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One-center trapping of the holes in alkali halide crystals

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The geometric and electronic structures and electron excitation energies for the one-center hole polaron state and several possible intermediate states corresponding to the hole relaxation in KI are calculated using the static embedded molecular cluster method. The calculated optical transition energies are close to the maxima of the transient optical-absorption spectra in KI which were observed experimentally using femto-second spectroscopy. The mechanism of the self-trapping of the holes in KI is discussed. It is demonstrated that the experimental spectra can be reasonably understood if we consider that the hole first localizes in the one-center state which then transforms into the two-center state, and finally into the V_K center. [S0163-1829(96)05726-8]

I. INTRODUCTION

Recently femtosecond scale pulse optical spectroscopic techniques have been applied to the study of the hole polaron self-trapping in KI and RbI.[1] The experiments were performed on the time domain from 0.3 to 100 ps after the excitation pulse at both room and liquid-nitrogen temperatures. The two-photon excitation with an energy of about 8 eV employed in these experiments first produces an electron-hole pair in the bulk of KI. The electron is quickly trapped by the NO_2^- impurity or is delocalized in the lattice. Optical-absorption spectra in the energy range from 1.5 to 3.2 eV have been observed both in pure samples of KI and those doped with the electron-trapping impurity (NO_2^-). Transformation of the optical-absorption spectrum in KI and RbI is attributed to the hole and takes place via three distinct stages. (i) At least two intense optical-absorption bands with maxima near 2.3 and >3.2 eV were already observed at 0.3 ps after the excitation pulse in doped crystals. Their intensity rises within approximately 1 ps. With some delay (about 0.5 ps) a third absorption band at about 2.6 eV begins to rise and broadens. (ii) About 3 ps after the pulse the whole spectrum transforms into a featureless broad band. (iii) After that the well-known optical absorption of the V_K center appears and rises during 10 ps with a time constant of about 3 ps. Similar transient optical absorption has been observed in RbI. In this paper we demonstrate that these results can be reasonably understood if we consider that the hole first localizes in the one-center state which then transforms into the two-center state, and finally into the V_K center.

Among plausible candidates for such a metastable hole state in alkali halides, the one-center state has the largest relaxation energy, S, (about 1 eV or more[2,3]) due to the polarization of the lattice by the strongly localized hole. The kinetic energy loss due to the hole localization in this state (localization energy), B, is determined by the structure of the upper valence band and may be roughly estimated as a half of its width,[4] which is more than 1 eV in many alkali halides (see Refs. 3, 5, and 6 for discussion). If the hole is equally delocalized between two or more lattice sites, the lattice polarization is smaller and these small polaron states are less favorable than the one-center state.[7] However, in alkali halides and in alkali-earth fluorides, possibly in alumina and other crystals the two-center state is stabilized by chemical bonding between the two anions sharing the hole.[6,8,9] This leads to formation of a quasimolecular X_2^- state (X is the anion) where the distance between anions is much smaller than that in the perfect lattice. The localization energy B in this state is smaller than in the one-center state because it is more delocalized. Thus the overall energy gain (the so-called self-trapping energy, $E_{\mathrm{st}}=B-S$) in the two-center state in these crystals is larger than in the one-center state and these are the only stable hole states observed so far in a pure lattice.

One can try to understand these experimental data from a different perspective. The most general approach would require consideration of the *time evolution* of the hole assuming different initial wave packets.[10] Sumi[11] studied the *probability* of the exciton localization in different ''nucleation states'' in alkali halides which can be calculated providing one knows the energetic parameters such as S and B for these states (see discussion below). However, since the only experimental information concerns the optical-absorption spectra in a narrow energy range, in this paper we focused on a simple model of the hole relaxation process using a static approach. This allows us to take into account the lattice polarization by the hole and to study the nature of the hole optical absorption. Since the small polaron theory predicts more favorable polaron trapping in one-center states than in more delocalized states, we first study the possibility of formation of the one-center metastable state of the hole in KI and make our argument on the basis of the static self-trapping criteria and comparison of the calculated optical transition energies with the experimental data.

The geometric structure and optical-absorption energies of the one-center hole state in KI were briefly reported in Ref. 1 assuming its formation on the first stage of the hole self-trapping. The calculated transition energies appeared to be close to the experimentally observed transient absorption spectrum before its transformation into the broad one. In this paper we present a detailed account of calculations on the hole in the one-center state in KI and consider its transformation into the two-center state and into the V_K center. The relaxation energies of the one- and two-center holes and their optical-absorption energies are calculated using a static many-electron quantum-mechanical approach successfully applied in recent studies of the models of self-trapped holes and excitons in several alkali haldies and oxides.[6,12–15] The results obtained are then used to discuss the mechanism of self-trapping of the holes in alkali halides.

