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Reaction-rate approach to the dipolar relaxation in alkali halides

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An alternative reaction-rate approach is suggested for dealing with the relaxation times of dipolar defects in alkali halides. It rests on an occurrence-probability definition of the transition rate, accounting for both classical and quantal effects. A simple model Hamiltonian is postulated to describe the reorientational motion of a dipole within the framework of the adiabatic approximation. Two infamous examples are considered from this point of view. In one of these, the OH^- dipole is assumed to couple only electronically to the neighboring cations, while all its remaining reorientational characteristics are, to a first approximation, independent of the host lattice. Assuming further that a single local oscillator drives the reorientational motion, this model agrees well with the experimental temperature dependence of the OH^- relaxation time in four host halides up to 10 K, as measured by Kapphan and Lüty. The other example is the off-center Ag^+ ion in RbBr and RbCl where a formal application of the reaction-rate method has been found to fit closely, over the entire range, the experimental temperature dependence of the relaxation time for 90° reorientation, measured by the same authors.

I. INTRODUCTION

This paper is aimed at presenting a new approach to dipolar relaxation times which is both alternative and complementary to the usual multiphonon treatments.[1,2] It makes use of the modern quantum-mechanical theory of chemical reaction rates.[3] The reaction-rate approach (RRA) rests on an occurrence-probability definition of the transition rates.[4,5] Details of the RRA formalism as applied to the polaron hopping is solids have recently been given elsewhere.[6] The RRA relaxation rate is defined as

$$k_{\rm if}=Z_i^{-1}\sum_{n,n',n''} W_{n'n''}(n)\exp(-E_{n'}/kT)\times\exp(-E_n/kT)(\Delta E_n/h)\ . \tag{1}$$

Here E_n is the energy for motion along the reaction coordinate, while the motions along the nonreactive orthogonal coordinates are quantized with n' and n'', representing the initial and final states, respectively. $W_{n'n''}$ is the transition probability, k is Boltzmann's constant, T is the absolute temperature, Z_i is the complete partition function of the initial state (assumed to be in thermal equilibrium), and $\Delta E_n=E_{n+1}-E_n$ is the energy level spacing along the reaction (relaxation) coordinate. Equation (1) has a simple physical meaning:[5] While $W_{n'n''}(n)$ is the transition probability at energy E_n along the reaction coordinate q, $(hZ_i)^{-1}\exp(-E_n/kT)\Delta E_n$ may be interpreted as the probability per unit time for an approach to the potential barrier between the initial and final state along q, with energy within the range ΔE_n. For a quantum-mechanical calculation of the relaxation rate, knowledge of the transition probability $W(n)$ is required. The latter can be computed given the potential surface governing the relaxation process.

II. DIPOLAR HAMILTONIAN

The Hamiltonian of a system composed of electrons and lattice oscillators contains electron H_e, lattice H_L, and electron-lattice H_{eL} terms, correspondingly,[6]

$$H=H_e+H_L+H_{eL}\ . \tag{2}$$

Assuming that the electron-phonon coupling is effected through modulating the electronic potential by the lattice vibrations, H_e+H_{eL} can be united to give

$$H_e+H_{eL}=\sum\left[\frac{\mathbf{p}_e^2}{2m_e}+V_e(\mathbf{r},\tilde{q})\right] \tag{3}$$

where $\mathbf{r}$ stands for the coordinate, $\mathbf{p}_e$ for the momentum, and m_e for the effective mass of an electron. The sum is over the coordinates and momenta of all the electrons. $\tilde{q}$ is the manifold of lattice coordinates. Expanding $V_e(\mathbf{r},\tilde{q})$ into a power series in $\tilde{q}$ we have

$$V_e(\mathbf{r},\tilde{q})=V_e(\mathbf{r},\tilde{0})+\tilde{b}(\mathbf{r})\cdot\tilde{q}+\cdots\ . \tag{4}$$

Comparing with (3) we get

$$H_e=\frac{\mathbf{p}_e^2}{2m_e}+V_e(\mathbf{r},\tilde{0})\ ,\qquad H_{eL}=\tilde{b}(\mathbf{r})\cdot\tilde{q}+\cdots\ . \tag{5}$$

