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OFF-CENTER DIPOLES IN ALKALI HALIDES: A REASSESSMENT

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ABSTRACT

Two "two-site" transition Hamiltonians are considered with regard to the off-center dipolar problem. One of these (H_S) effects static mixing of two degenerate electronic states to allow for a finite probability of transferring a dipole between neighboring reorientational sites. With the other (H_D), two states, split-off in energy, are mixed by coupling to a promoting mode. On solving the eigenvalue problem in the adiabatic approximation, both H_S and H_D lead to similar multiwell vibronic potential-energy surfaces, composed of lower (E_L) and upper (E_U) parts, whose extrema along the promoting-mode coordinate are displaced relative to each other, so that the minima on E_U occur where do the maxima on E_L, and viceversa. A single-frequency reaction-rate approach is applied to deriving the relaxation rate

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of horizontal energy-conserving transitions between any two neighboring reorientational sites. The resulting formula depends on three adjustable parameters: promoting-mode frequency, lattice-reorganization energy, and saddle-point energy splitting between E_U and E_L. The theoretical rate is then fitted to experimental data from various sources on off-center dipoles in several host crystals to obtain relevant values of the above parameters. Based on the obtained energy splittings, it is concluded that while H_D pertains to creating the off-centered displacements, H_S more likely applies to the reorientational motion. From the fitted-parameters data, the intrawell separations, the off-center dipole moments, the electron-phonon coupling constants, and the vibronic-level splittings are also calculated. These are found to compare reasonably well with experimental data, where available.

RESUMEN

Se resuelve el problema del dipolo "fuera de centro", considerando dos Hamiltonianos de transición de "doble-sitio". El Hamiltoniano (H_s) representa la mezcla estática de dos estados electrónicos degenerados, permitiendo determinar una probabilidad finita de transición entre posibles sitios de reorientación. El segundo Hamiltoniano (H_D), mezcla dos estados de Energía desdoblados, acomplándolos a un modo de oscilación promotor. La obtención de sus valores propios, utilizando la aproximación adiabática, conduce a superficies de energía vibracional parecidas. Estas superficies de pozos múltiples de potencial están compuestas de una parte baja E_L y otra parte alta E_U, cuyos extremos a lo largo de la coordenada del modo promotor se encuentran desplazados uno respecto al otro, en forma tal que el mínimo de E_U coincide con el máximo en E_L, y viceversa. Se usa el método de la "Razón de reacción monocromática" para derivar la razón de relajación de las transiciones de energía entre cualesquiera posibles sitios de reorientación. La fórmula obtenida depende de tres parámetros ajustables: La frecuencia del modo promotor, la energía de rearreglo de la red, y la separación entre E_U y E_L en el punto crítico (saddle-point). Los resultados obtenidos a través del modelo teórico se ajustan a los datos experimentales reportados para diferentes redes en las que se ha realizado estudios de dipolos "fuera de centro". En base a los valores obtenidos para la separación entre E_U y E_L se concluye que mientras D_H genera los desplazamientos del dipolo "fuera de centro", H_S se relaciona al movimiento de reorientación. De los parámetros ajustados también se pueden calcular: la separación entre los pozos de potencial, el momento del dipolo "fuera de Centro", las constantes de acoplamiento electrón-Fonón, y las separaciones entre niveles vibracionales. Se encuentra que éstas se comparan razonablemente bien con los datos experimentales con los que se cuenta.

1. INTRODUCTION

Off-center isovalent impurity ions in crystalline materials constitute an appealing object for solid state physics. Ever since their original discovery in 1965(1), it has been appreciated that these species can be used as model systems for studying atomic tunneling and quantum diffusion in condensed matter(2). This is largely due to the off-center ion's ability to perform reorientational transitions between equivalent positions around the regular lattice site involving low potential-energy barriers in-between. The purpose of the present paper being far from giving any comprehensive survey of the matter, the reader is referred to the available review and original literature(3,4,5).

We shall focus instead on the physics that leads to favoring an off-center position over a regular lattice site. From a classical point of view this is the interaction between the charge of the foreign ion and the electric dipole moment induced on the neighboring ions, the point-ion force not acting to displace that ion from the on-center position(6). The off-centered position is then stabilized by the balance between the polarization force and the repulsion arising from the overlap of the electronic charge clouds of adjacent ions according to the Pauli principle. Clearly, the off-center displacement would be the larger, the smaller the foreign ion's radius and the higher the polarizability. However, because of the close-packed structure, the off-center occurence is not a large effect in alkali halides. The equilibrium displacement from an on-center position gives rise to an electric dipole moment of the resulting structural entity that usually amounts to the order of 1 eÅ.

The quantum-mechanical explanation is based on the notion of the pseudo-Jahn-Teller effect (PJTE)(2,7). An equilibrium displacement from the on-centered position of an impurity ion in a degenerate electronic state may lead to a self-consistent removal of the degeneracy. Consequently, the circumstantial Jahn-Teller distortion will now be replaced by a PJTE. A phonon coupling of sufficient strength then mixes the resulting split-off states, say i and j, to promote the reorientational motion of the off-center entity. The success of calculations based on the classical model may be attributed to the fact that the shell model, designed to deal with the induced polarization, is approximately equivalent to the i-j admixture of the vibronic model. As long as that admixture is the essential physics, the classical calculations should do well(7).

An alternative quantum-mechanical treatment can be based on the notion of a reorientation-promoting mode that couples phase-shifted at 180° to two physically-equivalent electronic states i and j, corresponding to two neighboring equilibrium sites of an off-center ion(8). i and j split off at the transitional lattice configuration because of the electron-transfer interaction between the above sites.

The purpose of the present investigation is to reassess the quantum-mechanical approach to the off-center problem. For this purpose comparison of the theoretical predictions with available experimental data will be considered to be the crucial checkup of the virtues of either conceivable vibronic model. To simplify the theory so as to stress physics and make mathematics less formidable, single-frequency models will be discussed in either case. The authors are fully aware of the fact that such a simplification, even though permissible in some, may be too crude in other more complex experimental situations, and that it may not at all satisfy the taste of readers for more sophisticated mathematical formulae. In addition, the models to be considered will not at all incorporate any promoting mode - accepting modes interaction terms. This is by no means an absurd physical statement, for the relaxation of the excess energy through vertical vibronic transitions, made possible by these interactions, will be assumed sufficiently fast. Accordingly, the present analysis will deal with only a part of the overall problem, namely, the one of the horizontal tunneling transitions that lead to the redistribution of populations between neighboring potential-energy wells.

