Polaron effects on the dc- and ac-tunneling characteristics of molecular Josephson junctions

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We study the interplay of polaronic effect and superconductivity in transport through molecular Josephson junctions. The tunneling rates of electrons are dominated by vibronic replicas of the superconducting gap, which show up as prominent features in the differential conductance for the dc and ac current. For relatively large molecule-lead coupling, a features that appears when the Josephson frequency matches the vibron frequency can be identified with an over-the-gap structure observed by Marchenkov et al. [Nat. Nanotech. 2, 481 (2007)]. However, we are more concerned with the weak-coupling limit, where resonant tunneling through the molecular level dominates. We find that certain features involving both Andreev reflection and vibron emission show an unusual shift of the bias voltage at their maximum with the gate voltage $V_g$ as $V \sim (2/3) V_g$. Moreover, due to the polaronic effect, the ac Josephson current shows a phase shift of $\pi$ when the bias $eV$ is increased by one vibronic energy quantum $\hbar \omega_v$. This distinctive even-odd effect is explained in terms of the different sign of the coupling to vibrions of electrons and of Andreev-reflected holes.

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I. INTRODUCTION

Electron transport through quantum dots embedded in Josephson junctions is attracting increasing interest.1,2 Rich phenomena3–9 arise due to the competition of superconductivity and strong interactions. A crucial feature of molecular Josephson junctions (MJJs) is the interplay of the ac Josephson effect and molecular vibrations. Signatures in the transport can be expected when the Josephson frequency matches a vibration frequency. Since the Josephson frequency can be precisely controlled by the bias voltage, such signatures could be expected when the Josephson frequency matches a vibration frequency. We will see that signatures in transport do show up as prominent features in the differential conductance for the dc and ac Josephson effects, followed by a summary in Sec. IV.

II. MODEL AND METHOD

Our model Hamiltonian reads

$$H = \sum_{\alpha=L,R} H_\alpha + H_{\text{mol}} + H_T,$$

where the first term describes the left ($L$) and right ($R$) BCS superconducting leads,

$$H_\alpha = \sum_{k\sigma} \epsilon_{c_{\alpha k\sigma}}^\dagger c_{\alpha k\sigma} + \sum_{k\sigma} (\Delta_{\alpha}^c c_{\alpha \sigma}^\dagger c_{\alpha -k \sigma \uparrow} + \text{H.c.}),$$

with superconducting order parameter $\Delta_\alpha$, $c_{\alpha k\sigma}$ ($c_{\alpha k\sigma}^\dagger$) annihilates (creates) an electron of wave vector $k$ and spin $\sigma$ in lead $\alpha$.

The molecule with vibration degree of freedom is represented by

$$H_{\text{mol}} = \sum_{\sigma} \epsilon_m d_{\sigma}^\dagger d_{\sigma} + \hbar \omega_v a^\dagger a + \lambda (a^\dagger + a) \sum_{\sigma} \tilde{d}_{\sigma}^\dagger \tilde{d}_{\sigma},$$

where $\epsilon_m$ is the molecular energy level, $d_{\sigma}$ ($d_{\sigma}^\dagger$) is the annihilation (creation) operator of a spin-$\sigma$ electron in the molecular orbital, $a$ ($a^\dagger$) is the vibron annihilation (creation) operator, and $\lambda$ is the electron-vibron coupling strength. We neglect the Coulomb interaction in the molecule, which is justified if the charging energy is small compared to the coupling to the leads.10 The role of the Coulomb interaction in MJJs has recently been reviewed in Ref. 1.
The tunneling between the molecule and the leads is described by
\[
H_T = \frac{1}{\sqrt{N}} \sum_{\alpha \sigma} I_{\text{ad}} \exp \left[ i \left( \phi_\alpha + \frac{2eV_\alpha}{\hbar} t \right) \right] c_{\alpha \sigma}^{\dagger} d_{\sigma} + \text{H.c.},
\]
(4)
where \( \phi_\alpha \) is the initial phase of the superconducting order parameter at time \( t = 0 \), \( V_\alpha \) is the voltage in lead \( \alpha \), and \( I_{\text{ad}} \) is the tunneling matrix element. In the following we choose \( \phi_\alpha = 0 \), \( V_L = 0 \), and \( V_R = -V \), where \( V \) is the voltage drop across the junction. For symmetric capacitances between the molecule and the leads, as assumed here, the molecular energy level is then given by \( \epsilon_m = \epsilon_0 - eV/2 \).