II. METHOD OF CALCULATION

We employed the embedded molecular cluster model and semiempirical molecular-orbital linear combination of atomic orbitals (MO LCAO) Hartree-Fock method. They are implemented in a CLUSTER95 computer code which takes into account the polarization of the lattice by the defect. Although it is based on the algorithm which is broadly similar to those described in Refs. 14 and 16, it is instructive to briefly outline the details of the computational procedure which are necessary for understanding of the results of the present work.

The embedded cluster model employed in this study is based on the approximation that the perfect crystal can be divided into individual ions. It allows one to combine a quantum-mechanical treatment of a part of the crystal including a defect (quantum cluster) with the classical description of the rest of the crystal. This is made by substituting a number of classical ions by a quantum cluster and by using a ''self-consistency'' procedure based on consecutive iteration of two computational methods as schematically illustrated in Fig. 1 and discussed below. To be used together, both methods must give the same lattice constants of the perfect lattice and in the more general case must yield the same optimized structure.

In the CLUSTER95 code, the electronic structure of the system is calculated using the unrestricted Hartree-Fock (UHF) method within the approximation of intermediate neglect of differential overlap (INDO).[17] In this approximation some of the elements of the Fock matrix are calculated using semiempirical parameters.[18] In this study we employed a set of parameters which were optimized in order to reproduce the characteristics of the KI perfect crystal as well as those of the KI and I_2^- molecules. Calculations of the band structure and geometry of the perfect crystal were made using the large unit cell (LUC) method[18,19] for the periodic cell $K_{32}I_{32}$. This allows us to take into account 8 **k** points of the Brillouin zone. The lattice constant a of KI determined in our calculations is equal to 6.7 a.u. (6.676 is the experimental value). The band gap calculated using a configuration interaction technique for single-electron excitations[20] is equal to 5.9 eV, which is close to the experimental value of about 6.0 eV.[21] The INDO Hamiltonian does not include the spin-orbit interaction which is essential for the iodine ion.[21,22] The width of the upper p valence band obtained experimentally in Ref. 21 is equal to 2.8 eV. In our calculations, which do not include the spin-orbit splitting, it was obtained to be 2.05 eV.

The lattice outside the quantum-mechanical cluster is treated in the Mott-Littleton approximation using a shell model for ionic polarization.[23] The calculations are performed using the General Utility Lattice Program (GULP).[24] We employed the set of interatomic potentials developed in Ref. 25. The lattice surrounding the defect is divided into a number of spherical regions about a specified defect center which is located in the midpoint of the perturbed lattice sites. The quantum cluster is embedded in the middle of region I which encompasses all the ions that are strongly displaced by the defect. The system total energy is calculated as

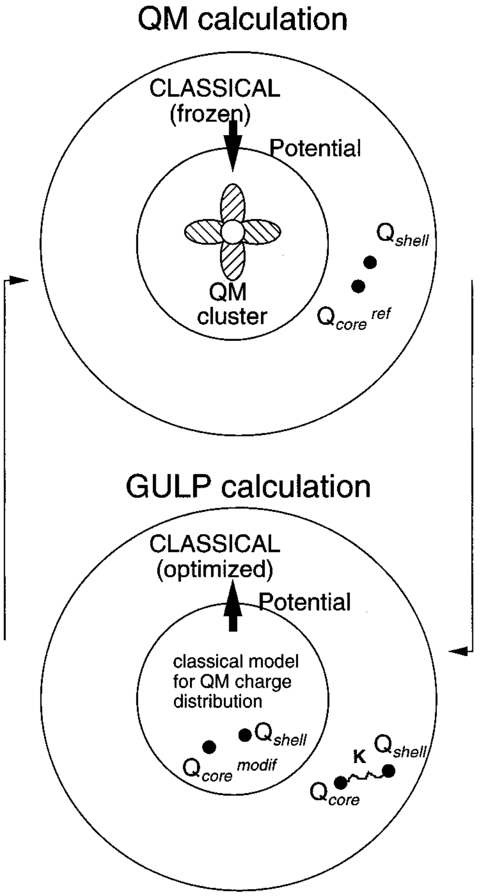

FIG. 1. Schematic presentation of the embedded molecular cluster technique employed in this study. In the QM calculation, the rest of the crystal treated classically is represented by an electrostatic potential ϕ_i produced by the cores and shells outside the cluster at the position of each nuclei, i, inside the quantum cluster. This potential is calculated using the ionic charges obtained for the perfect lattice using the same QM method. In the GULP calculation, the positions of the cores and shells of the classical region outside the QM cluster are optimized in the electric field produced by the modified charge distribution in the QM cluster. K is the spring constant of the shell model used to represent the polarization of the ions. The charges of the cores located at the nuclei positions of quantum ions are modified with respect to these in the perfect lattice as $Q_{\mathrm{core}} \Rightarrow Q_{\mathrm{core}} - [Q_{\mathrm{QM}} - Q_{\mathrm{QM}}(\mathrm{ref})]$, where Q_{QM} are effective ionic charges in the quantum cluster, and $Q_{\mathrm{QM}}(\mathrm{ref})$ are the effective ionic charge in the perfect lattice. The arrows indicate that calculation of the lattice polarization and of the electronic structure and the geometry of the quantum cluster embedded in the electrostatic potential of the polarized lattice are carried out iteratively until the total energy of the whole system does not change by more than a certain criterion.

