SPIN PROHIBITION AS A MECHANISM OF THE NEGATIVE DIFFERENTIAL RESISTANCE IN A SINGLE-MOLECULE MICROELECTRONIC DEVICE

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Introduction

Electron transport in microelectronic devices with a single molecule placed between two metal electrodes is well-known to show the complex voltage-current curve with switching of the system from the conducting state to the blocking one, where the latter corresponds to the negative differential resistance (NDR) effect. The NDR is that phenomenon, when the flowing through the molecule electrical current falls off steeply at definite voltage (V) values in the course of the voltage increasing. Similar processes can occur, in particular, in the scanning tunneling microscope (STM), when individual molecules placed on the STM electrode-substrate are investigated, as it was done by other authors some time ago for duroquinone being on the gold substrate [1,2]. NDR is that phenomenon which has important significance for microelectronic devices building. Therefore, it attracts persistently a considerable attention of many scientists [3-7]. In this work we present our results that, as we believe, can give insight into the major contributor of the NDR mechanism. We based on our gas phase study, performed with the negative ion mass spectrometry of the resonant electron capture by molecules (NIMS REC) [8-10], as applied to duroquinone. (The NIMS REC version used in the present work is described in [11,12].) Using NIMS REC, we revealed duroquinone unusual feature that is also observed sometimes in other compounds [13-15], but is a rarity in such experiments. That is the feature of formation by a molecule in the gas phase the negative molecular ions (M¯) with abnormally high lifetime (τ) relatively to the additional electron autodetachment, when the parent molecule captures the electron with nonzero energy, i.e., at E_{el} > 0. In other words, it is found that duroquinone molecule, being in the gas phase, has a pronounced property of delay the additional electron on itself. Since NDR can also be thought as the transferred electron retention on the molecule which is the same, but only placed between two electrodes, both phenomena are believed to have the similar origin. The present paper is devoted to examine this assumption. To do this, apart from the above-mentioned experimental facts themselves revealed in duroquinone, we used our recent explanation of this phenomenon, where a spin prohibition in M¯ was found as a cause of the abnormally long-lived M¯ [16-18]. In the present work, we investigated the problem: whether the same spin prohibition can be realized in the metal-molecule junctions under the STM conditions. This issue is considered
below, but before, the gas phase electron delay mechanism itself, as well as the corresponding duroquinone experimental data with the resonance states assignment should be shortly described.

**Long-lived ions of duroquinone. Spin prohibition**

NIMS REC shows that duroquinone forms in the gas phase a resonant state

![Diagram](image)

**FIG. 1.** Effective yield curves of $\bar{M}^-$ and $M^0$ from NIMS REC, $\tau$ is the lifetime of $\bar{M}^-$ ions (a). Effective yield curves of negative fragmental ions with m/z 46 and 112. Insert, duroquinone UV absorption spectrum in $n$-hexane, $E(S_1) = 2.86$ eV, $E(S_2) \approx 3.5$ eV, $E(S_3) = 3.75$ eV, the dashed arrows – the inter-shell resonances with $S_1$, $S_2$ and $S_3$ as the parent states (b). B3LYP/6-311+G** potential energy curves of $GS_{M^0}$, $GS_{\bar{M}^-}$, $Q_{M^-}$ and $M$ (EEFR$_3$), subscription “3” means the EEFR with electronic excitation from OMO. Circles on PECs present B3LYP/6-311+G** calculated points, the 1, 2, 3, 4 and 5 positions, the generalized coordinate of $GS_{M^0}$, $T$, $GS_{\bar{M}^-}$, $Q_{M^-}$-plane and $Q_{M^-}$-bent optimized geometry, respectively. The (r) and (l) letters point the right and the left EEFR$_3$ resonance edges limiting the energy range of the long-lived ions registration. Arrows: EEFR$_3 \rightarrow Q_{M^-}$ and $GS_{M^0} \rightarrow$ EEFR$_3$ transitions. Calculated zero vibration levels everywhere $\approx 5.2$ eV (c).