2. HAMILTONIAN

We consider a single isolated dipolar entity I embedded into a crystalline medium, regarded as a system of oscillators, each one associatted with a lattice ion in a given electronic state. The electronic state of the impurity will be assumed degenerate. The relevant Hamiltonian of the system is

$$H = H_e + H_L + H_{eL} \quad , \tag{1}$$

where

$$H_e = \sum \left\{\frac{1}{2}\,\vec{p}_e^{\,2}/m_e + V_e(\vec{r}_e, \tilde{0})\right) \quad , \tag{1'}$$

$$H_L = \sum \left\{\frac{1}{2}\,\vec{P}_1^{\,2}/M_1 + \frac{1}{2}\,M_1\omega_1^{\,2}q_1^{\,2}\right) + \dots \tag{1''}$$

and

$$H_{eL} = \sum \left(V_e(\vec{r}_e, q_1) - V_e(\vec{r}_e, \tilde{0})\right) \tag{1'''}$$

are, respectively, the electronic, lattice, and electron-lattice interaction energy operators. The sum in (1') is over all electronic coordinates $\vec{r}_e$ and momenta $\vec{p}_e$, in (1'') it is over the lattice coordinates q_1 and momenta $\vec{P}_1$, and (1''') sums over all $\vec{r}_e$ and q_1. The relevant masses are m_e (electronic) and M_1(nuclear), ω_1 are the oscillator's angular frequencies. $V_e(\vec{r}_e, q_1)$ is the electronic potential, and $\tilde{0}$ stands for the manifold of all $q_1 = 0$. The dots in (1'') will be discarded under the harmonicity-of-vibration assumption. For the reorientational transitions under consideration the interaction with the promoting mode at $q = q_I$ will be predominating, the remaining terms in (1) resulting in a constant contribution to the energy of the system will further be disregarded. This simplifies the Hamiltonian to give

$$H = H_e + H_{eI} + \frac{1}{2}\,\vec{P}_I^{\,2}/M_I + \frac{1}{2}\,M_I\omega_I^{\,2}q_I^{\,2} \quad . \tag{2}$$

Solving Schrödinger's equation

$$H\psi(\vec{r}_e, q) = E\psi(\vec{r}_e, q) \quad , \tag{3}$$

will further be made within the adiabatic approximation. Introducing

$$H_{AD} = H_e + H_{eI} + \frac{1}{2}\,M_I\omega_I^{\,2}q_I^{\,2} \quad , \tag{4}$$

the adiabatic Hamiltonian, we traditionally assume the total wave-function in (3) to factorize out into an electronic part $\psi(r_e, q_I)$, which only depends on q_I parametrically, and a nuclear component $\chi(q_I)$. Accordingly, Schrödinger's equation (3) splits into two eigenvalue equations, as follows:

$$H_{AD}\psi(\vec{r}_e, q_I) = E_t(q_I)\psi(\vec{r}_e, q_I) \tag{5}$$

and

$$\left(\frac{1}{2}\vec{P}_I{}^2/M_I + E_t(q_I)\right)\chi_{tn}(q_I) = E_{tn}\chi_{tn}(q_I) \quad . \tag{6}$$

Here t and n are the electronic and vibrational quantum numbers, respectively. Next, the static electronic states $\psi(\vec{r}_e, 0)$ will be defined as eigenstates of the electronic Hamiltonian H_e,

$$H_e\psi(\vec{r}_e, 0) = E_t^0\psi(\vec{r}_e, 0) \quad , \tag{7}$$

to find the adiabatic potential-energy surfaces as average values of (5) in the static states $\psi(\vec{r}_e, 0) = |t,0\rangle$. Assuming a linear coupling scheme confining to the first-order term in the expansion of H_{eI} in q_I, we obtain

$$V_{tt}(q) = \langle t,0|H_{AD}|t,0\rangle = \frac{1}{2}M\omega^2q^2 + b_{tt}q + E_t^0 \tag{8}$$

(subscript I thereon omitted), where

$$b_{tt} = \langle t,0|H_{eI}|t,0\rangle \tag{9}$$

is the diagonal matrix element of the first-order electron-phonon coupling operator. Equation (8) is that of a parabola whose minimum is at

$$q_t = -b_{tt}/M\omega^2 \quad . \tag{10}$$

For two different electronic states $t = i,j$ Eq. (8) defines two parabolae whose minima correspond to two neighboring reorientational sites.

These parabolae cross each other at

$$q_{ij} = (E_j^0 - E_i^0)/(b_{ii} - b_{jj}) \quad . \tag{11}$$

The energy difference between the minima of V_{jj} and V_{ii} is

$$Q = V_{ii}(q_i) - V_{jj}(q_j) = M\omega^2\left[\frac{1}{2}(q_j + q_i) - q_{ij}\right](q_j - q_i) \quad .$$

This is the "reaction heat" at 0°K. For a symmetric-well situation pertinent to the dipolarcase $Q = 0$, which gives

$$q_{ij} = \frac{1}{2}(q_j + q_i) \quad . \tag{12}$$

Eq. (8) gives but an approximate expression for the eigenvalues $E_t(q)$ of (4), since the static wavefunctions $|t,0\rangle$ differ considerably from their adiabatic counterparts $\psi(\vec{r}_e, q) = |t,q\rangle$ near the crossover point q_{ij}. Were it not the case, the diapole would have localized in one of the wells and no reorentational transitions between $E_i(q)$ and $E_j(q)$ would have been possible at all. On using the proper adiabatic eigenstates $|t,q\rangle$ the degeneracy at q_{ij} is lifted and the transitions made possible. It is to be stressed that the adiabatic formulation allows for the above transitions only because $|t,q\rangle$ are in fact quasi-stationary quantum states, being just approximate solutions to the Schrödinger equation (3).

Inasmuch as $|t,q\rangle$ are largely unknow, the relevant energy splitting at q_{ij} can be accounted for by considering appropriate models based on the static eigenstates $|t,0\rangle$, while modifying the adiabatic Hamiltonian (4). Physically the splitting results from the dipole-transfer interaction between $E_i(q)$ and $E_j(q)$ due to the mixing-up of states $|i,0\rangle$ and $|j,0\rangle$. We shall next consider two such models based on static and dynamic mixing types, respectively. In both of them solutions of the eigenvalue equation (5) will be sought in terms of a linear combination

$$|t,q\rangle = A|i,0\rangle + B|j,0\rangle \quad , \tag{13}$$

where $|1,0\rangle$ and $|j,0\rangle$ will be assumed orthonormal.

2.1 *Static mixing*

The relevant Hamiltonian (4) is modified in a two-site formulation to read

$$H_{AD} = H_e + H_{eI} + \frac{1}{2} M\omega^2 q^2 + K_{ij}(q)(|i,0\rangle\langle j,0| + |j,0\rangle\langle i,0|) \quad . \quad (14)$$

From (14) we get

$$V_{ij}(q) = \langle i,0|H_{AD}|j,0\rangle = b_{ij}q + K_{ij}(q) \qquad , \qquad (15)$$

where

$$b_{ij} = \langle i,0|H_{eI}|j,0\rangle \qquad (16)$$

is the off-diagonal matrix element of the linear electron-phonon coupling operator. Next we solve Schrödinger's equation (5) with H_{AD} from (14) and using (13) to obtain the following eigenvalues:

$$\begin{aligned} E_{U/L}(q) &= \frac{1}{2} (V_{ii}(q) + V_{jj}(q) \pm ((V_{ii}(q) - V_{jj}(q))^2 + 4|V_{ij}|^2)^{\frac{1}{2}}) \\ &= \frac{1}{2} (M\omega^2 q^2 + (b_{ii} + b_{jj})q + (E_i^0 + E_j^0) \pm \qquad (17) \\ &\qquad ((b_{ii} - b_{jj})^2 (q - q_{ij})^2 + 4|V_{ij}|^2)^{\frac{1}{2}}) \qquad , \end{aligned}$$

where $V_{ii}(q)$, etc. as given by Eq. (8) are the adiabatic surfaces. $E_U(q)$ and $E_L(q)$ define two adiabatic surfaces, upper and lower, respectively. They split by $2|V_{ij}(q_{ij})|$ at the crossover coordinate.