A linear coupling will be adopted throughout omitting the terms represented by the ellipses in (5). On the other hand,

$$H_L=\sum_L \left[\frac{\mathbf{p}_L^2}{2M_L}+\tfrac{1}{2}M_L\omega_L^2 q_L^2\right]+\frac{\mathbf{p}^2}{2M}+\tfrac{1}{2}M\omega^2 q^2+\cdots \, . \tag{6}$$

q_L, $\mathbf{p}_L$, M_L, and ω_L stand for the coordinates, momenta, masses, and angular frequencies of the lattice oscillators, respectively. Extracted from the overall sum in (6) are the terms (subscripts omitted) which refer to the mode that promotes the reorientational motion of the dipole. These terms will, undoubtedly, lead to dominating matrix elements when solving quantitatively the reorientational problem. Consequently, the sum in (6) will not be taken into account explicitly, that is, the reorientating dipole will be assumed to couple to a single local mode and all other modes will be considered unimportant for the relaxation process. Also omitted are terms [represented by the ellipses in (6)] which express intervibrational coupling to the L labeled oscillators, the accepting modes. However, all these terms securing the distribution of the surplus energy during relaxation must always be implied. Under the above conditions the Hamiltonian appropriate to the reorientational problem is, finally,

$$H=H_e+b(\mathbf{r})q+\frac{\mathbf{p}^2}{2M}+\tfrac{1}{2}M\omega^2 q^2 \, . \tag{7}$$

Also implied is that the electron-phonon coupling to the reorientation-promoting mode predominates too.

We further define an "adiabatic Hamiltonian" H_{ad} by subtracting from (7) the nuclear kinetic energy operator:

$$H_{\text{ad}}=H_e+b(\mathbf{r})q+\tfrac{1}{2}M\omega^2 q^2 \, . \tag{8}$$

Using (8) we get the "diabatic surfaces" for two electronic states $|i,0\rangle$ and $|f,0\rangle$:

$$V_t(q)=\langle t,0\,|\,H_{\text{ad}}\,|\,t,0\rangle=E_t^0+b_t q+\tfrac{1}{2}M\omega^2 q^2 \tag{9}$$

for $t=i,f$. The $|\,t,0\rangle$'s are both eigenstates of "diabatic" electronic Hamiltonian H_e with eigenvalues

$$E_t^0=\langle t,0\,|\,H_e\,|\,t,0\rangle \, . \tag{10}$$

The b_t's are the average electron-phonon coupling coefficients

$$b_t=\langle t,0\,|\,b(\mathbf{r})\,|\,t,o\rangle \, . \tag{11}$$

The minima of $V_t(q)$ amount to

$$V_{t\,\min}(q_t)=E_t^0-\tfrac{1}{2}M\omega^2 q_t^2 \quad \text{at } q_t=-b_t/M\omega^2 \, . \tag{12}$$

The difference between them is

$$Q_{\text{if}}=-\tfrac{1}{2}M\omega^2(q_f^2-q_i^2)+E_f^0-E_i^0 \, . \tag{13}$$

This is the "reaction heat" at 0 K. A physical requirement for the relaxation problem is that the reaction heat be vanishing for a transition between two neighboring reorientational sites along the reaction coordinate. Solving for $Q_{if}=0$, one obtains two distinct cases:

(i) $E_f^0=E_i^0$, $q_f=-q_i$. The transition is between two physically equivalent electronic states, whose only difference may be, e.g., in the spatial orientation of their respective electron clouds.

(ii) $E_f^0-E_i^0=\frac{1}{2}M\omega^2(q_f^2-q_i^2)$. Now, the transition involves two different electronic states which couple with different strengths b_t to the promoting mode. Transitions of this type can arise between excited F centers and bound polarons.[7]

Case (i) pertains to the dipolar relaxation. However, for the reorientational transition to occur there has to be a finite electronic coupling between the eigenstates $|\,i,q\rangle$ and $|\,f,q\rangle$ of the adiabatic Hamiltonian H_{ad}, in the sense that the electron-exchange matrix element

$$V_{\text{if}}(q)=\langle f,q\,|\,H_{\text{ad}}\,|\,i,q\rangle \tag{14}$$

should be finite at least around the crossover configuration q_c between $V_i(q)$ and $V_f(q)$.[6] This would bring about a splitting which results in the appearance of two "adiabatic surfaces," lower,

$$E_L(q)=\tfrac{1}{2}\{V_i+V_f-[(V_f-V_i)^2+4V_{if}^2]^{1/2}\} \, , \tag{15}$$

and upper,

$$E_U(q)=\tfrac{1}{2}\{V_i+V_f+[(V_f-V_i)^2+4V_{if}^2]^{1/2}\} \tag{16}$$

as illustrated in Fig. 1, the difference $E_U(q_c)-E_L(q_c)$ amounting to $2V_{if}(q_c)$ at the crossover coordinate. For the sake of simplicity, $V_{if}(q)=V_{if}(q_c)$ is often assumed to hold in the entire range of q.[6]