To go beyond perturbative approaches, we employ the unitary Lang-Firsov transformation to diagonalize \( H_{\text{mol}} \). The transformed Hamiltonian reads
\[
\tilde{H} = H_a + \sum_\sigma \left( \tilde{\epsilon}_\sigma - \frac{eV}{2} \right) d_\sigma^{\dagger} d_\sigma + \hbar \omega_v a^{\dagger} a + \tilde{H}_T,
\]
(5)
where the molecular energy level is shifted to \( \tilde{\epsilon}_\sigma = \epsilon_0 - \lambda/\hbar \omega_v \) by the polaron binding energy. To simplify notation we now take \( \tilde{\epsilon}_0 = 0 \) to denote the shifted level. In principle, the electron-electron interaction is also renormalized by the transformation but we neglect this shift together with the bare Coulomb interaction. We do not expect the on-site interaction to qualitatively change our results, which are concerned with transport outside of the Coulomb-blockade regime. \( \tilde{H}_T \) has the same form as \( H_T \), except that the tunneling matrix elements are dressed by the polaronic effect as \( I_{\text{ad}} = I_{\text{ad}} \tilde{X} \), where
\[
X = \exp \left[ -\frac{\lambda}{\hbar \omega_v} (a^{\dagger} - a) \right]
\]
is the polaron-shift operator.

The transport properties are obtained by the nonequilibrium-Green-function method. In the Nambu representation we introduce the contour-ordered Green function \( G(t,t') = -i \langle T_\varepsilon (t\psi(t')\bar{\psi}(t')) \rangle \) with the contour-ordering directive \( T_\varepsilon \) and \( \psi = (d_\uparrow, d_\downarrow)^T \). The particle current through the lead \( \alpha \) is
\[
I_\alpha(t) = \frac{2e}{\hbar} \text{Re} \int dt_1 \text{Tr} \left[ \sigma_\varepsilon [G^{-}(t,t_1)] \Sigma^\alpha_{\varepsilon}(t_1,t) \right. \\
+ \left. G^{+}(t,t_1) \Sigma^{-\alpha}_{\varepsilon}(t_1,t) \right],
\]
(7)
where the trace is over Nambu space, \( \sigma_\varepsilon \) is a Pauli matrix, and \( \Sigma^\alpha_{\varepsilon} \) and \( \Sigma^{-\alpha}_{\varepsilon} \) are, respectively, the advanced and lesser self-energies due to the coupling to lead \( \alpha \). The advanced self-energy is related to the retarded one through \( \Sigma^\alpha_{\varepsilon}(t,t') = [\Sigma^\varepsilon(t',t)]^\dagger \).

The current measured in, say, the left lead consists of the particle current \( I_\ell(t) \) plus the displacement current due to the formation of image charges. This contribution vanishes in the stationary state but must be taken into account in the time-dependent case to ensure gauge invariance and current conservation. This requires proper partitioning of the displacement current. Since we assume symmetric coupling, the displacement currents are symmetric, in which case the measured current equals the symmetrized current \( I = (I_L - I_R)/2 \). Due to the ac Josephson effect, the current can be expanded as \( I(t) = \sum_n I_n e^{i\omega_n t} \), where the Josephson frequency is \( \omega_J = 2eV/\hbar \) and \( I_n = (I_{L,n} - I_{R,n})/2 \). The Fourier components \( I_{\alpha,n} \) are
\[
I_{\alpha,n} = \frac{2e}{\hbar} \int dt \text{Re} \text{Tr} \left[ \sigma_\varepsilon [G_{\alpha,n}(\epsilon) \Sigma^\alpha_{\varepsilon}\otimes\Sigma^{-\alpha}_{\varepsilon}(\epsilon)] \right],
\]
(8)
where \( G_{\alpha,n}(\epsilon) \equiv G_{\alpha,n}(\epsilon) + \Sigma_n^{\alpha,n}(\epsilon) \) and analogously for the self-energies. The current can be decomposed into dissipative \( (I_n^D) \) and nondissipative \( (I_n^S) \) contributions,
\[
I(t) = I_0 + \sum_{n>0} \left( I_n^D \cos n\omega_J t + I_n^S \sin n\omega_J t \right),
\]
(9)
where \( I_n^D = \text{Re} \left( I_{\alpha,n} - I_n \right) \) and \( I_n^S = 1m(\alpha,n - I_\alpha) \).