For $b_{ii} = -b_{jj}$, $q_i = -q_j$, and from (12) and (11) we get $q_{ij} = 0$ and $E_i^0 = E_j^0$. Now,

$$E_{U/L}(q) = \frac{1}{2} M\omega^2 q^2 + E_i^0 \pm \frac{1}{2} (4b_{ii}{}^2 q^2 + 4|V_{ij}|^2)^{\frac{1}{2}} \quad . \qquad (18)$$

Physically, this is the case when the promoting mode, in driving the dipole from site i to site j, produces compression at j, while causing extension at i. Consequently, the average force exerted by the surrounding lattice on the outer shells of the impurity ion is dephased at 180° for i and j. Note that the electronic states $|i,0>$ and $|j,0>$ are degenerate with the same energy E_j^0. On going to $|t,q>$ the degeneracy is lifted because of the electron-transfer interaction at crossover.

Because of the symmetry hermiteicity can be assumed so that $|V_{ij}|^2 = V_{ij}{}^2$. The static mixing parameter

$$K_{ij}(q) = V_{ij}(q) - b_{ij}q$$

does not contain any electron-phonon interaction terms. In a donor-acceptor model $2|K_{ij}(q_{ij})|$ is simply the tunneling splitting of the electron-energy level of a DA pair proportional to the square-root electron-transfer probability W_e at crossover$^{(9)}$

$$|K_{ij}(q_{ij})| = (h\nu_e/\pi)W_e^{\frac{1}{2}} \quad , \tag{19}$$

where ν_e is the electron beating-frequency. Assuming coulombic potentials, $K_{ij}(q_{ij})$ has been calculated within the BWK quasiclassical approximation to give$^{(10)}$

$$|K_{ij}(q_{ij})| = (h\nu_e/\pi)\exp{-\alpha(R)} \quad , \tag{20}$$

where

$$\alpha(R) = 4R_0(-2m_eE_e/\hbar^2)^{\frac{1}{2}} \left[\frac{E(k)}{1 - k^2} - K(k)\right] \quad , \tag{21}$$

with

$$R_0 = -e^2/\varepsilon E_e \quad ,$$

$$k = (1 - 4R_0)R)^{\frac{1}{2}} \quad .$$

K(k) and E(k) are the complete elliptic integrals of first and second kind, respectively, of modulus k, ε is the dielectric constant of the host crystal. The electron frequency is given by

$$\nu_e = \varepsilon(-E_e)^{\frac{3}{2}}/2\pi e(2m_e)^{\frac{1}{2}} \tag{22}$$

E_e is the electron energy at crossover.

Generally, the dependence of $K_{ij}(q)$ on the promoting-mode coordinate q is unknown. It depends on the mode symmetry in the particular case. Nevertheless, K_{ij} can be expected to be significant at the crossover only, and to drop rapidly on both sides of it. On the other hand, the dynamic-mixing parameter (16) will be assumed small, $|b_{ij}| \ll |b_{ii}|$, in a static-mixing scheme. Under these conditions $E_U(q)$ and $E_L(q)$ will tend asymptotically to the corresponding diabatic branches far from crossover. The extrema of the adiabatic surfaces are easily found from (18) then. There is one at $q = 0$ (minimum of $E_U(q)$ and maximum of $E_L(q)$), as well as two additional extrema (minima) on $E_L(q)$ at q_i and q_j ($q_i = -q_j$), respectively. The maximum at $q = 0$ (the crossover) on $E_L(q)$ is that of the barrier between the two reorientational sites at q_i and q_j. The barrier energy (at $q = 0$) is $E_b' = E_i^0 - |K_{ij}(0)|$. The barrier height relative to the minima on $E_L(q)$ is $E_b = (1/2)M\omega^2 q_i^2 - |K_{ij}(0)|$.

2.2. *Dynamic mixing*

Now a promoting mode of sufficient strength mixes the two different-parity electronic states, $|i,0\rangle$ and $|j,0\rangle$, already split in energy by $E_{ij} = E_i - E_j$. Following Fowler(7), the relevant adiabatic Hamiltonian of the system is

$$\begin{aligned} H_{AD} = \frac{1}{2} E_{ij}(|i,0\rangle\langle i,0| \; - \; |j,0\rangle\langle j,0|) + \frac{1}{2} M\omega^2 q^2 \; + \\ g_{ij} q(|i,0\rangle\langle j,0| \; + \; |j,0\rangle\langle i,0| \qquad , \end{aligned} \tag{23}$$

where g_{ij} is a linear-coupling constant. Solving again Schrödinger's equation (5) by means of (13) we obtain the eigenvalues

$$E_{U/L}(q) = \frac{1}{2}\left(M\omega^2 q^2 \pm (4g^2_{ij}q^2 + E^2_{ij})^{\frac{1}{2}}\right) \tag{24}$$

Equation (24) resembles (18) except for the fact that E_{ij} is independent of q, while K_{ij} is not. The extrema of (24) are: one at $q = 0$ (minimum of $E_U(q)$ and maximum of $E_L(q)$), as well as two minima on $E_L(q)$ at

$$q_{i/j} = \mp((4g_{ij}^2/2M\omega^2)^2 - E_{ij}^2)^{\frac{1}{2}}/2g_{ij} \quad . \tag{25}$$

The condition for the existence of the latter extrema is

$$E_{JT} > \frac{1}{4}\,|E_{ij}| \quad , \tag{26}$$

where

$$E_{JT} = g_{ij}^2/2M\omega^2 \tag{27}$$

is the Jahn-Teller energy. E_{JT} should, therefore, exceed a quarter of the energy splitting between $|i,0>$ and $|j,0>$ for the off-center sites to occur at q_i and q_j. In the absence of splitting ($E_{ij} = 0$) the dipole stabilizes in one of the wells, say i, and no transitions to well j are possible.

2.3. *Static versus dynamic mixing*

Clearly, while the Jahn-Teller distortion is the main factor that determines the off-center displacement of the impurity ion, it is the electron-energy splitting $|E_{ij}|$ which makes finite the probability of reorientational transitions between neighboring off-center sites. In the static-mixing model the off-center sites are determined by the nonmixing electron-phonon interaction, while the transfer probability is finite because of the electron-tunneling splitting $2|K_{ij}(q_{ij})|$ at crossover. Comparing Eqs. (18) and (24) reveals the formal conversion relationship between the corresponding static and dynamic parameters in the two cases:

$$|K_{ij}| \to \frac{1}{2}\,|E_{ij}|$$

$$|b_{ii}| \to |g_{ij}| \quad , \tag{28}$$

$$E_R = E_{JT} \quad ,$$

where

$$E_R = \frac{1}{2} M\omega^2 (q_i - q_j)^2 \tag{29}$$

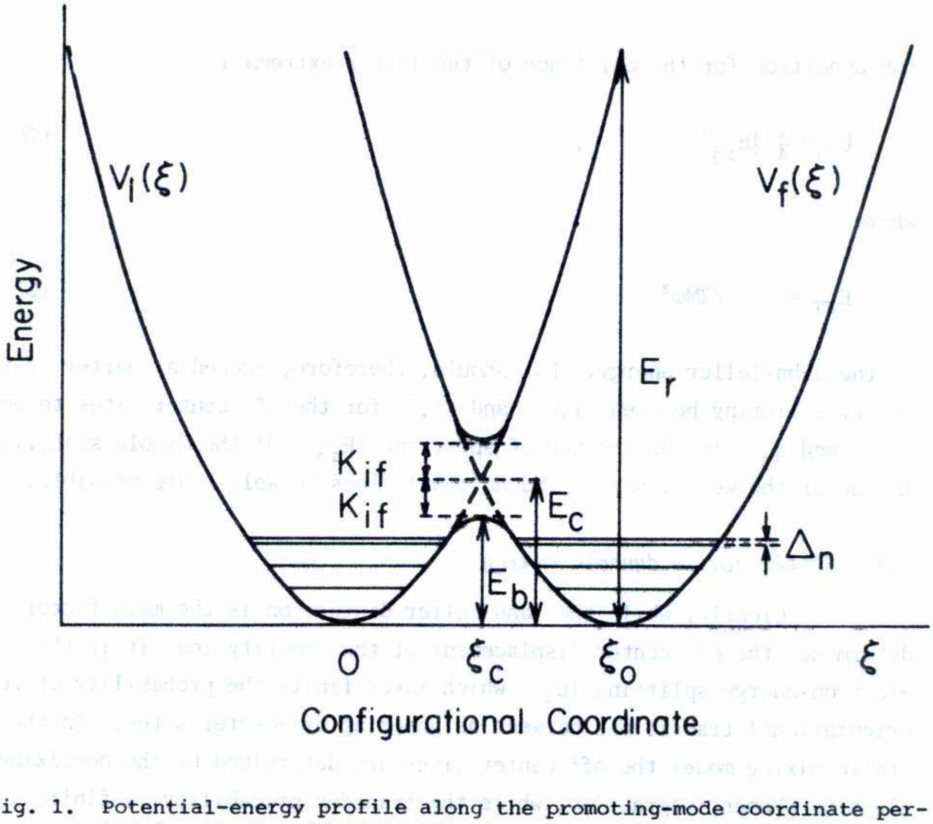

Fig. 1. Potential-energy profile along the promoting-mode coordinate pertaining to the off-center dipole motion. The upper and lower adiabatic surfaces are sectioned by solid lines. The diabatic surfaces are depicted by dashed lines in the vicinity of the crossover configuration only; far from the crossover these coincide with the corresponding adiabatic branches. Transitions between the two wells are only possible at finite crossover splitting between the adiabatic energies. See the text for further details.

is the lattice-reorganization energy of any pair of diabatic parabolae. It should be stressed, however, that different physics is involved in the two cases. Inasmuch as the two models lead to two pairs of adiabatic surfaces each which are experimentally indistinguishable, preference to one or the other can only be given based on the obtained values of the parameters (28). The latter can be determined by measuring the rate of attaining thermal equilibrium after a population difference between reorientational sites has been created by some initial external perturbation. The potencial-energy profile along the promoting-mode coordinate ξ is exemplified in Fig. 1 applying to both the static and dynamic mixing models.

3. RELAXATION RATE

The overall two-site rate of energy-conserving horizontal dipolar relaxation transitions at the quantized energy levels of the potential-energy profile composed of $E_L(q)$ and $E_U(q)$ along the promoting-mode (relaxation) coordinate q will be calculated using the reaction-rate method$^{(11)}$, as done elsewhere$^{(8,12)}$. The reaction-rate constant is given by

$$k_{ij}(T) = 2\nu\sinh(h\nu/2k_BT) \sum_n W_L(E_n)W_e(E_n)\exp-(E_n/k_BT) \quad , \qquad (30)$$

where $W_L(E_n)$ and $W_e(E_n)$ are, respectively, the probabilities for lattice rearrangement and electron transfer at level E_n, ν is the mode frequency, and T is the temperature. h and k_B are Planck's and Boltzmann's constants, respectively. For overbarrier transitions ($E_n >> E_b$),

$$W_L(E_n) = 1 \quad , \qquad (31)$$

$$W_e(E_n) = 2(1 - \exp-(2\Pi\gamma_n))/(2 - \exp-(2\Pi\gamma_n)) \quad , \qquad (32)$$

while for subbarrier ones ($E_n << E_b$)

$$W_L(E_n) = \Pi \frac{F_{nn}(\xi_0,\xi_c)^2}{2^{2n}(n!)^2} \exp-(E_R/h\nu) \quad ,$$

$$W_e(E_n) = 2\pi(\gamma_n)^{2\gamma_n} \exp-(2\gamma_n)/\Gamma(\gamma_n)^2\,\gamma_n \quad . \tag{32}$$

Here

$$\gamma_n = (K_{ij}{}^2/2h\nu)(E_R|E_n - E_c|)^{-\frac{1}{2}} \quad , \tag{33}$$

where $E_c = E_b + |K_{ij}|$ is the crossover energy of the diabatic parabolae relative to their common minima, $E_R = 4E_c$. The quantized energy levels $E_n = E_{nt}$ are, strictly speaking, to be obtained as eigenvalues of the vibronic equation (6) with $E_t(q) = E_{U/L}(q)$. These will, however, be approximated by the harmonic-oscillator eigenvalues,

$$E_n = h\nu\left(n + \frac{1}{2}\right) \quad , \tag{34}$$

along the entire energy axis. Relaxation of the excess energy during the reorientational process occurs through vertical intralevel transitions, which, as stated before, will be considered fast enough to give that energy away to the lattice by virtue of strong promoting-mode -accepting-modes coupling. In (32)

$$F_{nn}(\xi_o,\xi_c) = \xi_0 H_o(\xi_c)H_n(\xi_c-\xi_0) - 2n\,H_{n-1}(\xi_c)H_{n-1}(\xi_c-\xi_0) + 2n\,H_n(\xi_c)H_{n-1}(\xi_c-\xi_0) \tag{35}$$

is a binary form composed of Hermitian polynomials $H_n(\xi)$,

$$\xi = (M\omega^2/h\nu)^{\frac{1}{2}}\,(q - q_i) \tag{36}$$

is a dimensionless mode coordinate, ξ_0 and ξ_c are those coordinates, corresponding to the minimum of well j ($q_j - q_i = 2q_j$) and the crossover point ($q_{ij} - q_i = -q_i$), respectively, all relative to the minimum of well i at q_i.

Eq. (30) is often presented in an equivalent form:

$$k_{ij}(T) = \chi(T)\ (2k_BT/h\nu)\sinh(h\nu/2k_BT)\nu\exp-(E_b/k_BT) \tag{37}$$

$$\chi(T) = \sum_n W_L(E_n)W_e(E_n)\ \exp-((E_n - E_b)/k_BT)\Delta(E_n/k_BT) \quad . \tag{38}$$

$\chi(T)$ is a quantum or adiabaticity correction to the rate constant, presented otherwise in its conventional classical form. For adiabatic transitions ($W_e = 1$) around Christov's characteristic temperature T_c, $\chi(T)$ is well approximated by

$$\chi(T) = (\pi/2)(T_c/T)/\sin((\pi/2)(T_c/T)) \quad , \tag{39}$$

for $\frac{1}{2}T_c < T < \infty$, at which temperature T_c the overall rate is due to equal-weight overbarrier (classical) and subbarrier (quantal) transitions. For a strongly nonadiabatic process ($W_e \ll 1$) occuring through classical overbarrier jumps ($W_L = 1$), $\chi(T)$ has been shown to be (for a weakly-quantized system ($h\nu \ll E_b$)$^{(12)}$

$$\chi(T) = 2\ (K_{ij}{}^2/h\nu)(\pi^3/E_Rk_BT)^{\frac{1}{2}} \tag{40}$$

for $|K_{ij}| \ll E_b$.