III. TRANSITION PROBABILITIES

The reaction rate (1) can also be rewritten in the form[6]

$$k_{if}=2\sinh(h\nu/2kT)\nu\sum_n W(n)\exp(-E_n/kT) \, , \tag{17}$$

where $\nu=\omega/2\pi$ is the vibrational frequency. In most cases of practical importance the transition probability $W(n)$ can be represented as the product

$$W(n)=W_L(n)\times W_e(n) \tag{18}$$

of the probability W_L for lattice rearrangement times the probability W_e for a change of the electronic state from i to f. To derive an expression for $W(n)$ would require solving a system of coupled vibronic equations.[3] Various expressions have been obtained depending on the magnitude of $\epsilon_n=E_n-E_c$, the excess energy relative to the barrier peak E_c. We next introduce

$$\gamma_n=(V_{if}^2/2h\nu)(E_r\,|\,E_n-E_c'\,|\,)^{-1/2} \, , \tag{19}$$

where

$$E_r=V_f(q_i)-V_f(q_f)=\tfrac{1}{2}M\omega^2(q_f-q_i)^2 \quad \text{for } Q_{if}=0 \tag{20}$$

is the lattice reorganization energy,

$$E_c'=(E_r+Q_{if})^2/4E_r=E_r/4 \quad \text{for } Q_{if}=0 \tag{21}$$

is the crossover diabatic potential $V_f(q_c)-V_i(q_i)$ relative to the minimum of $V_i(q)$,

$$E_c=E_c'-V_{if} \tag{22}$$

is the saddle-point potential barrier at q_c along the lower adiabatic surface (15). All the relevant quantities are explained in Fig. 1. Now, the expressions derived for a strongly quantized vibronic system read[6]

$$W_e = 2[1-\exp(-2\pi\gamma_n)]/[2-\exp(-2\pi\gamma_n)] \ ,$$
$$W_L = 1 \quad \text{for } \epsilon_n \gg 0 \ , \qquad (23)$$

that is, for overbarrier transitions, and

$$W_e = 2\pi\gamma_n^{2\gamma_n}\exp(-2\gamma_n)/\Gamma(\gamma_n)^2\gamma_n \ ,$$
$$W_L = \pi\frac{F_{n_i n_f}(\xi_0,\xi_c)^2}{2^{n_i+n_f}n_i!n_f!} \times\exp[-(n_i-n_f)^2 h\nu/E_r]\exp(-E_r/h\nu) \quad \text{for } \epsilon_n \ll 0 \qquad (24)$$

for subbarrier transitions. Here Γ is Euler's gamma function, while

$$F_{n_i n_f}(\xi_0,\xi_c) = \xi_0 H_{n_i}(\xi_c)H_{n_f}(\xi_c-\xi_0) - 2n_i H_{n_i-1}(\xi_c)H_{n_f-1}(\xi_c-\xi_0) + 2n_f H_{n_i}(\xi_c)H_{n_f-1}(\xi_c-\xi_0) \ , \qquad (24')$$