Before turning to transport properties, we show that the molecule-lead coupling is drastically modified by the polaronic effect. We employ the standard decoupling approximation, which assumes that averages of products of two polaron-shift operators can be taken out of electronic Green functions and evaluated in equilibrium. This approximation is valid if \( \hbar \omega_v \) is large compared to the molecule-lead coupling. It is known that beyond its range of quantitative reliability, the approximation predicts resonant features that are too broad and too low, but that are centered at the same energy as obtained from a more advanced treatment. In contrast to previous studies for normal leads, we encounter not only the correlation function \( \langle X(t)X(t') \rangle \) but also \( \langle X(t)X(t') \rangle \). These functions are given by
\[
\langle X(t)X(t') \rangle = \langle X^{\dagger}(t)X \rangle = \sum_i L_i e^{-i\omega_{\text{m,n},i} t},
\]
(11)
\[
\langle X(t)X \rangle = \langle X^{\dagger}(t)X^{\dagger} \rangle = \sum_i (-1)^i L_i e^{-i\omega_{\text{m,n},i} t},
\]
(12)
where
\[
L_i = e^{-i(\omega_{\text{m,n},i})^2(2N_i+1)} \exp \left( \frac{\hbar \omega_v}{2k_B T} \right) I_i(\eta),
\]
(13)
with the modified Bessel function \( I_\ell \) of the argument \( \eta = 2(\lambda/\hbar \omega_v)^2 \sqrt{N_i(N_i+1)} \). \( N_i \) is the average vibron number at temperature \( T \) determined by the Bose-Einstein distribution function. The correlation functions can be evaluated analytically. While the normal one has the well-known form
\[
\langle X(t)X^{\dagger} \rangle = \exp\left[ -g^2 \left[ (1 - e^{-\omega_{\text{m,n},i} t})N_i + 1 \right] \right] + N_i(1 - e^{i\omega_{\text{m,n},i} t}),
\]
(14)
the anomalous one is
\[
\langle X(t)X \rangle = \exp\left[ -g^2 \left[ (1 + e^{-\omega_{\text{m,n},i} t})N_i + 1 \right] \right] + N_i(1 + e^{i\omega_{\text{m,n},i} t}).
\]
(15)
The two correlation functions differ by a phase shift of half a vibration period. This phase shift will turn out to be crucial for the polaron effect on the Josephson current. Its origin can be traced back to the factor of \( (-1)^i \) under the sum in Eq. (12). This factor stems from Andreev reflection: An electron tunneling out of the molecule transmutes into a hole before it tunnels back in, which couples to the vibron with the opposite sign, as seen by inspecting the last term in Eq. (3).
Under the decoupling approximation, we obtain the retarded and lesser self-energies due to the coupling to superconducting lead $\alpha$ as

$$\left[\Sigma_{\alpha,mm}^{r}\right]_{ij} (\epsilon) = \sum_{l=-\infty}^{\infty} (-1)^{l(i-j)} L_{i} \left\{ \left[\Sigma_{\alpha,mm}^{r}\right]_{lj}(\epsilon_{-}) + \frac{1}{2} \left( \Sigma_{\alpha,mm}^{<}lj(\epsilon_{-}) - \Sigma_{\alpha,mm}^{<}lj(\epsilon_{+}) \right) \right\}$$

$$+ \frac{1}{2\tau} \left\{ H\left[\Sigma_{\alpha,mm}^{<}\right]_{lj}(\epsilon_{-}) - H\left[\Sigma_{\alpha,mm}^{<}\right]_{lj}(\epsilon_{+}) \right\}$$

(16)

and

$$\left[\Sigma_{\alpha,mm}^{<}\right]_{ij} = \sum_{l=-\infty}^{\infty} (-1)^{l(i-j)} L_{i} \left[\Sigma_{\alpha,mm}^{<}\right]_{lj}(\epsilon + i\omega_{p})$$

(17)

respectively, where $\epsilon_{+} = \epsilon \pm \hbar\omega_{v}$, and $i, j = 1, 2$ are Nambu indices. Here, $\Sigma_{\alpha}$ is the self-energy in the absence of electron-vibron coupling. Taking the wide-band limit and making use of our choice of vanishing initial phases $\phi_{\alpha}$ at time $\tau = 0$, $\Sigma_{\alpha}$ is given by

$$\Sigma_{L,mn}(\epsilon) = -\frac{i}{\tau} \Gamma_{L} \beta_{L}(\epsilon_{m}) \left( \frac{1}{\epsilon} - \frac{\Delta_{L}}{\epsilon_{m}} \right)$$