$$E_{\text{tot}}=E_{\text{GULP}}-E_{\text{GULP}}(\text{cluster})-E_{\text{Coul}}(\text{cluster-environment}) + E_{\text{QM}}(\text{cluster}), \quad (1)$$

where E_{GULP} is the total energy of the crystal with defect calculated using the Mott-Littleton method; $E_{\text{GULP}}(\text{cluster})$ is the total energy of the part of the region I which is substituted by the quantum cluster calculated as a free molecule with frozen positions of the cores and shells using the interatomic potentials; $E_{\text{Coul}}(\text{cluster-environment})$ is the Coulomb part of the interaction of the classical cores substituted by quantum ions with the rest of the crystal; and $E_{\text{QM}}(\text{cluster})$ is the total energy of quantum cluster including its interaction with the rest of the crystal. In this approach, the contribution $E_{\text{GULP}}-E_{\text{GULP}}(\text{cluster})-E_{\text{Coul}}(\text{cluster-environment})$ includes (i) the short-range interactions between the cluster ions and the surrounding lattice, represented by the interatomic potentials; and (ii) the polarization energy of the lattice outside the cluster.

To calculate the lattice polarization by the defect, the whole system is treated using the Mott-Littleton technique. To simulate the defect-induced changes of the charge distribution inside the quantum cluster, the classical cores are located at the positions of the nuclei of quantum ions with the corresponding shells attached to them (see Fig. 1). The charge distribution in the perfect crystal calculated using the same quantum-mechanical method in a periodic model is used as a reference. The charges of the cores located at the nuclei positions of quantum ions are modified with respect to these in the perfect lattice as $Q_{\text{core}} \Rightarrow Q_{\text{core}}-[Q_{\text{QM}}-Q_{\text{QM}}(\text{ref})]$, where Q_{QM} are effective ionic charges in the quantum cluster, and $Q_{\text{QM}}(\text{ref})$ are the effective ionic charge in the perfect lattice obtained by the LUC method, both calculated in INDO approximation.[17] The GULP code uses the modified effective charges and positions of the cores in order to adjust the positions of the shells inside and of the cores and shells outside the cluster. This simple approximation is adequate for the present case because the hole is well localized in both one- and two-center states. More explicit representation of the electron density using, for instance, multipole moments must be used in more complex cases.

The response of the polarized lattice is then given in a form of the lattice polarization energy and an electrostatic potential ϕ_i produced by the cores and shells outside the cluster at the position of each nuclei i inside the quantum cluster. This potential, though, is calculated using not the formal ionic charges employed in the parametrization of the shell model, but those obtained for the perfect lattice using the LUC method (see Fig. 1). Since the quantum-mechanical charges are different from the formal ionic charges used in the Mott-Littleton model, this ensures a homogeneous charge distribution across the cluster border. Note that ϕ_i includes both the Madelung term and the dipole polarization term which were both subtracted in Eq. (1) to avoid double counting. The diagonal matrix elements of this potential calculated on atomic orbitals μ, $\langle\mu|\phi_i|\mu\rangle$, are then added to the Fock matrix for the calculation of $E_{\text{QM}}(\text{cluster})$. The total energy of the whole system including the quantum cluster embedded in the infinite polarizable lattice is minimized with respect to the LCAO coefficients, positions of the nuclei inside the cluster and of the cores and shells of the rest of the crystal. Use of the approximate INDO method allows us to calculate large quantum clusters (up to 150 ions in this study) and to make sure that ions on the cluster border are not significantly perturbed by the defect. Therefore the described method provides a smooth boundary for the embedded cluster. Inside the cluster, the inertial part of the lattice polarization is accounted for completely whereas the electronic part is treated in the INDO approximation. The calculation of the lattice polarization and of the electronic structure and the geometry of the quantum cluster embedded in the electrostatic potential of the polarized lattice are carried out iteratively until the total energy of the whole system does not change by more than a certain criterion (usually 0.001 eV).

Optical-absorption energies for the hole states were calculated using the configuration interaction method taking into account single-electron excitations (CIS).[20] In embedded molecular cluster calculations boundary effects and the symmetry of the quantum cluster can affect the symmetry of delocalized states of the hole. To eliminate this effect, we also made calculations using periodic boundary conditions for a unit cell $K_{32}I_{32}$. Since the unit cell for the system with a hole should be neutral it included an Ag^+ ion on one of the cation sites which is known as a good electron-trapping center. The INDO parameters for this ion were taken from our previous calculations[26] of the hole trapping in AgCl. In the triplet state of the system the excited electron becomes completely localized in the Ag^0 state where the hole is delocalized by the unit cell if no special lattice relaxation is included.