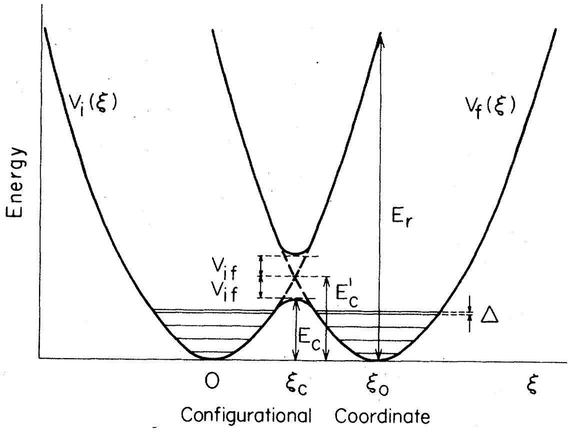

FIG. 1. General potential-energy profile along the relaxation coordinate believed to properly describe a dipolar reorientation transition. The diabatic potentials labeled V_i and V_f relate to the initial and final electronic states, respectively. Because of the electron-exchange interaction, V_i and V_f split by $2|V_{if}|$ at the crossover energy E_c' to give rise to lower and upper adiabatic potential surfaces, as shown by the solid lines. Accordingly, the diabatic curves are extrapolated by dashed lines near the crossover. Far from crossover, however, the corresponding diabatic and adiabatic branches practically coincide with each other. A barrier of magnitude $E_c = E_c' - |V_{if}|$ forms on the lower adiabatic surface. If the splitting is large, it is this barrier that confines the reorientation rate and the transition is called adiabatic. For very small splittings, however, the chance that the system might not change its electronic state during a hopping attempt is high, rendering the relaxation rate, now termed nonadiabatic, very low. In this way, low barriers E_c for tunneling do not always imply high relaxation rates. E_r is the lattice reorganization energy, Δ is the vibronic splitting.

H_m being the Hermite polynomials of mth order. As is customary, a reduced lattice coordinate

$$\xi = (M\omega/\hbar)^{1/2}q \qquad (25)$$

has been used to put (24) in a more compact form. ξ_0 and ξ_c stand for the positions of the minima of $V_f(\xi)$ and of the $V_i(\xi)\rightarrow V_f(\xi)$ crossover, respectively, relative to the configuration of the $V_i(\xi)$ minimum at $\xi=0$, Fig. 1.

The electronic transfer is called *adiabatic* for $\gamma_n \gg 1$ ($W_e=1$) and *nonadiabatic* for $\gamma_n \ll 1$ ($W_e \ll 1$); otherwise it is not *adiabatic*. Adiabaticity is mainly controlled by the magnitude of the electron-exchange integral V_{if}.

IV. RELAXATION OF ON-CENTER DIPOLES

In all the actual cases to be considered in this section the equilibrium positions q_i and q_f of the potential energy wells are regular orientational positions, while the component defects of the dipole remain in regular lattice sites. These *on-center* dipoles apparently reorientate under the conditions of case (i) of Sec. II. Because of $q_f=-q_i$, the electron-phonon coupling is phase shifted at 180 °C for the two otherwise equivalent electronic states i and f. Namely, the average force (coupling) coefficient $b=b_i=-b_f$ from (12), even though of the same magnitude, is of the opposite sign for i and f. Physically, the promoting mode, while tending to push the rotating entity out of site q_i thereby causing, e.g., extension at that site, aims at placing it in site q_f, causing compression there. Consequently, the diabatic parabolas are

$$V_i(q) = \tfrac{1}{2}M\omega^2q^2 + bq + E^0 \ ,$$
$$V_f(q) = \tfrac{1}{2}M\omega^2q^2 - bq + E^0 \ , \qquad (26)$$

with equilibrium positions at $q_{i,f} = \mp b/M\omega^2$ ($b>0$), which are symmetric relative to the crossover coordinate at $q=0$. Furthermore, if the respective electron clouds in states i and f are displaced at R when the lattice coordinate is at crossover q_c, the electron-exchange integral V_{if} will be generally proportional to $\exp(-\text{const}\times R)$.[7] The zero-point transition rate of a *nonadiabatic* process is also proportional to $\exp(-\text{const}\times R)$,

$$k_{if}(0) = \nu W_e(0)W_L(0) = 2\pi\gamma_0\nu\pi(M\omega^2/h\nu)(q_f-q_i)^2\exp(-E_r/h\nu) \propto V_{if}^2 \ , \qquad (27)$$

as it follows from (24) and (24') at $n_i=n_f=0$.