(18)

$$\Sigma_{R,mn}(\epsilon) = \frac{i}{\tau} \Gamma_{R} \beta_{R}(\epsilon_{m}) \left( \frac{1}{\epsilon} - \frac{\Delta_{R}}{\epsilon_{m}} \right)$$

(19)

$$\Sigma_{L,mn}^{<}(\epsilon) = \frac{i}{\tau} \Delta_{L} \epsilon_{m} f(\epsilon_{m}) \beta_{L}(\epsilon_{m}) \left( \frac{1}{\epsilon} - \frac{\Delta_{L}}{\epsilon_{m}} \right)$$

(20)

$$\Sigma_{R,mn}^{<}(\epsilon) = \frac{i}{\tau} \Delta_{R} \epsilon_{m} f(\epsilon_{m}) \beta_{R}(\epsilon_{m}) \left( \frac{1}{\epsilon} - \frac{\Delta_{R}}{\epsilon_{m}} \right)$$

(21)

where $\epsilon_{m} = \epsilon + \hbar\omega_{J}$ and $f(\epsilon) \equiv (e^{\epsilon/k_{B}T} + 1)^{-1}$ is the Fermi-Dirac distribution function, where the chemical potential in the left lead is independent of the bias voltage due to our assumption of $V_{L} = 0$ and has been absorbed into $\epsilon$. The shifts in the arguments $\epsilon_{m+1/2}$ of the Fermi functions in Eq. (21) account for the potential difference between the leads.

$\Gamma_{\alpha} \equiv 2\pi |\rho_{N}|^{2} \rho_{N}^{2}$ describes the coupling of the molecule to lead $\alpha$, where $\rho_{N}$ is the density of states in lead $\alpha$ in the normal state. In the wide-band limit, $\Gamma_{\alpha}$ is independent of energy. Also, for symmetric coupling we have $\Gamma_{L} = \Gamma_{R} \equiv \Gamma$.

The expressions for $\beta_{\alpha}$ and $\bar{\beta}_{\alpha}$ read

$$\beta_{\alpha}(\epsilon) = \left\{ \begin{array}{ll}
\frac{\epsilon}{i\sqrt{\Delta_{\alpha}^{2} - \epsilon^{2}}} & \text{for } \Delta_{\alpha} > |\epsilon|, \\
\frac{|\epsilon|}{\sqrt{\epsilon^{2} - \Delta_{\alpha}^{2}}} & \text{for } \Delta_{\alpha} < |\epsilon|,
\end{array} \right. \quad (22)$$

$$\bar{\beta}_{\alpha}(\epsilon) = \theta(|\epsilon| - \Delta_{\alpha}) \frac{|\epsilon|}{\sqrt{\epsilon^{2} - \Delta_{\alpha}^{2}}}$$

(23)

respectively. Furthermore,

$$H[F](\omega) \equiv \frac{1}{\pi} \int P \left( \frac{d\epsilon}{\omega - \epsilon} F(\epsilon) \right)$$

(24)

is the Hilbert transform of the function $F$, where $P$ denotes the principal value. The above results are valid for fast vibron relaxation so that the averages of bosonic operators can be taken in equilibrium. Figure 1 shows $-\text{Im}(\Sigma_{L}^{r})_{11}$ for various electron-vibron coupling strengths $\lambda$. Without electron-vibron coupling, $-\text{Im}(\Sigma_{L}^{r})_{11}$ exhibits the superconducting gap of the left lead. In the presence of electron-vibron coupling, $-\text{Im}(\Sigma_{L}^{r})_{11}$ develops vibronic replicas of the gap edges, separated by integer multiples of $\hbar\omega_{v}$, which open inelastic transport channels beyond the usual Andreev reflection. They enable electrons with energies above the superconducting gap to undergo Andreev reflection under emission or absorption of vibrons.

