagnetic center, which affects tunneling analogously to PMC; these possibilities are discussed in one of the recent publications.[7]

Detection of SS ESR of triplet molecules

Problems analogous to those of detection of monospin paramagnetic species and associated with small differences in the populations of Zeeman levels and, hence, with small contribution of the microwave pumping to changes in the populations arise in this case.

It will suffice to analyze two limiting cases. Let the triplet states (*e.g.*, pairs of phosphorus surface atoms) be virtually degenerate with singlet states, *i.e.*, the exchange energy $J \ll kT$. Since the microwave pumping induces only transitions between the $T_{\pm}$—T_0 Zeeman levels of the triplet state and has no effect on the T—S transitions, it cannot be used for changing relative populations of the singlet and triplet states even if the efficiencies of their detection with respect to the tunneling current differ substantially (for instance, the tunneling electrons are "scattered" by the triplet state, whereas the singlet state is "transparent" to them). It is clear that irrespective of the spin conversion between the singlet and triplet states (due to hyperfine interaction, difference in the Zeeman energies, or relaxation) the populations of these states cannot be considerably changed by microwave pumping and the result appears to be even worse than in the case of SS ESR considered in the preceding section.

It should be noted that this conclusion is also valid in the case of rigorous solution of this problem, which implies performance of analysis of the spin states in a three-electron system consisting of two PMC electrons (in the singlet or triplet states) on the surface and a tunneling electron. In this case, eight new spin states appear instead of triplet and singlet states: four doublet states "transparent" to tunneling and four "scattering" quartet states. Rigorous solution of this problem gives the same answer as that mentioned above, *viz.*, the magnitude of the effect of microwave pumping does not exceed one part per million.

An analogous conclusion can also be drawn for the other limiting case, *i.e.*, for singlet and triplet states strongly differing in energies ($J \gg kT$). In this case, too, the microwave pumping only changes the populations of Zeeman levels of the triplet states (T_0 and $T_{\pm}$) to a very small extent, but has no effect on the singlet/triplet ratio.

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The following general conclusion can be drawn based on the discussed above. The effect of microwave pumping on the tunneling current is determined only by the difference in the populations of Zeeman levels affected by pumping. This difference is very small ($\sim 10^{-3}$) under typical conditions (H = 3000 G, T = 300 K) and therefore the contribution of pumping to the change in the tunneling current is negligible (less than one part per million). It becomes noticeable only under extremal conditions (high magnetic fields, low temperatures) when one succeeds in almost complete destruction of one of the Zeeman levels.

Two circumstances deserve attention. First, unlike the classical ESR where the absorption of the energy of microwave pumping is detected, the tunneling current as a function of pumping is measured in the SS ESR. Tunneling of the electrons through the paramagnetic center can be considered as a spin-selective "reaction" which either allows tunneling or forbids it. Such an interpretation of the SS ESR shows that, in fact, it is a version of the known RYDMR method,[5] in which the tunnelled electrons play the role of a "product" of the spin-selective reaction.

Second, the idea of developing the time-resolved tunneling scanning microscopy technique arises. By measuring the density of the tunneling current in unit time (with resolution of the order of one nanosecond), one would be able to experimentally observe the modulation of current by the spin triplet-singlet transitions as a function of time, *i.e.*, to detect quantum beats in the two-spin system. In fact, the potentialities of such a time-resolved tunneling spectroscopy in the chemistry of single molecules are almost limitless.

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