producing the $\bar{M}^-$ ions with $\tau \approx 200$ $\mu$s at $E_{el} = 1.7$ eV (Fig. 1 a). The value $\tau \approx 200$ $\mu$s is abnormally high in this case because in NIMS REC experiment, $\bar{M}^-$ ions are formed in fine vacuum, and, consequently, cannot dissipate by any way the
excess energy introduced into the ion with the captured electron. So, $M^-$ ion, formed at $E_{el} > 0$ lies in total energy ($E_t$) above the parent molecule of the ground state ($^{GS}M^0$) by $E_{el}$, during all period of the ion lifetime, and this ion should rapidly release the additional electron, for $\tau \approx 10^{-12}$–$10^{-15}$ s, falling easily into $^{GS}M^0$ [19]. Such, indeed, is the case, but not with some molecules including duroquinone. The violation of the rule was revealed first by Christophorou in para-benzoquinone [13]. But the explanation of this phenomenon was found only recently [16-18]. In works [16-18] it was shown that in some compounds, $M^-$ ions generated originally as ions-doublets (of multiplicity $M = 2$) are converted into the ions-quartets ($^{QM}$), of $M = 4$, with three unpaired electrons with parallel spins. The conversion occurs as a result of the doublet-quartet intersystem crossing with nonradiative transition of the ion at the intersection point of the corresponding potential energy curves (PEC), with spin flip of one of the electrons. The $^{QM}$ ion has a high $\tau$ value because it can decay back into $^{GS}M^0$ only with the analogous spin flip that takes time. Besides, it cannot decay into a molecular triplet (without spin flip) because in the given compound, all triplets lie in total energy above $^{QM}$. Applying this conception to duroquinone, we have that duroquinone long-lived $M^-$ ions are the $^{QM}$ ions. B3LYP/6-311+G** [20] calculations confirm this: $E_t^{calc}(^{QM}) > E_t^{calc}(^{GS}M^0)$ by 1.5 eV. This calculated difference of 1.5 eV between $E_t$ values is close to experimental 1.7 eV. The 1.5 eV value determines also the relative positions of the calculated PECs of $^{QM}$ and $^{GS}M^0$ for the gas phase that are depicted in Fig. 1c together with PECs of the molecular ion of the ground state ($^{GS}M^-$) and $M^-$ formed from the electronically-excited Feshbach resonance (EEFR). The geometry optimization of $^{QM}$ indicates that the most stable $^{QM}$ conformer has a severely nonplanar structure of the ring (Fig. 2; II) that differs markedly from the plane ring structure of $^{GS}M^0$ and $^{GS}M^-$ (Fig. 2; I). Although, the stable $^{QM}$ with the plane ring structure exists also. The views and the energies (with correction of 2 eV [21]) of the calculated orbitals of $^{GS}M^0$, $^{GS}M^-$ and $^{QM}$ are also presented in Fig. 2. Besides, the experimental energies of the occupied molecular orbitals (OMOs) of $^{GS}M^0$, that are the ionization energies (IE) from duroquinone photoelectron spectrum (PES) obtained in the present work (insert in Fig. 2), are given in Fig. 2. PES was recorded for controlling the quantum-chemical calculations reliability, and, together with recorded herein UV absorption spectrum (insert in Fig. 1 b), was used for NIMS REC data interpretation.