FIG. 1. Imaginary part of the first diagonal element of the retarded self-energy $-\text{Im}(\Sigma_{L}^{r})_{11}$, which represents scattering of electrons between the molecule and lead $L$, for various electron-vibron coupling strengths $\lambda$. We have taken $\hbar\omega_{v} = 8 \Delta$ and $\Gamma = 0.2 \hbar\omega_{v}$. With increasing $\lambda$, multiple vibronic replicas of the superconducting gap edges appear.
III. RESULTS AND DISCUSSION

A. Differential conductance of the dc Josephson current

We now discuss the modification of the Josephson current due to the polaronic effect. In this study we assume the two leads to be identical superconductors and take the amplitude of the order parameters to be $\Delta = |\Delta_L| = |\Delta_R|$. In Fig. 2 we first present density plots of the dc differential conductance $dI_0/dV$ as a function of the bias voltage $V$ and the on-site energy $\varepsilon_0$, which in a break-junction setup could be controlled by a gate voltage. Different polaronic features are observed depending on the molecule-lead coupling $\Gamma$. For large $\Gamma$, dc transport is dominated by coherent tunneling across the molecule without requiring the energy of the electron to be aligned with the molecular level. For Fig. 2(a) we have chosen $\Gamma = \lambda = \hbar \omega_v$. As noted above, in this regime the decoupling approximation is expected to underestimate the polaronic effect on transport but to show resonances at the correct voltages. The numerical results thus provide a reasonable qualitative description to the vibrion-assisted tunneling features. In Fig. 2(a) we find several features at fixed bias voltage, insensitive to $\varepsilon_0$. The feature labeled by “1” at $eV = \hbar \omega_v/3 = \Delta$ is due to single Andreev reflection without vibron emission or absorption. This process is illustrated by the left panel in Fig. 3. The feature labeled by “2” at $eV = 2\hbar \omega_v/3 = 2\Delta$ is due to direct tunneling from the lower gap edge at one side to the upper gap edge at the other, illustrated by the right panel in Fig. 3.

The features labeled by the letters “a”–“h” in Fig. 2(a) involve vibrons. All these features and their replicas shifted by integer multiples of $\hbar \omega_v$ can be explained by the onset of vibron-assisted Andreev reflections or coherent-tunneling processes sketched in Fig. 4, where the density of states (DOS) has been modified compared to the conventional picture of Andreev reflection to account for the polaronic effect. For instance, the weak feature “a” located at $\omega_v = \omega_J$ arises from the resonance of the vibron and Josephson frequencies and has been invoked by Marchenkov et al. to interpret the observed over-the-gap structure. The process is sketched in Fig. 4(a), where another electron from a singular edge of the left lead undergoes one Andreev reflection at the right lead and arrives at a singular edge of the left lead. In this process, one electron is emitted.

On the other hand, for small $\Gamma$, where the decoupling approximation gives quantitatively reliable results, the tunneling processes are sensitive to the position of the molecular energy level. Pronounced features arise when singular edges of the DOS are aligned with the level $\varepsilon_0$. In Fig. 2(b) we show $dI_0/dV$ vs $V$ and $\varepsilon_0$ for weak coupling, $\Gamma = 0.05\hbar \omega_v$. As the nonresonant tunneling is strongly suppressed, the features seen in Fig. 2(a) become much weaker or are even invisible in Fig. 2(b). Instead we see vibron-induced features with peak bias voltages depending not only on $\omega_v$ and $\Delta$ but also on $\varepsilon_0$. Two features, labeled by “f” and “g,” satisfy $\partial eV/\partial \varepsilon_0 = -2$. They are due to the alignment of the gap edges with the molecular level where resonant sequential tunneling through the molecule plays a dominant role. The corresponding processes are depicted in Figs. 4(f) and 4(g). Note that the level positions are renormalized due to the electron-vibron coupling. One can see that feature g displays a sharp rise in $dI_0/dV$ followed by a narrow region of negative differential conductance. This is due to the onset of resonance sequential tunneling.
FIG. 4. (Color online) Schematic representation of various vibron-assisted tunneling and Andreev-reflection processes in the MJJ. The labels are the same as in Fig. 2. The DOS of both leads is modified due to the polaronic effect. The filled (empty) shapes represent the energy states of the superconducting leads below (above) the Fermi energy. The molecular level \( \epsilon_0 \) (blue/gray) is broadened due to the coupling to the leads. Energy scales of the superconducting gap \( \Delta \), the vibron energy \( \hbar \omega_v \), and the bias voltage \( \epsilon \) are indicated. The arrows denote possible transitions of the electron or hole.