Examples of on-center dipolar defects are the IV dipoles formed by an aliovalent impurity ion and the compensating vacancy. Such defects can form in both the cationic and anionic sublattices. For the time being there seems to be no experimental evidence whatsoever for the occurrence of quantal effects in the orientational behavior of the dipoles, at least when the impurity is in its electronic ground state. Accordingly, the experimental data have mostly been interpreted in terms of purely classical overbarrier transitions. This implies barriers which are overly high, of the order of several tenths of an eV or more. However, lower barriers have been revealed when the impurity is in its excited electronic states, permitting much easier reorientation.[8,9] Apparently more experiments are needed to unravel eventual quantal effects during photoinduced reorientation. Another notorious example is the type-I F_A center in its various charge states.[10] Here too, quantal effects may be expected to occur at low temperatures in the excited state of the F_A electron. However, there certainly is a dipolar type which does exhibit a quantum-mechanical reorientation at low temperatures. It forms when a substitutional molecular ion with an intrinsic electric dipole moment, such as OH^-, occupies a regular lattice site. This is a $\langle 100 \rangle$-oriented molecular dipole in the alkali-halide lattice.

A further attempt will be made to compare the RRA formalism with what has been found experimentally for the OH^- dipoles.[11] Before all, the optical relaxation time $\tau_{\text{rel}}=(6k_{if})^{-1}$ in several hosts has been found to vary as $\exp(+\text{const}\times\alpha)$ with the interionic separation α at low temperature. The conventional explanation is based on the notion of a *phonon-dressed dipole,* an elastic dipole creating large noncubic lattice distortion around itself. This increases the effective moment of inertia of the entity thus hindering its reorientational motion. The elastic dressing effect increases with the size of the host anion rendering the relaxation rate lower.[11] Assuming a *nonadiabatic* reorientational transition for the OH^- ion, the RRA would rather ascribe the observed dependence on the host material to corresponding variations of the electron-exchange term V_{if}, in accordance with (27), provided R constitutes some constant portion of the interionic distance. However, this latter statement has to be elaborated further.

The overall temperature dependence of τ_{rel} has also been measured experimentally.[12] Now, the theoretical rate (17) in each case is fitted to the experimental data by adapting the values of three parameters: ν, E_r, and V_{if}. A discrete-level strongly quantized system was assumed to make direct use of Eqs. (23) and (24). To obtain the best fits to the lower-temperature portions of the experimental curves, a simple model had to be adopted allowing for the same vibrational frequency $\nu=2.66\times10^{11}$ Hz for all the hosts. This frequency is therefore characteristic of the dipole, not the host. Similar assumptions were made regarding the lattice reorganization energy E_r and the crossover energy E_c'. The following values were found appropriate: $E_r=6$ meV, $E_c'=1.5$ meV, independent of the host type. In other words, the relaxation is assumed to occur within a potential energy configuration (in the double-well analysis), which is almost identical for all the host materials, with only the electron-exchange integral V_{if} differing from host to host, according to Table I. V_{if} is seen to generally decrease as the interionic distance is increased. The overall result of this test of RRA applicability to the OH^- relaxation-time data is shown in Fig. 2. However, the agreement between theory and experiment is not as good at temperatures in excess of 10 K. The RRA curve apparently lacks steepness which may well result from the actual inclusion of another vibrational mode in that range. This would imply that the present single-oscillator model of Sec. II may be oversimplified.

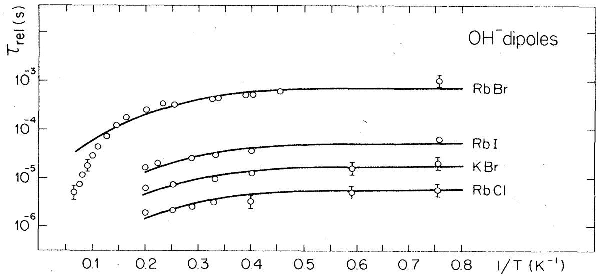

FIG. 2. Relaxation time τ_{rel} versus reciprocal temperature for OH^- molecular ions in several alkali halides. The circles are experimental data (Ref. 12), while the RRA best fits are represented by solid lines. These differ from each other only in that the electron-exchange interaction varies from host to host in a nonadiabatic electron transfer.