III. RESULTS OF CALCULATIONS

We apply the static approach described above first to consider the one-center hole polaron state and then a model of its transformation into the state where the hole is delocalized by two nearest anions.

A. The one-center state

To find the geometric and electronic structures of the hole in one-center state, we first fixed the position of the I atom carrying the hole in the lattice site whereas all other crystal ions were allowed to relax. For comparison, the relaxed configuration of this state was calculated using both a cluster model, accounting for the lattice polarization, and periodic LUC model. $[K_{24}I_{24}]$ quantum cluster and a $\{K_{31}I_{32}Ag\}$ unit cell were used in these studies. The two calculations gave very similar results for the displacements of ions nearest to the I atom carrying the hole (see Fig. 2); the difference in ionic displacements for completely relaxed state does not exceed $0.01a$. The nearest-neighbor cations are displaced outwards by about $0.1a$ and the next nearest-neighbor anions are displaced inwards by about $0.015a$. The relaxation energy S calculated using the cluster model as a difference between the energy of the completely relaxed state and that without core displacements from their perfect lattice sites, when only the electronic polarization responds to the presence of the hole, is equal to 1.3 eV.

The hole in the one-center relaxed configuration almost completely occupies one of the three p spin orbitals (let us for convenience consider the p_z spin orbital). The spin density on this orbital is about $0.95e$ (e is the electron charge).

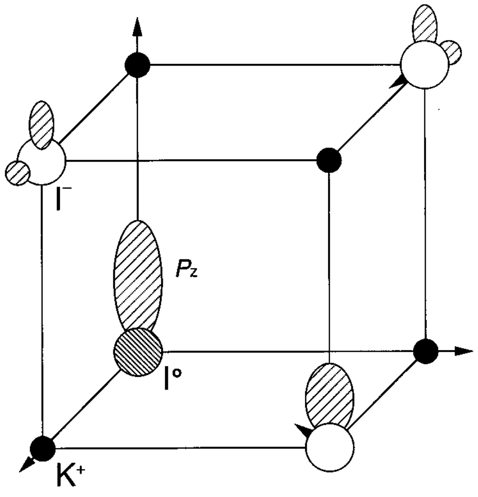

FIG. 2. Schematic representing the first, second, and third neighbors of the I atom carrying the hole in KI and the nature of the hole (unoccupied molecular orbital). The arrows point into the directions of the ionic displacements. Only a symmetry unique portion of the local defect structure is shown.

This hole state is threefold degenerate and the ionic configuration has D_{4h} symmetry due to a Jahn-Teller lattice distortion. This distortion is mainly induced by the difference in the interaction of the singly occupied p atomic spin-orbital of the central anion with the nearest cations and the p orbitals of the four anions located in the xy plane perpendicular to the hole orientation and the eight nearest-neighbor anions in the xz and yz planes (see Fig. 2). However, the calculated displacements of the latter anions are only about 0.015 Å larger than those in the xy plane. The energy difference between the completely symmetric (O_h) and distorted (D_{4h}) configurations (which is the adiabatic barrier between the three equivalent minima) in our calculations does not exceed 0.01 eV.

The perturbation produced by the hole charge and the lattice distortion induces a series of electronic states having the defect symmetry. However, in a finite embedded molecular cluster, where all electronic states are localized within the cluster, the degree of localization of the states due to defect-induced perturbation can be exaggerated. To check this point, we compared the calculations for the completely relaxed one-center hole in the clusters $(3\times3\times3)$ $[K_{14}I_{13}]$, $(4\times4\times3)$ $[K_{24}I_{24}]$, and $(6\times5\times5)$ $[K_{75}I_{75}]$ and a periodic cell $\{K_{31}I_{32}Ag\}$ which have different numbers of electrons, symmetry, and boundary conditions. In the first of them, the hole was localized on the central I ion. In the three other systems, the center of symmetry was not located on the lattice site and the symmetry of the cluster with the localized hole was much lower. In all four cases hole-induced electronic states are formed. They can be identified by the symmetry of their molecular orbitals which corresponds to the hole symmetry, D_{4h}, and by the energies and matrix elements of the electronic transitions from these states to the single-occupied hole state. The latter depend entirely on the strength of the defect-induced perturbation. The values of the polarization potential are different on the anion carrying the hole and on surrounding anions. This leads to an additional splitting of the hole electronic states and affects optical-absorption energies of the hole especially in the one-center state.