**Types of ions-doublets transforming themselves into the ions-quartets $^{QM}$ in the gas phase**

Further, duroquinone $M^-$-doublets which convert themselves into the $^{QM}$ ions in the gas phase were found. To do this, the resonant states at $E_{el} = 0$–$4$ eV (Fig. 1 a, b) were assigned with B3LYP/6-311+G** calculations of $^{GS}M^0$, $^{GS}M^-$, $^{QM}$, the lowest triplet and the $M^-$ electronically-excited states by technique like used earlier [13,14]. PES and UV absorption spectroscopy were implemented at a time, like it
was done previously [22-26]. The relationship between UV spectra and NIMS REC allowed to assign the resonant states at $E_{el} > 2.5$ eV to inter-shell resonances [23-25,27,28], the resonance at $E_{el} \approx 0$ was ascribed to nuclear-excited Feshbach resonance [29,30], and the resonances at $E_{el} \approx 0.2$ and 0.8 eV (m/z 46, Fig. 1 b) were found as shape resonances [8,10]. The resonant states at $E_{el} \approx 1.2-2.0$ eV, producing finally the long-lived $Q^M$ ions, were assigned to four EEFRs [34]. EEFRs are identified herein at rather low energies, but this is confirmed by the similar results of Honda et al. for para-benzoquinone [31]. Thus, it was obtained that the $M^-$ ions-doublets formed via EEFRs are the protosource of duroquinone $Q^M$ ions in the gas phase.

**FIG. 2.** Ionization energies from photoelectron spectrum of duroquinone, insert (a). B3LYP/6-311+G** orbitals of $GS^M^0$ (b), $GS^M^-$ (c), and bent $Q^M$ (d). The calculated energy scale (on the right) is shifted down by 2 eV in accordance with PES data, as made in [21]. Correspondingly, digits above the lines at columns (b), (c) and (d) present the calculated orbital energies reduced by 2 eV. Plane conformation is typical for $GS^M^0$ and $GS^M^-$ (I), the bent one is peculiar to $Q^M$ (II).

**Ion stabilization in the STM**

From the aforesaid, it may be seen that the principal problem of the present work is whether duroquinone $Q^M^-$ ions can be formed on the metal surface under the STM conditions. The problem arises because in the gas phase, duroquinone $Q^M^-$ ions are formed above $GS^M^0$ in total energy. But in the STM, any negative molecular ion
can only be formed below \( \text{GS} \text{M}^o \), since the molecule captures the additional electron therein always with the negative energy. This is the case because it comes to the molecule by tunneling from the negative energy level of the metal [32].

Thus, duroquinone \( \text{Q} \text{M}^- \) formation in the STM is possible only if there is a mechanism of the ion stabilization in the STM. And such mechanism, indeed, does exist that follows from the case of Cl-benzene investigated under both conditions in the gas phase and in the STM. In the gas phase, Cl-benzene forms its lowest in energy resonance (shape resonance) with the \( \text{M}^- \) ions formation above molecule [33-35] by \( E_{\text{cl}} = 0.73 \text{ eV} \) [35]. And, at the same time, it forms \( \text{M}^- \) ions on the Si surface in the STM [36-39] “via the gas-phase-like resonant electron attachment” as noted in [39], i.e. below the parent molecule in total energy. By this is meant that the similar effect can also take place for duroquinone \( \text{Q} \text{M}^- \), and we need only to estimate the value of this stabilization. This is done below. But initially it is necessary to indicate the \( \text{M}^- \) ions-doublets which can be the parent ions (the protosource) of \( \text{Q} \text{M}^- \) at the STM experiment.

\( \text{OC} \text{M}^- \) is the parent ion for \( \text{Q} \text{M}^- \) in the STM. Stabilization of the \( \text{OC} \text{M}^- \) parent ion by two electrodes metal surfaces image-charges