Although all the above equations in Section 3 have been presented in terms of the quantities relevant to the static-mixing model, the transition to the dynamic-mixing counterparts can easily be performed by means of (28).

For an experimental determination of the relaxation rate, one of the wells, say i, is overpopulated by some appropriate initial perturbation, while j is depopulated. The method is measuring the rate of reattaining thermal equilibrium as the perturbation is switched off. On applying the rate equations of this Section to experimental data obtained in the above manner, it will be assumed that the transition rate does not depend appreciably on the magnitude of the perturbation. Clearly, this holds true for small perturbations only.

4. COMPARISON WITH EXPERIMENTAL DATA

4.1. *Quantal dipoles*

Experimental relaxation time vs. temperature data, available from the literature or from previous work, on three off-center ions: F^{-}(13), Ag^{+}(14,15), and Li^{+}(16), all exhibiting evidence of quantal reorientation at low temperature, were processed by means of the reaction-rate equation. In applying the two-site formula (30) to data obtained for an otherwise multiwell energy surface, the experimental relaxation time was assumed to relate to k_{ij} by way of

$$\tau_{rel} = (g\ k_{ij})^{-1} \quad ,$$

where g was set equal to 4 for all the <110>-symmetry dipoles, and to 1 for the one of <111>-symmetry. In each case the procedure involved fitting Eq. (30), dependent on three free parameters: rotational frequency ν, lattice-rearrangement energy E_r, and electron-energy splitting term $|K_{ij}|$, to the corresponding experimental data by means of an appropriate computer program. Fits obtained in this way are shown in Fig's 2 through 7. In some cases (Li^{+} in KCl, F^{-} in NaBr) they are to be considered preliminary. The resulting values of ν, E_r, and $|K_{ij}|$ from those fits are listed in Table I. All the data for <110> dipoles pertain to a 90° hopping.

Using the Table I values we calculated the interwell separation

$$\Delta q = (2E_R/M\omega^2)^{\frac{1}{2}} \quad , \tag{41}$$

the off-center dipole moment

$$p_d = e\Delta q/\sqrt{2} \text{ for <110> and } p_d = e\Delta q\times(\sqrt{3}/2\ ) \text{ for <111>} , \tag{42}$$

the linear electron-phonon coupling constant

$$|b_{ii}| = \frac{1}{2}\,\Delta q\,M\omega^2 \quad , \tag{43}$$

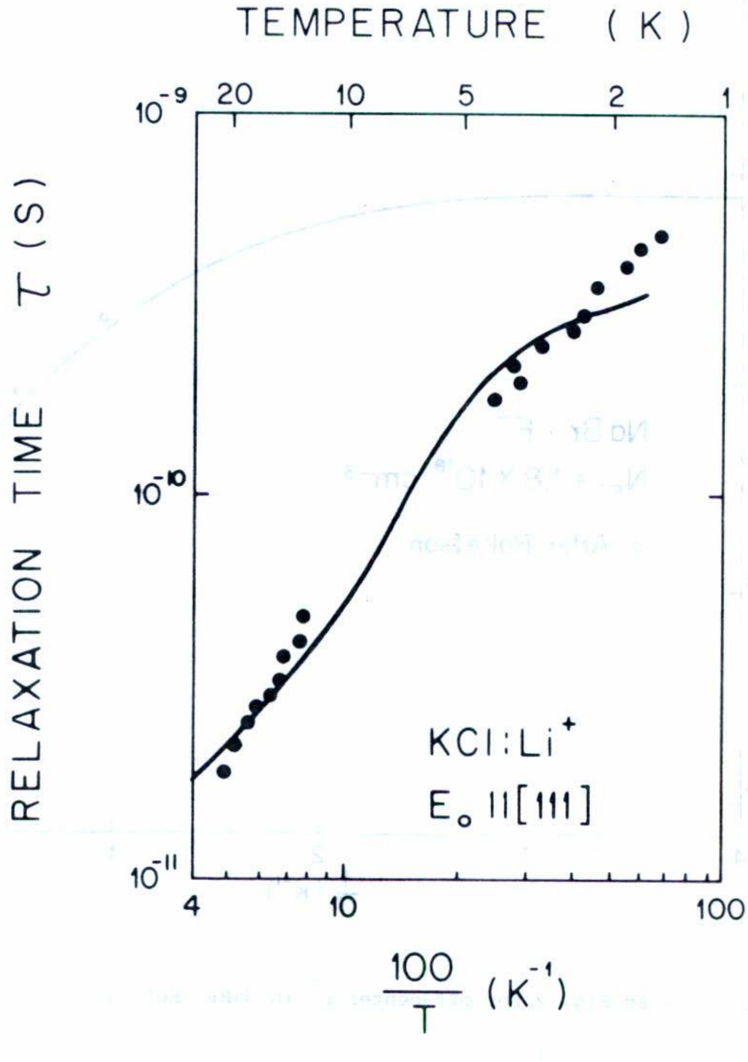

Fig. 2. Fit of the reaction-rate equation (30) (solid line) to experimental relaxation-time data (circles) on off-center Li$^+$ in KCl (Ref. 16). The fitted parameters are listed in Table I.

as well as an upper limit to the vibronic splitting from

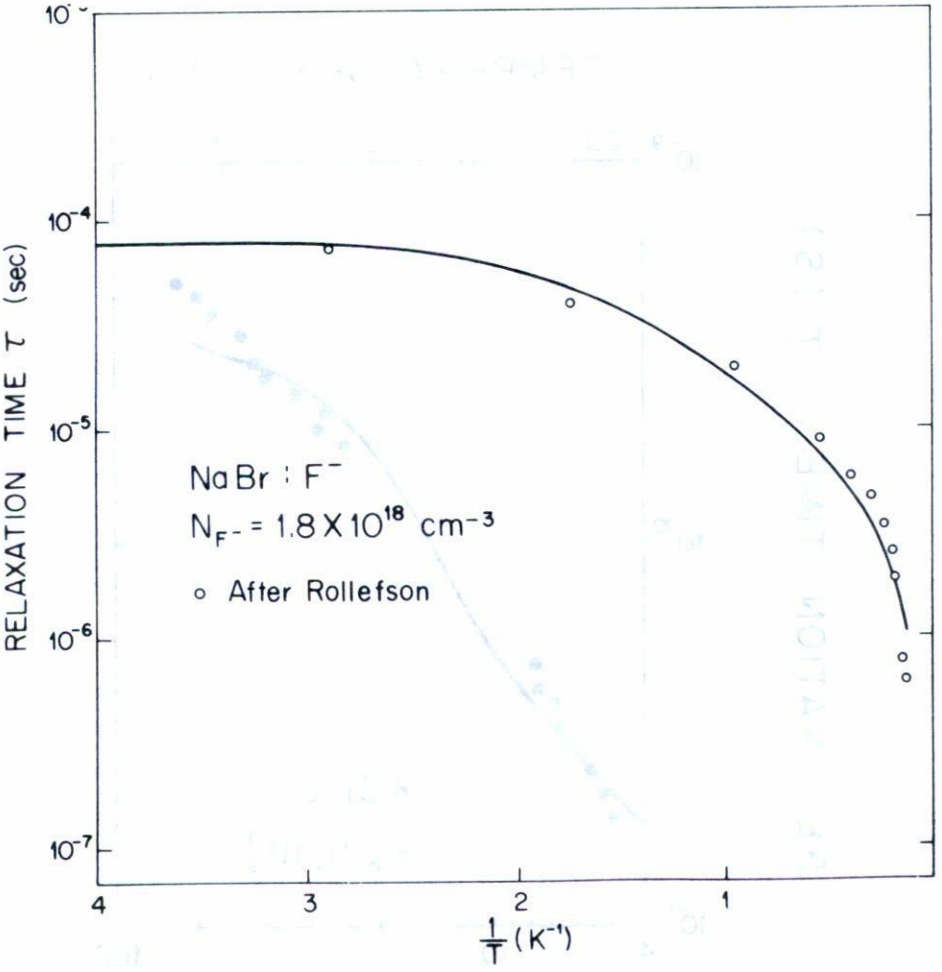

Fig. 3. Same as Fig. 2 for off-center F^- in NaBr (Ref. 17).