Optical absorption by a small radius polaron has been considered by many workers in conjunction with the polaron conductivity (see, for example, Refs. 27 and 28) and polaron holes trapped by defects in oxides.[29] In a two-site model, the optical absorption was considered to be due to a Franck-Condon electron excitation to the state localized on another polaron site. For the stationary one-center polaron case, our model generalizes this picture as it takes into account the possibility of the hole delocalization by all nearest-neighbor sites and considers a more realistic hole wave function. In the completely symmetrical configuration, the allowed transitions are from E_{1g} and A_{1g} states to the single occupied E_{1u} hole state. Accordingly, instead of a single transition one should expect two groups of allowed transitions. These are indeed observed in our calculations.

Calculations of the optical-absorption energies and the matrix elements of the corresponding dipole electronic transitions for the relaxed state of the one-center hole were made using the CIS method. For the cluster $[K_{14}I_{13}]$ the CIS calculations were performed for all p states of anions and all empty states of cations (that is to say for the I $5p$ valence and K $4s$ conduction bands). For two other clusters, the same number (about 900) of excited configurations were used which were chosen according to the local defect symmetry in order to include all potentially important states. The transitions with the largest matrix elements for the cluster $[K_{14}I_{13}]$ include a z-polarized transition with the energy 2.0 eV, two degenerate x and y polarized transitions of 2.1 eV, and one z and two degenerate x, y transitions with close energies of 2.8 eV. Two larger clusters gave similar results with energies of 2.2, 2.4, and about 3.6 eV and the matrix elements having very similar relative values to those obtained for the former case. Quantitative differences in the transition energies and matrix elements are considerable mainly because of the difference in the cluster charges which imposes a shift in the energy levels. Nevertheless, the agreement between transition energies and their splitting calculated for different clusters is satisfactory.

The nature of these charge-transfer transitions can be described in terms of local and resonance defect electronic states. Local states are usually split from the bands whereas resonance states are more delocalized and their energies are located within the bands. We should note that the notion of resonance states induced in occupied or empty electron bands by a defect is well defined only for an infinite crystal[30] (see also discussion in Ref. 15). To classify the defect states in a cluster model, one needs to estimate the position of the hole ground state E_h with respect to the optical excitation from the top of the valence band. This is the lower limit of the ''optical'' hole delocalization energy which determines an approximate energy range within which electronic transitions are originated from the local states. One way to determine E_h is to calculate the electron affinity A of the center and then to subtract it from the energy of the interband optical excitation, E_g. In this case $E_h = E_g - A$. Alternatively, one can calculate the energies of the electron transitions from the delocalized electronic states (simulating the ‘‘band’’ states in the cluster calculation) to the single-occupied hole state.

For comparison, we calculated E_h using both methods in the cluster $[K_{24}I_{24}]$. The value of A calculated at core positions fixed in the relaxed one-center hole configuration and shells allowed to relax was found to be equal 5.9 eV. The optical band calculated in the same cluster is 7.8 eV. This gives $E_h = 1.9$ eV. On the other hand, the smallest optical excitation energies from the delocalized cluster states to the single-occupied hole state calculated using CIS are about 2.2 eV. The reasonable agreement between the two methods suggests that E_h equal to about 2 eV can be a realistic estimate. The optical transitions of the one-center hole state have larger energies than E_h which implies that they originated from the resonance states and should lead to hole delocalization.

This hole delocalization from one site over several lattice sites should be accompanied by the change in the lattice polarization which was not taken into account in our CIS calculations. To check how this can affect the calculated optical-absorption energies, we used the self-consistent-field (ΔSCF) technique, i.e., calculated some of the transitions as the difference between the total energies of the ground and excited hole states with the self-consistent account of the lattice polarization in both states. We should note that because of the hole delocalization these calculations are difficult to converge. Therefore our estimate is based on a successful calculation for one transition corresponding to that with an energy of about 3.6 eV. We compared the transition energy calculated for the electron excitation at the same positions of the cores and shells as in the ground state (as in the CIS calculations) with that in which the shells were allowed to relax in the excited state and the self-consistency procedure has been completed. After the shell relaxation according to the new hole distribution the transition energy became smaller by 0.3 eV. If we apply this shift to all transitions calculated using CIS in the same cluster, they become 1.9, 2.1, and 3.3 eV.

Obtained optical-absorption energies are in the range of the splitting and positions of the maxima of the absorption bands observed at 0.3 ps after the excitation pulse at both room and liquid-nitrogen temperature in KI.[1] However, since the real stage of the hole relaxation process at each measurement time is unknown, it is impossible to establish a direct correspondence between the theoretical results and the experimental transient absorption spectra. In particular, the experimental spectra[1] demonstrate a clear shift of the maximum of the lower energy absorption band to higher energies by about 0.1 eV on the time domain from 0.3 to 0.7 ps. One natural explanation of this observation could be that the spectrum at 0.3 ps does not correspond to a completely relaxed state. In terms of our model, this would mean that the average positions of the ions surrounding the I bearing the hole have not yet displaced to their ‘‘equilibrium’’ positions (it makes sense to speak about averaging because 0.7 ps already corresponds to several lattice vibrations). The equilibrium displacements of cations in a completely symmetrical configuration of the hole (0.35 Å) are much larger than these of the next-nearest-neighbor anions. To check a qualitative tendency, we assumed that the cations were those which did not relax and calculated the optical absorption of the one-center state corresponding to the displacements of the nearest cations by 0.30 and 0.25 Å in the embedded cluster $[K_{24}I_{24}]$. In qualitative agreement with the experiment, the calculated spectrum demonstrated an almost heterogeneous shift by about 0.2 and 0.4 eV to smaller energies with respect to the fully symmetrical configuration.