In the STM, \( \text{Q} \text{M}^- \) can be produced, probably, mostly from \( \text{GS} \text{M}^- \), in contrast with the gas phase where EEFRs are the source of \( \text{Q} \text{M}^- \), because, in the STM, at the electron tunneling only \( \text{GS} \text{M}^- \) can be initially generated. This statement is a consequence of two principles: i) the equality in energy of two levels between which the tunneling electron passes [40,41]; ii) the energy conservation law. Only \( \text{GS} \text{M}^- \) can provide both principles simultaneously, because only its semi-occupied molecular orbital (SOMO, Fig 2 c) that is the lowest unoccupied molecular orbital (LUMO) with the additional electron, significantly differing from the latter (by 3.65 eV for duroquinone in the gas phase), provides the relationship of its energy \( E(\text{SOMO}) \) with the total energy changes (\( \Delta E_t \)) occurring after the electron tunneling. Indeed, as regards the molecule accepting the electron, in general, we can write:

\[
E(\text{SOMO}) = E_t(\text{GS} \text{M}^-) - E_t(\text{GS} \text{M}^o) = \Delta E_t = -E_A \quad (1)
\]

where \( E_A \) is the molecule vertical electron affinity. For duroquinone in the gas phase \( E_A = 1.67 \text{ eV} \) from our B3LYP/6-311+G** calculations. Thus, from (1) we have:

\[
E(\text{SOMO}) = -E_A \quad (2)
\]

For a molecule being on a surface, the same equation can be written as follows:

\[
E(\text{SOMO}^{\text{SUR}}) = -E_A^{\text{SUR}} \quad (3)
\]

As regards the metal (Mt) losing the electron:

\[
\mu_1 = -\Delta E_t(\text{Mt}) \quad (4)
\]
where $\mu_1$ is the energy of the metal level donating the electron onto the molecule. It is the electrochemical potential defined from the well-known equation:

$$\mu = E_f \pm V/2 \quad (\mu_1 = E_f + V/2, \mu_2 = E_f - V/2) \quad (5)$$

where $E_f$ is Fermi level and $V$ is the bias voltage between the substrate and the tip. If we take $V = +1.5$ V (which produces duroquinone NDR states of number 2 [1]) and $E_f(Au) = -5.52$ eV [42], the value

$$\mu_1 = -4.78 \text{ eV} \quad (6)$$

is obtained (Fig. 3). In accordance with the energy conservation law, the right parts of equations (3) and (4) are equal, so the left ones of them are equal too. Then, considering also (6) we obtain:

$$\mu_1 = E(\text{SOMO}^{\text{SUR}}) = -4.78 \text{ eV} \quad (7)$$

First, equation (7) indicates that the levels alignment in the STM occurs for $\mu_1$ with SOMO$^{\text{SUR}}$ (but not with LUMO, as is the convention), and, second, together with (3) it gives:

$$E_A^{\text{SUR}} = 4.78 \text{ eV} \quad (8)$$
Equation (8), in its turn, states that the vertical electron affinity of duroquinone molecule on the gold surface under the $V = +1.5$ V voltage in the STM is 4.78 eV. In other words, $^{G_S}M^-$ is formed below the molecule in total energy by 4.78 eV under these conditions. Since in the gas phase it is formed below the molecule by 1.67 eV, the STM conditions stabilize $^{G_S}M^-$ by $4.78 - 1.67 \approx 3$ eV. The value of 3 eV ion stabilization is fully reliable because it corresponds to well-known image-charge effect [43], which is described, e.g., for O produced from O$_2$ on the Pt substrate, with the energy lowering by this effect on 2.5 eV [44]. Benzene shows the stabilization of the resonance on the Pd surface by 2.3 eV [45]. Duroquinone $^{G_S}M^-$ is stabilized slightly more by virtue of two metal surfaces in the STM, where each produces the image charges.