$$\Delta_n = (h\nu/\pi)W_L(E_n)^{\frac{1}{2}} \quad , \tag{44}$$

where E_n is the highest-lying subbarrier vibronic level used for obtaining the Table I data. The results are presented in Table II, as compared with

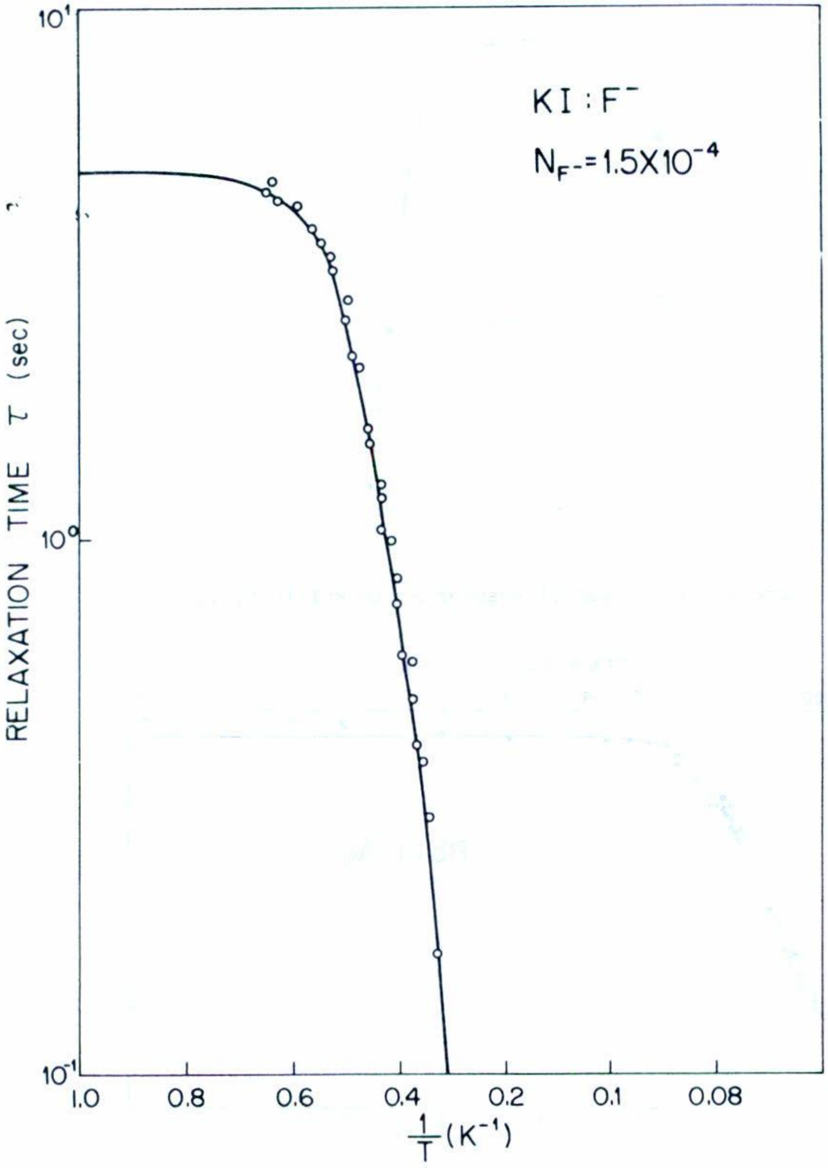

Fig. 4. Same as Fig. 2 for off-center F^- in KI (Ref. 13).

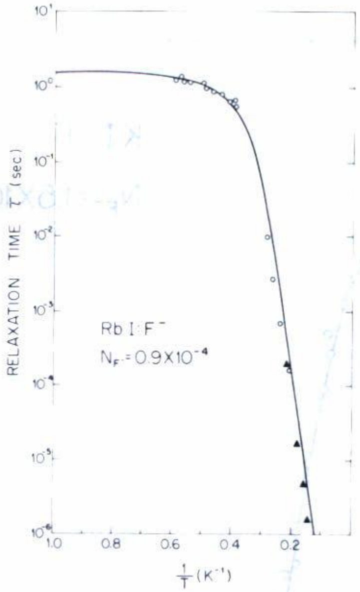

Fig. 5. Same as Fig. 2 for off-center F$^-$ in RbI (Ref. 13).

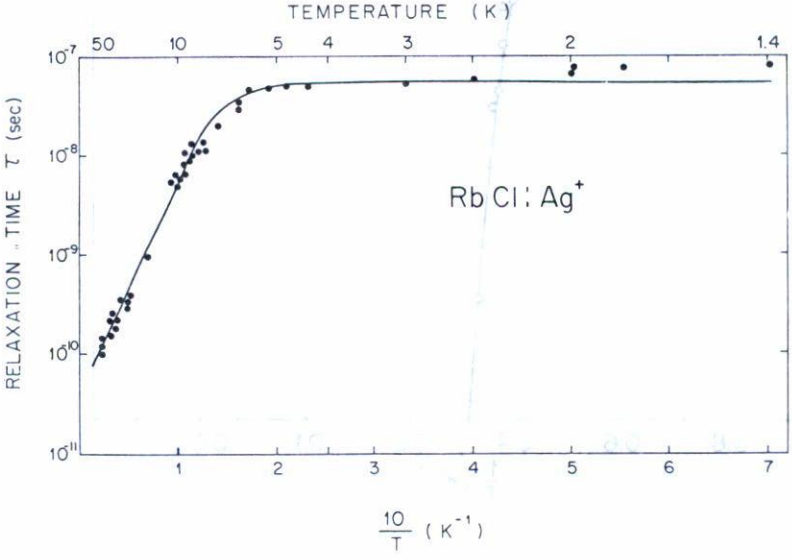

Fig. 6. Same as Fig. 2 for off-center Ag$^+$ in RbBr (Ref. 15).