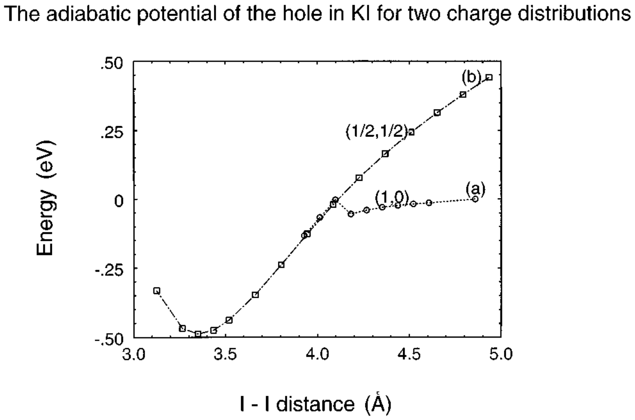

FIG. 3. The adiabatic potential with respect to the symmetrical displacements of the two I ions towards each other and all other polarizable ions adjusting their positions. In (a) the hole is initially localized on one of the I ions and remains strongly localized on it until the two curves cross; in (b) the hole is equally shared throughout by two I ions.

B. Transformation from one-center into two-center state

The total energy of the fully symmetrical one-center hole polaron state in KI is 0.44 eV lower than that for the state where the hole is equally shared between the two nearest anions located in the perfect lattice sites and the positions of all other ions are optimized. However, both of these states are not stable with respect to the displacement of the two anions closer to each other. Sections of the adiabatic potential with respect to the symmetrical displacements of the two I ions towards each other and all other polarizable ions adjusting their positions are shown in Fig. 3. Curves (a) and (b) differ in the hole distribution: in (a) the hole is initially localized on one of the I ions and remains strongly localized on it until the two curves cross; in (b) the hole is equally shared throughout by two I ions. One can see that the curve (a) is very flat before the crossing point at 4.1 Å which coincides with the change of the electronic configuration from (1,0) to (1/2,1/2). This behavior of the adiabatic potentials results from the competition between two main factors: (i) the chemical bonding between two iodines, and (ii) the lattice polarization. The latter factor is treated self-consistently with respect to the charge-density distribution and favors the one-center hole localization. Therefore chemical bond formation is a crucial factor which requires accurate treatment.

As has been shown in our recent study of Cl_2^- molecular ion, without the symmetry constraint, the UHF equations always have a broken symmetry solution at distances which are larger than the equilibrium interatomic distance.[31] It has lower energy than a symmetrical one and corresponds to the predominant localization of the excess electron on one of the atoms. This effect has been observed in other systems (see, for example, Ref. 32) and has a simple explanation.[33] However, the dissociation energy corresponding to the broken symmetry solution of Cl_2^- was obtained to be only 0.4 eV, which is 0.8 eV smaller than the experimental value. As has been demonstrated in Ref. 31, this can be improved if one takes into account electron correlation. After the correlation correction has been added to the total energy, the symmetrical solution became lower than the broken symmetry one, and the energy difference between them was less than 0.1 eV. A similar effect must take place also in the case of I_2^- molecular ion, however correlated calculations are yet to be performed.

The semiempirical technique allows us to mimic qualitatively correct behavior of both broken symmetry and symmetrical solutions due to the restricted basis set employed and the choice of parameters. In our calculations, the free I_2^- molecular ion has an equilibrium distance of 3.3 Å and a dissociation energy of 1.24 eV which are close to 3.28 Å and 1.08 eV calculated by Tasker, Balint-Kurti, and Dixon for the symmetrical solution using an *ab initio* UHF method.[34] The symmetrical solution has a lower energy than the broken symmetry solution and the latter does not exist at I-I separations smaller than 5 Å . In KI crystal, when two iodines are displaced towards each other to a distance more than 4.1 Å the one-center hole localization can be therefore imposed only by the lattice polarization. At shorter distances, formation of the chemical bond between iodines enforces a symmetrical charge distribution. This technique allows us to check this effect numerically by starting from the symmetrical charge density distribution between the two iodines and allowing the system to find the energy minimum corresponding to a consistent charge distribution and lattice polarization without additional constraints. Although this method is not rigorous and does not properly take into account the electron correlation, it nevertheless allows us to demonstrate an important qualitative effect that the one-center hole polaron state once formed will not collapse into the two-center state immediately, but this requires the iodine ions to come closer than some critical distance. Before that happens, the hole will remain localized on one of the ions. Dynamics of the system relaxation from the one-center into the two-center state is beyond the scope of this paper. We should note that a similar effect has recently been demonstrated in the calculations of $I^- + I$ combination in polar solutions.[35,36]