**Double stabilization of the $^{Q_M^-}$ daughter ion: 1) by two electrodes metal surfaces image-charges; 2) by shifting toward the positively charged substrate**

As to $^{Q_M^-}$, in order to be formed in the STM, it should be approximately aligned in energy with $^{G_S}M^-$ therein, because it should have a possibility of the nonradiative, “horizontal” transition from its parent ion $^{G_S}M^-$. It lies higher $^{G_S}M^o$ in the gas phase at least by 1.25 eV (Fig. 1 a, b). Therefore, it should be stabilized in the STM at least by $4.78 + 1.25 \approx 6$ eV. One-half this value is provided by the same, above-mentioned image-charge effect of 3 eV. One more part of stabilization energy of 3 eV, $^{Q_M^-}$ can get from the voltage action that exist in the STM, but is lacking in the experiments cited above. Under the voltage action, the parent $^{G_S}M^-$ ion, after formation, should shift towards the positively charged substrate. Then, the substrate-$^{G_S}M^-$ ion distance is shortened, and the stabilizing electrostatic interaction of $^{G_S}M^-$ (as well as of the daughter $^{Q_M^-}$) with this electrode increases, while their destabilizing interaction with the negatively charged electrode (the tip) decreases. The balance between two interactions is broken in favour of the stabilization.

**Numerical evaluation of the $^{Q_M^-}$ ion stabilization under the STM conditions**

Duroquinone molecule is held between two electrodes spaced by 7 Å in the STM [2]. Therefore, to a first approximation, the initial distance between the neutral duroquinone ring plane and the substrate can be taken as 3.5 Å. Our B3LYP/6-311+G** calculations show that shifting of $^{G_S}M^-$ toward the positive charge (simulated by the potassium cation) occurs up to $\approx 2.4$ Å. In this case the energy of the system is lowered by $\approx 2$ eV. Thus, the calculations show that the direct voltage effect in the STM concerned to the ions stabilization can be rather great. And now we need only to find a possible source of $\approx 1$ eV remaining part. There is a good probability that it is generated by increased intimation contact of CH$_3$ groups of the ion with the substrate (which was not taken into account in the above-mentioned calculations) after the ion-substrate distance shortening. The similar effects of the adsorbate-surface distance shortening and the corresponding binding energy increase was found, for instance, for C$_{60}$ studied on the Si surface in the STM,
when the adsorbate-surface distance of 4.7 Å was changed to 3.3 Å with the covalent bonding formation [46]. The covalent binding energy contribution of \( \approx 1 \) eV was found for the equilibrium \( \Gamma^-\text{-Cu} \) distance of 2.65 Å [47] and of \( \approx 3-6 \) eV for \( K^+\text{-Cu} \) interaction [48] (see Table IV in Ref. [48]). The value of \( \approx 5 \) eV was found in the case of the O-Si covalent binding [49]. It follows herefrom that the cited data, obviously, overlap the required addition of \( \approx 1 \) eV. The hydrogen atoms of duroquinone CH\(_3\) groups in \( {^G}M \) and \( Q\) , maybe, do not form pure covalent

![Diagram](image)

**FIG. 4.** The sections of \( {^G}M^o, {^G}M^- \) and \( Q^- \) potential energy curves by the tip-substrate distance coordinate, for the case of \( V = +1.5 \) V. Vertical down arrow shows the \( {^G}M^o \rightarrow {^G}M^- \) transition, horizontal arrow indicates the \( {^G}M^- \rightarrow Q^- \) one. Value of 4.78 eV at the vertical arrow corresponds to \( \mu_1 = -4.78 \) eV.

bond with the Au surface, forming, probably, mainly the ionic one. But the ionic bonding can also be strengthened as a result of the distance shortening between the atoms of the negative ion and the positively charged surface. One way or the other, we can conclude, likely, from these estimations that there is a good probability for \( Q^- \) to be formed under the STM conditions (Fig. 4) with subsequent producing of NDR. It is pertinent to note that this conclusion is supported by the fact that NDR was found to be absent in duroquinone at \( V < 0 \) [1]. Since at \( V < 0 \) tunneling
current in the STM is well-known to flow via the positive molecular ion \([50]\), the absence of NDR at \(V < 0\) is obvious: simply, \(Q^-M^+\) cannot be formed from \(M^-\).