FIG. 5. (Color online) Density plot of the ac differential conductance of (a) the dissipative Josephson current \( I^D_1 \) and (b) the nondissipative Josephson current \( I^S_1 \) vs the molecular energy level \( \epsilon_0 \) and the bias voltage \( \epsilon \). The parameters are identical to those used for Fig. 2(b).

of resonant tunneling at the gap edges with singular DOS.\(^1\) Feature f instead shows a broader structure without negative differential conductance since the occupation of the final state is different, namely nearly empty for f and nearly full for g. Moreover, we identify another pronounced feature “h” moving with \( \epsilon_0 \), as well as one of its replicas. The underlying picture is shown in Fig. 4(h). An electron starting from the molecular level emits a vibron and is Andreev reflected. One could say that the electron traverses the bias voltage \( \epsilon \) one and a half times. Accordingly, the feature has an unusual slope of \( \partial \epsilon / \partial \epsilon_0 = -2/3 \). Accordingly, the feature has an unusual slope of \( \partial \epsilon / \partial \epsilon_0 = -2/3 \). Assuming that the molecular level is shifted by a gate voltage \( \epsilon_g \) as \( \epsilon_0 = \epsilon_0' - \epsilon_g \), we predict the distinctive slope \( \partial \epsilon / \partial \epsilon_g = 2/3 \) of this feature in a bias-voltage/gate-voltage map. Interestingly, the feature is confined to the voltage range \( \hbar \omega_v \leq \epsilon \leq \hbar \omega_v + 2\Delta \). This is due to the fact that for \( \epsilon > \hbar \omega_v + 2\Delta \), electrons prefer direct tunneling, while for \( \epsilon < \hbar \omega_v \), the process is blocked due to the Pauli principle.

B. Differential conductance of the ac Josephson current

We finally turn to the ac Josephson current. In Fig. 5 we plot the differential conductances of the dissipative and nondissipative components as functions of \( \epsilon \) and \( \epsilon_0 \) for small \( \Gamma' \), where the decoupling approximation is valid. The features seen in Fig. 2(b) for the dc current are found again. However, their appearance is different: Feature f becomes blurred in the ac case and feature h is visible in a much broader voltage range.

More interestingly, we observe an approximate antiperiodic behavior of both the dissipative and the nondissipative components of the ac differential conductance as functions of the bias voltage. The ac current itself exhibits the same antiperiodicity (not shown). The antiperiod in \( \epsilon \) is the vibron energy \( \hbar \omega_v \).
This means that the alternating current and the ac differential conductance change their phase by $\pi$ whenever $eV$ is increased by $\hbar\omega_v$. This antiperiodicity is a direct consequence of the polaronic effect: The anomalous (off-diagonal) self-energies in Eqs. (16) and (17) contain a factor $(-1)^l$. This factor stems from the corresponding factor in the anomalous correlation function of the polaron-shift operators, Eq. (11). As noted above, the factor is due to Andreev reflection since an outgoing electron and an Andreev-reflected hole couple to the vibron with opposite sign. For the weak molecule-lead coupling considered here, the current is dominated by processes involving a single vibron number $l$. The phase of the ac components can be measured with established techniques, or employing the coupling to a charge qubit, as proposed recently. Our results are related to the long-standing $\cos \varphi$ problem. It was found that the measured result for the phase of the ac Josephson current does not agree with theoretical predictions. In the present work we have identified a mechanism by which this phase could even change periodically as a function of the bias voltage.

IV. SUMMARY

In summary we have studied the transport properties of MJJs for which the electronic tunneling rates are modified by polaron formation. Pronounced features due to its interplay with the superconductivity in the leads have been identified in the differential conductance of both the dc and ac Josephson currents. We have explained these features in terms of vibron-assisted Andreev reflection. The combination of sequential tunneling and Andreev reflection leads to conductance peaks that show an unusual shift of their peak bias voltage with the molecular energy level or gate voltage, $V \sim (2/3)V_g$. Furthermore, the opposite sign of the coupling of electrons and Andreev-reflected holes to vibrons induces periodic phase changes of the ac components of the Josephson current—their phase changes by $\pi$ when the bias voltage $eV$ is increased by one vibrational energy quantum $\hbar\omega_v$. We propose to search for this clear-cut polaronic effect by measuring the ac Josephson current through molecular junctions.

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