On the other hand, however, the good RRA fits below 10 K may give a clue for understanding the physical significance of the above independent-of-the-host diabatic-well approach to the OH^- relaxation. Indeed, it suggests that the exchange term V_{if} alone varies as the anion radius is changed. Increasing the size of the anion, however, would mean a larger separation from the six nearest-neighbor cations surrounding the dipole. The wavefunction overlap in V_{if} is between two physically equivalent electronic states at the saddle-point (crossover) configuration. At this point the valent OH^- electron is shared between a dissipating $|\, i,q_c \rangle$ state and an incipient $|\, f,q_c \rangle$ state. For a given $\langle 100 \rangle$-orientational position of the dipole, e.g., at $q=q_i$, that electron may overlap considerably with the nearby $\langle 100 \rangle$ cation to secure the dipole-lattice coupling. At the saddle point the overlap is divided in half between two such cations, the $\langle 100 \rangle$ and, say, the $\langle 010 \rangle$, if the dipole is to perform a reorientational hopping to a neighboring $\langle 010 \rangle$ position at $q=q_f$. This division of the electron cloud between the two cations materializes through electron tunneling and it is intuitively clear that the tunneling distance, proportional to R, should be a certain portion of the $\langle 100 \rangle$-to-$\langle 010 \rangle$ ionic separation, and thereby, of the lattice constant. As a result, the smaller the interionic separation, the higher the hopping expectancy. The exponential factor $\exp(-\text{const}\times\alpha)$ due to V_{if} will undoubtedly be the main α-dependent term in Eq. (27) for the low-temperature rate

TABLE I. Interionic separation α and fitted values of the electron-exchange integral V_{if} for OH^- relaxation in several alkali halides.

Host	RbCl	KBr	RbBr	RbI
α (Å)	3.291	3.298	3.445	3.671
V_{if} (eV)	7.7175×10^{-7}	4.3951×10^{-7}	6.8681×10^{-8}	2.5725×10^{-7}

constant. These simple considerations may help to reveal the physics of a reorientation process. However, before doing that they surely have to be substantiated by detailed quantum-mechanical calculations. We are unable at this time to arrive at any quantitative conclusions regarding the numerical value of the constant in the above exponent.

To conclude, the present model assumes that the OH^- dipole substituting for a host anion couples only electronically (through V_{if}) to the lattice, to a first approximation, all its remaining reorientational characteristics (ν, E_r, E_c') being intrinsic of the dipole, not the host. The promoting mode of frequency ν is a local mode which couples relatively weakly to the lattice modes to secure the redistribution of surplus energy during relaxation.

V. OFF-CENTER DIPOLES

Following Fowler,[13] it is the pseudo-Jahn-Teller effect that renders an off-center impurity ion. Now, a phonon coupling of sufficient strength mixes two different-parity electronic states, say $|s\rangle$ and $|p\rangle$. This leads to the following adiabatic surfaces relevant to the reorientational problem:

$$E_L(q)=\tfrac{1}{2}[M\omega^2q^2-(4G^2q^2-E_{sp}^2)^{1/2}] ,$$
$$E_U(q)=\tfrac{1}{2}[M\omega^2q^2+(4G^2q^2-E_{sp}^2)^{1/2}] . \tag{28}$$

Here G is the coupling constant, while E_{sp} is the energy separation between $|s\rangle$ and $|p\rangle$ at $q=0$. The corresponding diabatic surfaces obtain at $E_{sp}=0$.

Comparing with (15), (16), (26), and (20), one obtains the formal conversion to the RRA parameters ($b=G$):

$$E_r=4E_{JT} ,$$
$$E_c'=E_{JT} , \tag{29}$$
$$V_{if}=\tfrac{1}{2}|E_{sp}| ,$$

where

$$E_{JT}=G^2/2M\omega^2 \tag{30}$$

is the Jahn-Teller energy. The condition that a diagram such as the one in Fig. 1 results at all is

$$E_{JT}>\tfrac{1}{4}|E_{sp}| . \tag{31}$$

With the conversion formula (29) in mind, one can apply the RRA to calculating the relaxation rates of off-center dipoles. This would require the knowledge of three parameters: ν, E_{JT}, and E_{sp}. However, this would merely be a formal calculation before RRA is further elaborated to physically adapt to the problem.

A prominent example of an off-center impurity dipole which reorientates quantum mechanically at low temperatures is the Ag^+ ion in the rubidium salts. The off-center Ag^+ gives rise to a $\langle 110\rangle$ dipole with predominantly 90° reorientation over 60° reorientation. This has been attributed to dressing by a strong E_g lattice distortion allowing an easy rotation in a $\{100\}$ plane, while inhibiting a change of that plane by 60° reorientation.[11] For this reason the 60° reorientation occurs via classical overbarrier transitions mainly, due to the higher barriers involved. The RRA may possibly suggest its own clue to an explanation based on substantial differences in the E_{sp} energy for the two reorientational angles, provided both transitions are regarded as nonadiabatic.