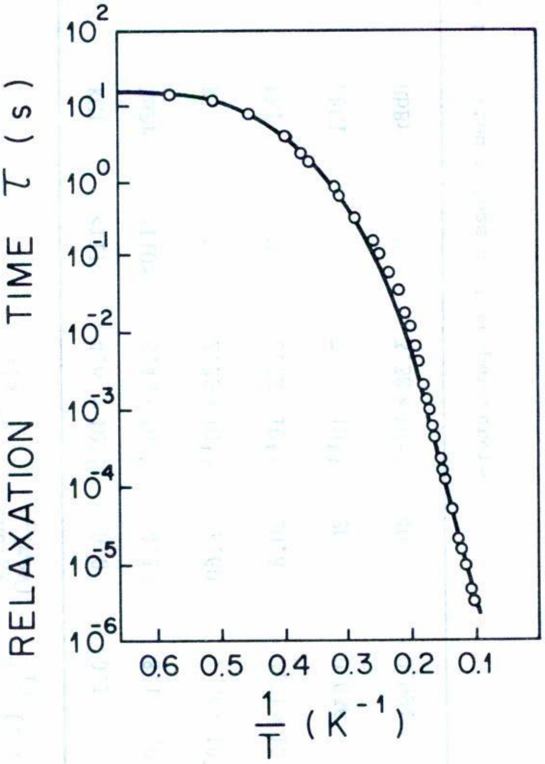

Fig. 7. Same as Fig. 2 for off-center Ag^+ in RbBr (Ref. 14).

experimental data where available.

One striking feature of the fitted values for the splitting term $|K_{ij}|$ in Table I is the nearly perfect nonadiabaticity of the electron transfer exhibited in all the cases listed therein. Generally, the splitting magnitude $2|K_{ij}|$ seems too small to be attributed to any energy separation $|E_{ij}|$ between two static states $|i,0>$ and $|j,0>$ at crossover. Alternatively, we attempted to interpret the calculated splitting in terms of the static mixing parameter $|K_{ij}|$. On using the quasiclassical formulae (20) - (22), $|K_{ij}|$ depends on both the diabatic energy $E_e = E_i^0$ of the degenerate electronic system at crossover and the donor-acceptor separation

TABLE I

Impurity ion	Host crystal	Symmetry of dipole	Promoting-mode frequency $\nu(s^{-1})$	Lattice-reorganizational energy E_r(meV)	Energy-splitting parameter K_{ij} (meV)	Barrier height E_b(meV)	Number of levels used $N^{\text{overbarrier}}_{\text{subbarrier}}$	Reference to experimental data	Fitting of Eq. (30) in:
Li^+	KCl	<111>	4.6×10^{11}	6.0	0.1	1.4	6^5_1	16	This work
F^-	NaBr	<110>	8.45×10^{10}	4.12	8.1×10^{-4}	1.03	2^0_2	17	"
	KI	"	2.25×10^{11}	8.60	1.34×10^{-4}	2.15	6^4_2	13	"
	RbI	"	2.75×10^{11}	20.8	2.71×10^{-4}	5.2	6^1_5	"	"
Ag^+	RbCl	"	7×10^{11}	20	0.036	5	6^4_2	15	"
	RbBr	"	3.38×10^{11}	40	0.091	9.9	7^3_4	14	18

Table I. Fitted values of free parameters

TABLE II

Ion	Host	Mass M (at.u.) (Ref. 20)	Force constant $M\omega^2$ (meV/Å^2)	Well-separation Δq(Å)	Dipole moment p_d(eÅ)		Electron-phonon coupling constant $\lvert b_{ii} \rvert$ (meV/Å)	Vibronic splitting Δ(cm^{-1})	
					Calculated	Experimental		Calculated	Experimental
Li^+	KCl	6.941	6.0091	1.41309	1.22	1.16 [5]	4.48270	2.21070	∿0.8 [5]
F^-	NaBr	18.99840	0.55505	3.85298	2.72		1.06930	0.00557	
	KI	"	3.93536	2.09061	1.48		4.11364	1.63486	
	RbI	"	5.87874	2.66014	1.88		7.81914	5.70248	
Ag^+	RbCl	107.868	216.267	0.43006	0.30	0.78	46.5045	9.67902	≦0.1[19]
	RbBr	"	50.4229	1.25959	0.89	0.95	31.7562	0.08 [18]	

Table II. Calculated parameters of off-center dipoles

R. Neither of these is precisely known. Nevertheless, R can be interpreted as the difference between the average electronic radial coordinate r in states $|i,0>$ and $|j,0>$ at the crossover configuration q = 0. Using the proper adiabatic eigenstates pertaining to the lower potential-energy surface $E_L(q)$, that difference can be shown to be equal to the one between the average r in states $|i,q_i>$ and $|j,q_j>$, corresponding to the bottoms of the two wells, which is given by the interwell separation Δq. However, substituting Δq for R in Eq's (20) - (22) and solving numerically for $|E_e|$, leads to values of the crossover diabatic energy which are too high to be taken as realistic. It follows that the quasiclassical equation simply does not work which is not surprising when donor-acceptor separations of the order of the interionic spacing are involved. At such separations a quantum-mechanical analysis would do much better.

4.2. *Discussion*

In any event, small electron-exchange matrix elements may well result from the static mixing of different-parity states. Consequently, the Table I data on $|K_{ij}|$ seem to give the preference to the static-mixing model of Section 2.1. This implies that the transition Hamiltonian (14) therein may be the one *driving the reorientational process*. Even though the apparent Jahn-Teller energy (E_R) exceeds abundantly the quarter of the crossover splitting ($2|K_{ij}|$), as required by (26), for all the cases listed in Table I, the dynamic reorientational model can be considered unrealiable based on the low splittings obtained. At the same time, however, the dynamic-mixing Hamiltonian (23) of Section 2.2 may be regarded as rather the one responsible for *creating the off-centered sites*.

Different modes may be expected to be involved in the above two processes: While off-centered displacements may mainly result from coupling to some A_{1g}-type vibration, coupling to both A_{1g}- and T_{1g}- simmetry modes is conceivable as the driving force in rotating an <110> dipole. Generally, the curvature along the transition path in lattice-configurational space between any two reorientational sites will be the more significant, the larger the A_{1g}-contribution. Thus the present single-mode analysis, based on Eq. (30) assuming in effect motion along the chord bet ween those sites, has underestimated both the interwell separation and the related off-centered displacement. This is clear from the Table II data where the calculated dipole moments are often inferior to the measured ones. The misfit can undoubtedly be expected to be dependent on the relative magnitudes of the coupling to the modes promoting the dipolar motion. Similar considerations apply to the fitted values of ν, which is then to be regarded as an effective frequency which results when approximating for a multimode-driven motion, characterized by more than one frequency. Nevertheless, the estimated frequencies are of the expected order of magnitude, being generally some ten times smaller than the longitudinal-optic phonon frequencies of the corresponding host materials. At the same time, however, the obtained barrier heights E_b are quite realistic, as long as the quality of the fits to the experimental rates extends to the higher-temperature range, the Arrhenius range in particular.

Under the above circumstances, the purpose of the present study has mainly been to check whether the reaction-rate method works at all, as applied to off-center reorientation, even though at the expense of introducing some effective frequency to describing the otherwise multimode-promoted motion. Clearly, although the net result is encouraging, future theoretical work will have to concentrate on extending the reaction-rate equation, so as to account for coupling to several promoting vibrations of various frequencies.

The rotation of all the quantal dipoles examined presently involves a nonadiabatic electron transfer, characterized by very small values of the electron-exchange matrix element $|K_{ij}|$. Consequently, the reorientational motion of an off-center dipole is significantly impeded relative to the one of a free rotor because of the low probability for changing the electronic state, even though the barrier height is relatively low. This introduces novel physics, as compared to previous treatments, since now the dipole is also "dressed electronically" in addition to being coupled to the lattice, the more effective the dressing, the more easily the dipole rotates. Clearly the "electron dressing" is spatially anisotropic which may account for some of the marked difference in reorientational rates of <110> dipoles between 90° and 60° jumps(13,14).