The result that the one-center state is in fact a saddle point and the flatness of the adiabatic potential suggest that the geometry of the one-center state will be always distorted and therefore it is interesting to check how the results of the previous section will change for some plausible distortions. Assuming that the one-center state, if formed, will relax into the two-center state we have calculated the optical absorption at several I-I distances during the initial stages of this process. We first considered displacements of one I ion towards the iodine bearing the hole by 0.025, 0.07, and 0.17 Å and secondly the symmetrical displacement of the ion with the hole and another ion towards each other to a distance of 4.34 Å. The results can be summarized as follows. At small displacements of one ion the main features of the spectrum discussed for the fully symmetrical configuration remain the same except that the degenerate states split. In addition, a transition corresponding to the hole transfer from the I^0 to the displaced ion appears. The energy of this transition is about 2.8 eV. In the case of the strong displacement of the ions towards each other, the original spectrum is more perturbed with several transitions occurring in the energy range between 2.1 and 3.1 eV. It is interesting to compare these energies with the polaron theory[28] which predicts the energy of the optical transition from small radius polaron as twice the polaron lattice relaxation energy $2S$. This value in our calculations is equal to 2.6 eV which is in the range of the experimentally observed optical transition energies.

It is plausible to assume that when the interaction or some vibrational fluctuation brings two anions to a distance which is shorter than the critical distance necessary for formation of the symmetrical electronic state, the latter gradually relaxes into the V_K-center configuration. This process is mainly determined by the cooling relaxation of the valence vibration of I_2^- molecular ion (the wave number of this vibration obtained in our calculations is 150 cm^{-1}, which is larger than experimentally detected[37] 115 cm^{-1}). This should correspond to the broad adsorption band due to the loss of coherence between different relaxing centers. Calculation of the characteristic time of this process performed in Ref. 38 has demonstrated that it takes several picoseconds. This is in good agreement with the observation[1] that the time of the second stage of the spectrum transformation, characterized by the broad featureless band, and appearance of the optical absorption of the V_K center, is about 4 ps at liquid-nitrogen temperature.

The relaxed two-center state of the hole which corresponds to the V_K-center configuration was calculated in the same quantum clusters as the one-center state. The energy of this configuration is lower than that for the one-center state by about 0.3 eV. This value is similar to 0.27 eV, which is the activation energy of the V_K-center diffusion in KI.[39] As has been shown in the study of the mechanism of a 60° reorientation of V_K centers in KCl,[40] the saddle point for this process has an energy close to the one-center state of the hole. Therefore we consider 0.3 eV to be a good estimate of this quantity. The optical absorption of the V_K center in KI is discussed in Ref. 15.

IV. DISCUSSION

The optical transition energies for the one-center hole polaron state and several possible intermediate states corresponding to the hole relaxation calculated in this paper are close to the maxima of the experimentally observed transient optical-absorption spectra in KI. This implies that this state can be considered as a candidate for the transition hole state corresponding to the first stage of the hole self-trapping in this crystal. Let us now discuss possible reasons for and the mechanisms of the hole trapping in this state.

The static criterion

One simple argument is based on the static energetic criterion that the self-trapped state should have the energy lower than the bottom of the free hole band, i.e., E_{st} should be negative. The band-structure calculation of the KI using a relativistic technique[22] has demonstrated that spin-orbit effects split the upper p valence band into two nonoverlapping subbands. The two-photon excitation with an energy of 8 eV produces holes in the upper subband with the angular momentum $J=3/2$. The width of this subband calculated using a relativistic mixed basis method and a ''muffin-tin'' potential[22] was found to be equal to about 1 eV whereas the width of the spin-orbit split valence band is 1.82 eV. This is about 1 eV smaller than the experimental value[21] of 2.8 eV. The valence band width obtained in our calculation without the spin-orbit interaction is 2.05 eV, which with the addition of the spin-orbit splitting gives 2.95 eV.