**Ions-quartets and four NDR states in duroquinone**

It is given in the paper \([1]\) that duroquinone forms 1, 2, and 3 states in the STM at \(V = +1.3, +1.5\) and \(+1.7\) \(V\), respectively, with the NDR effect arising; 0 state is produced at \(V = –1.7\) without NDR. Each of 1, 2, and 3 states is saved during few minutes at the corresponding voltage and is switched to 0 state if the voltage is changed to \(V = –1.7\) \(V\). Besides, it is observed that duroquinone CH\(_3\) groups rotate themselves at the switching. We suppose that 1, 2, and 3 states can be the neutral duroquinone molecules with different CH\(_3\) groups positions among five stable molecule conformers (I–V, Fig. 5) obtained by B3LYP/6-311+G** calculations. We think that in the STM, each of 1, 2, and 3 states can be formed as one of these five conformers in consequence of decay of \(Q^-M^+\) ions which, in turn, are formed with different vibration excitations from the different vibration levels of the parent

![FIG. 5. Five conformations of duroquinone molecule. Three projections for each conformation: top view (in the centre) and two side views. The digits at the bottom, the total energies (eV) of the molecule in the given conformation.](image)

\(\text{GS}^-M^-\). The 0 state is presented by the most stable conformation I. When, at \(V = +1.3, +1.5\) or \(+1.7\) \(V\), the next electron comes from the tip onto corresponding neutral conformer, each of them forms again “its own” \(Q^-M^+\) (via \(\text{GS}^-M^-\)) by virtue of the proper CH\(_3\) groups positions and fixation of these positions by the surface. And these \(Q^-M^+\) ions formation lowers the conductivity of the system, producing the NDR effect. When the voltage is changed to \(V = –1.7\) \(V\), the negatively charged (in this case) substrate repels the negative parent \(\text{GS}^-M^-\) ion. Then, its CH\(_3\) groups became freer, thus getting possibility to be transformed to the positions of the most
stable conformer I providing by this way the 0 state formation. The system switches with CH₃ groups rotation, as it was observed in the work [1].

**Delay mechanism of the electron transition by the QM⁻ ion in the STM**

In any case, QM⁻ should suppress the tunneling electron transfer if it is formed in the STM. For instance, in the case of the molecule triplet to fall within the “voltage window” (Ve), the additional electron could pass to the second electrode directly from QM⁻ without spin flip, because there would be sufficient energy for the molecule to be left in the triplet-excited state. But the triplet-exciting molecule would create unfavorable conditions for accepting the electron by this molecule from the first electrode. That is: i) the level alignment breaking; ii) the presence of electron on LUMO; iii) the absence of the correspondence between the levels energies and the total energies changes. For one of these reasons alone the process should stop. If no triplet falls within the “voltage window” (that is more probable), the additional electron cannot be detached from QM⁻ directly (without spin flip of the remaining molecule electron) onto the second electrode, since in this case the molecule should remain in the triplet state which in this case is impossible because of higher position in energy of the triplet relatively QM⁻. Then, the electron can go away onto the second electrode either via parent GS⁻M, after the spin forbidden returning QM⁻ → GS⁻M, or via spin inversion of the remaining molecule at the instant the electron leaves the ion-quartet. It is obviously that both events takes time, and the electron transfer will be delayed, by full analogy with the gas phase.

**Conclusion**

In conclusion it may be noted that the probability of the QM⁻ formation in the metal-molecule junctions, if allowed in energy, should be immeasurably higher than in the gas phase it takes place. The cause is the metal atoms presence in the junction. The metal atoms enhance the spin-orbital coupling which is the well-known factor promoting the intersystem transitions. Therefore, the QM⁻ formation can be of widespread occurrence in the metal-molecule devices. As regards the molecule NDR behavior therein, we think that it can be predicted from the ability of the molecule to produce the abnormally long-lived negative molecular ions at nonzero electron energies in the gas phase.

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Literature