4.3. *Off-center* Cu^+

The temperature dependences of the dipolar relaxation time of off-center Cu^+ in three host materials, KCl, KBr, and KI, have been measured using the ITC technique(21). These have been interpreted in terms of an apparent classical behavior, the experimental points falling well along the straight line in the Arrhenius plot in all the three cases. The pre-exponential frequency factors and activation energies obtained from the plots are listed in Table III along with the ITC peak temperatures The respective LO-phonon frequencies ν_{LO} are also listed for the sake of comparison.

TABLE III

Host crystal	LO-phonon frequency $\nu_{LO}(s^{-1})$ $(\times 10^{12})$	Frequency factor $\nu_{eff}(s^{-1})$ $(\times 10^{12})$	Activation energy E_A(eV)	ITC-peak temperature T_M(K)
KCl	6.40	2.1029	0.177	62
KBr	5.11	3.7560	0.196	70
KI	4.30	1.3191	0.232	83

TABLE III. Experimental frequency factors and activation energies for reorientation of off-center Cu^+ (data from Ref. 21).

All the three frequency factors are seen to be of the order of ν_{LO}. Inasmuch as the actual promoting-mode frequencies ν are expected to be lower, and alternative analysis in terms of the adiabatic intermediate-dipole ocurrence was attempted(12), using instead Eqs. (37) and (39) to process the experimental arrays of points. The result is presented in Fig. 8, while the corresponding mode frequencies ν, characteristic temperatures T_c, and barrier heights E_b, regarded as fitting parameters in Eqs. (37) and (39), are given in Table IV. Also listed in that table are the values of the electron-exchange matrix element $|K_{ij}|$, calculated from(12)

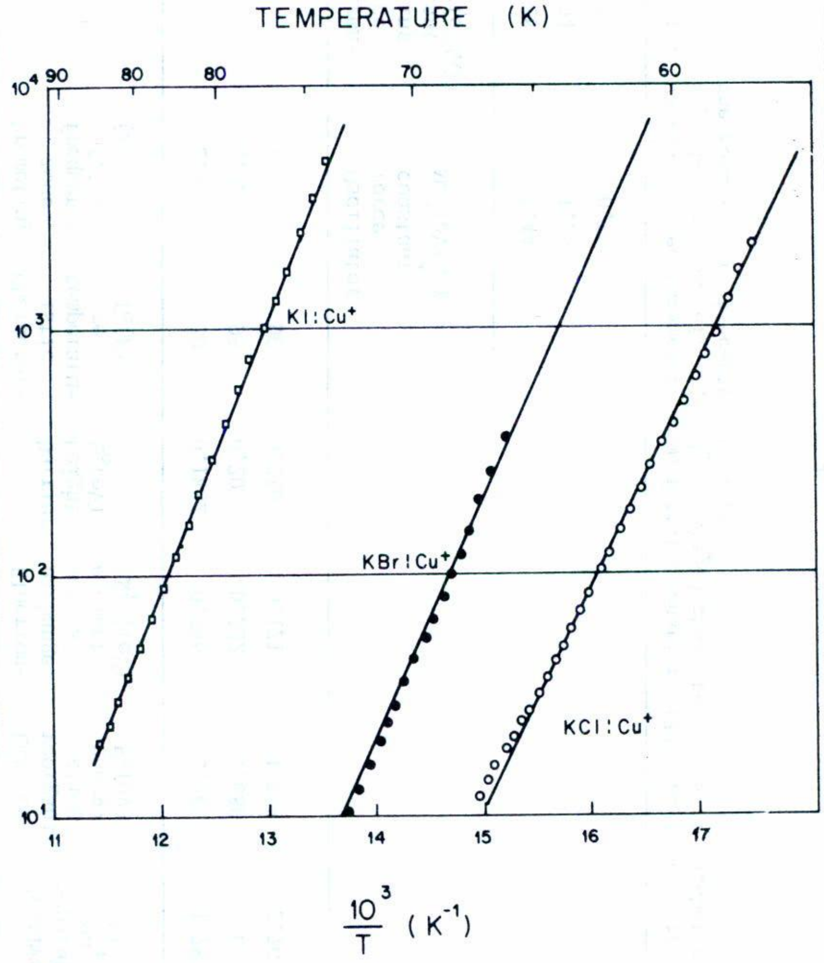

Fig. 8. Fits of reaction-rate equations (37) and (39) (solid lines) to experimental relaxation-time data on off-center Cu^+ in KCl, KBr, and KI (Ref. 21) (circles). The fitted parameters are listed in Table IV.

$$|K_{ij}| = 2E_b/(\pi k_B T_c/h\nu - 1) \quad . \tag{45}$$

TABLE IV

Host	Promoting mode frequency $\nu(v^{-1})$ ($\times 10^{12}$)	Characteristic temperature T_c(K)	Barrier height E_b(eV)	Electron-exchange matrix element $\lvert K_{ij} \rvert$(eV)	Lattice-reorganization energy E_R(eV)	Interwell separation Δq(Å)	Dipole moment p_d(eÅ)		Electron-lattice coupling constant $\lvert b_{ii} \rvert$(eV/Å)	Oscillator force constant $M\omega^2$(eV/Å^2)
							calculated	experimental		
KCl	2.35	70	0.1832	0.386	2.28	1.78	1.54	1.49 ± 0.20	1.28	1.44
KBr	2.22	95	0.20	0.222	1.688	1.62	1.41	1.92 ± 0.1	1.04	1.28
KI	1.2	90	0.236	0.121	1.428	2.76	2.39	2.6 ± 0.13	0.52	0.37

Table IV. Values of free parameters from fitting equations (37) and (39) to the experimental temperature dependences from Ref. 21, and calculated characteristics of adiabatic potentials pertinent to the rotation of off-center Cu^+ dipole*

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* Oscillator mass assumed equal to the Cu^+ atom mass, M = 63.546 atom units.

Using the data on E_b, $|K_{ij}|$, and ν, the interwell separations Δq and the dipole moments p_d were also computed from (41) and (42), respectively, the latter based on the presumed <111> symmetry of the Cu^+ off-center dipole, as well as the resulting values of the electron-phonon coupling constant $|b_{ii}|$ from (43).

Again, in view of the single-mode approximation adopted presently the fitted values of the free parameters ν, T_c, and E_b in Table IV should be regarded as effective ones, particularly the mode frequencies and the resulting interwell separations and dipole moments. Nevertheless, the relatively good fits obtained all reveal quantal effects due to tunneling near the barrier top which is almost as effective as the over-barrier jumps in the vicinity of the characteristic temperature T_c (12). This comes to stress several important features, namely

i) the apparent arrangement of relaxation times along a straight line in the Arrhenius plot do not always imply a purely classical behavior;

ii) the slope of an Arrhenius plot may be some percent lower than the one corresponding to the actual barrier height;

iii) quantum-mechanical tunneling is not the sole feature of low temperatures only.

Another remarkable implication is that the rotational motion of the off-center Cu^+ dipole involves an *adiabatic* electron transfer, unlike the quantal dipoles of Section 4.1. Clearly, more theoretical work is needed before this peculiar behavior is further clarified.

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