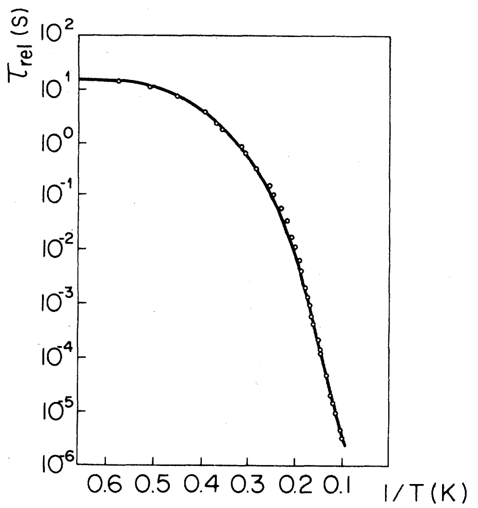

FIG. 3. Relaxation time τ_{rel} versus reciprocal temperature for off-center Ag^+ in RbBr (90° reorientation). The circles are experimental points (Ref. 14), while the solid line is the RRA best fit for a nonadiabatic electron transfer (Ref. 15).

Assuming $\tau_{rel}=(4k_{if})^{-1}$, a very good agreement has been found between experiment[14] and theory[15] for a 90° reorientation in RbBr, as shown in Fig. 3. The fitted values of the free parameters are presented in Table II. The resulting value of the Jahn-Teller energy E_{JT} is about 10^{-2} eV, while $|E_{sp}|$ is only about 10^{-4} eV. Consequently, condition (31) holds good.

VI. CONCLUDING DISCUSSION

Stressing that the main aim of this paper has been to *suggest* an alternative approach to the relaxation times of dipolar defects in alkali halides, it seems safe to conclude that the goal has been achieved. While the usual treatment of relaxation phenomena is confined to considering adiabatic transitions only, disregarding the upper adiabatic surface in Fig. 1, the present reaction-rate theory allows for an active role of that surface through the inclusion of the electron-exchange interaction, thus covering *all* kinds of transitions between the adiabatic and nonadiabatic extrema. That such an approach is not unreasonable is indicated by the good agreement between experiment and theory exemplified above, revealing that nonadiabatic dipolar relaxation may not be a rare occurrence at all.

TABLE II. Fitted parameters for off-center Ag^+ reorientation in RbBr through 90° hopping: angular frequency ω, reorganization energy E_r, resonance energy V_{if}, barrier height E_c, and tunneling splitting $\Delta=(h\nu/\pi)W_L^{1/2}$.

ω (s^{-1})	E_r (eV)	V_{if} (eV)	E_c (eV)	Δ (cm^{-1})
2.127×10^{12}	0.04	9.09×10^{-5}	0.01	0.08

It should be emphasized that the present reaction-rate formalism is applicable to systems composed of harmonic oscillators, provided the relaxation coordinate is dynamically separable from the domain of all nuclear coordinates. Undoubtedly, none of these conditions is being violated by the model Hamiltonian of Sec. II. However, the reaction-rate theory has a more general significance and is by no means confined by the limitations imposed by the model, which was simplified merely in order to stress physics and make the mathematics less formidable.

At the same time, not all the quantitative aspects of the present reaction-rate approach to the dipolar relaxation have been worked out. Such is, for instance, the quantum-mechanical justification of the $V_{if} \propto \exp(-\text{const} \times \alpha)$ statement, so far only intuitively deduced. Nevertheless, RRA can be presumed inherently applicable to the on-center dipoles. Another problem awaiting physical elaboration is the approach to the off centers dealt with a bit schematically at present. Nevertheless, there seems to be no immediate reason as to why Fowler's mixing-up Hamiltonian[13] should not be included in a model energy operator of the type in Sec. II to eventually lead to the anticipated splitting of magnitude $|E_{sp}|$, as required by the pseudo-Jahn-Teller proposition. In this way, the present paper, while falling short of providing a solution to all the problems raised, can be expected to stimulate further research.

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