The localization energy B for the localized one-center state in the Wannier representation is determined by the position of the ''center of mass'' of the density of states (DOS) in the valence band. For a symmetrical DOS it can be calculated as a half of the valence band width.[3,6] As has been shown in calculations of B which were made for KCl,[5] AgCl,[26] and MgO,[13] a more accurate value is usually smaller than this estimate by abut 20%. This is due to an angular dependence of transfer integrals for p orbitals which is neglected in this simple approximation.[5] Therefore a conservative estimate for the upper limit of the localization energy B of the one-center hole is half of one of the two split subbands <1.0 eV. Then the self-trapping energy for the one-center hole states can be estimated as $B-S\leqslant-0.3$ eV. This is close to the results obtained in previous calculations for other cubic crystals such as KCl (-0.2 eV),[40] MgO (-0.4 eV),[13] AgCl (-0.1 eV).[26] We should note that the spin-orbit splitting does not affect the value of the relaxation energy which depends on ionic polarizabilities. In particular, the S value in KI is larger than in KCl, where it was calculated using the same technique to be 1.1 eV. However, in KCl the valence band is effectively wider, which gives the smaller E_{st} than in KI.

These estimates suggest that the self-trapping energy of the one-center polaron state in KI can be negative and therefore it can exist as a metastable state. However, this does not answer the question why holes produced by crystal excitation prefer to be trapped first in this state but not, for instance, in the two-center state.

''Nucleation state''

Sumi considered a similar problem with respect to exciton self-trapping[11] and proposed that at low temperatures the free exciton should first tunnel into some so-called ''nucleation state.'' This is essentially an already appreciably relaxed state corresponding to a certain degree of localization of the particle. Using the phenomenological approach and the theory of nonradiative tunneling transitions he calculated the tunneling rate between the free and different nucleation states of the exciton as a function of the parameters of the Hamiltonian (localization and relaxation energies) and temperature, and has demonstrated that the nucleation state should have the scale of a lattice constant. These calculations demonstrated that the tunneling rate is extremely sensitive to the energetic parameters. Apparently at some their combination one can obtain a rate close to the experimental value, but in reality one should consider a distribution of energetic parameters corresponding to the lattice fluctuations at a given temperature.

These fluctuations are of the same nature as those leading to the exponential behavior of the one-electron density of states and the Urbach optical-absorption edge in alkali halides and other crystals (see, for example, Refs. 28 and 41). For three-dimensional crystals, a critical strength of a Gaussian fluctuation of potential necessary to produce a bound state has been evaluated in Ref. 42. For a fluctuation parametrized by a depth V_0 and a range α, a dimensionless quantity $2m\alpha^2V_0/h^2$ has been found to be equal 2.95, where m is the electron mass. If one assumes the range of the fluctuation α equal to the lattice constant, in KI this would correspond to $V_0=0.231$ eV. For a simple estimate one can assume further that this fluctuation is produced by a symmetrical outward displacement of the six cations surrounding one iodine ion. For the formal ionic charge of $1.0e$, the displacement necessary to produce such a fluctuation of the potential is about $0.01a$, where a is the interionic distance. Although such fluctuations are readily available even at low temperatures,[43] they correspond to rather delocalized states centered at one lattice site which are impossible to study using the present technique and localized basis set. Therefore more detailed studies of the lattice fluctuations and corresponding holes states are needed to elaborate this point.

Another effect which has not yet been properly understood is the much lower optical density of the V_K centers with respect to the initial absorption spectrum. One of the possibilities is that, since the self-trapping energy for the one-center hole state is small, i.e., it is close to the bottom of the free hole band, part of the holes can be thermally delocalized. This can correspond to the intermediate case which has been discussed by Sumi:[44] while the small polaron state is energetically stable, the thermally populated large polaron states play a dominant role in polaron conduction. This would explain the considerable decay of the number of holes by their fast band motion to the acceptors. However, we should note that this process competes with the two-center state formation which immobilizes the hole. Therefore, more data for different crystals, temperatures, and concentrations of impurity are needed to understand this phenomenon in more details.

Since our method does not take into account the spin-orbit interaction on I and employs a valence-only approximation, it can be considered as representing some general cubic MX (M is alkali atom) crystal with a relatively narrow valence band. From the point of view of the model discussed in this paper, there is no reason why similar temporal evolution of the hole cannot occur in other crystals providing the static criterion for the one-center polaron state is fulfilled, i.e., the relaxation energy is larger than the localization energy. However, this depends on individual crystal. Likely candidates could be KCl where E_{st} was found to be -0.2 eV, or KBr which has similar dielectric constants to that in KI and relatively narrow valence band [2.6 eV (Ref. 21)].

Finally, we would like to note the similarity of the processes of the hole transformation from the one-center state into the V_K center in KI with the $\text{I}+\text{I}^-\leftrightarrow\text{I}_2^-$ combination reaction in solutions. As has been calculated in Refs. 35 and 36, because of the competition between the solvent polarization and chemical bond formation, in the latter process the transformation from (1,0) into (1/2,1/2) state also occurs at some critical distance (3.45 Å in acetonitrile). However, since the dielectric constant of the acetonitrile is 37.5, which is several times larger than in KI, the combination process even has some small barrier and the critical distance is much smaller than found in this paper for KI.

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