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MOTION OF OH⁻ IMPURITY IN KCl†

M. E. Baur and W. R. Salzman*
Department of Chemistry, University of California, Los Angeles, California
(Received 16 December 1966)

Evidence has accumulated indicating the presence of a complicated motional state structure for the impurity species OH⁻ in KCl.[1-5] Interpretations of the available data have made use of both the Devonshire model for rotation in an octahedral field[5] and the alternative picture of tunneling between localized "pocket" states.[6-9] From optical,[2] paraelectric resonance,[4] and dielectric[1,10] data, it seems very likely that the OH⁻ ion in KCl experiences a minimum in potential when the center of mass is on a $\langle 100 \rangle$ axis, leading to a lowest motional manifold comprising six states split into $A_{1g} + T_{1u} + E_g$ with characteristic energy separations between these levels on the order of 0.3 cm⁻¹. Recent spectroscopic data[5] show in addition the presence of levels near 32 and 293 cm⁻¹ in OH⁻-KCl; both these features exhibit shifts upon substitution of D for H in the impurity ion by a factor close to the $2^{-1/2}$ to be expected if the states involved are those of a librator. The 293-cm⁻¹ level was assigned to the second motional manifold predicted by the Devonshire theory,[5] in which purely angular motion of the impurity ion with center of mass fixed at the cavity center is assumed. Numerical agreement of the energy of this level with that predicted by the Devonshire theory is, however, poor on this assignment, although it has been shown that the discrepancy could be associated with the effect of quasistatic lattice distortion.[8] Moreover, the doublet feature near 32 cm⁻¹ then falls entirely outside the framework of the Devonshire model.

The object of this note is to propose an alternative simple model for the motion of OH⁻ in a KCl cavity which accounts in a natural way for both the 32- and 293-cm⁻¹ features and is in at least qualitative accord with other experimental observations. Basic to our model is the assumption that the effect of interactions between impurity ions can be neglected, that is, that the spectrum of Ref. 5 can be taken to be that for an isolated OH⁻ impurity in the lattice. We also accept the assignment of the 293-cm⁻¹ feature to a librational level, as proposed in Ref. 5; we do not, however, make the additional assumption that it corresponds to a transition to states in the second manifold of Devonshire theory. Phonon interactions with the impurity are left out of consideration.

It has been noted[9] that there is a reason to believe that the OH⁻ ion in KCl experiences minima in potential when its center of mass is displaced from the cavity center along $\langle 100 \rangle$ and that in such a case both angular and center-of-mass motion of the ion must be considered. This appears to complicate the description of the system; but since OH⁻ has a small moment of inertia,[11] strong coupling between these two modes of motion may be expected, in a way analogous to the strong coupling between electronic and nuclear motion in molecules within the Born-Oppenheimer approximation.[12] The motional wave function for OH⁻ may therefore be approximately separated into parts depending on angular orientation and center-of-mass position, respectively. Accordingly, we write for the Hamiltonian of the OH⁻ ion in a cavity

$$H = (-\hbar^2/2m)\{\nabla^2 + [(m/M)^{1/2}\nabla_\gamma]^2\} + V(\Omega, \vec{r}), \quad (1)$$

where $M = 17$ amu is the total mass of the ion,

$m = 0.94$ amu is the reduced mass, r is the position vector of the ion center of mass, and $\Omega = (\theta, \varphi)$ is the angular orientation of the O-H axis referred to a laboratory frame.[13] The operator ∇^2 is the angular part of the Laplacian. We now assume that the total wave function $\psi(\vec{r}, \Omega)$ factors according to

$$\psi = \chi(\vec{r})\Phi(\Omega:\vec{r}) \tag{2}$$

with Φ and χ eigenfunctions of

$$H_\Omega = -(\hbar^2/2m)\nabla_\Omega{}^2 + V(\Omega:\vec{r}) \tag{3}$$

and

$$H_\gamma = -(\hbar^2/2M)\nabla_\gamma{}^2 + U(\vec{r}:\Phi), \tag{4}$$

respectively. In (3), the potential V is to be that for angular motion with a fixed value of $\vec{r}$; in (4), U is a potential for motion in $\vec{r}$ averaged over the rotational state Φ. Equation (1) shows that we are in fact carrying out a series expansion in powers of $(m/M)^{1/2} = 0.2$ and retaining the first term.

We shall not write an explicit form for U, but we postulate that U has minima at six equivalent points $\vec{r}_{min}$ off center on the $\langle 100 \rangle$ axes, with barriers between these minima sufficiently high so that the ion center-of-mass motion may be regarded as tunneling between the minimum positions. The approach developed in Ref. 9 is then valid for analysis of this motion, and it follows that the lowest set of center-of-mass motional states comprises (A_{1g}, T_{1u}, E_g); we assign the narrowly split set of levels lying within 0.3 cm^{-1} of the ground state in OH$^-$-KCl to these states. Assuming that $\vec{r}_{min}$ corresponds to a configuration in which the oxygen atom is in contact with a nearest-neighbor K$^+$ ion, with OH$^-$ center of mass then about 0.4 Å off center, the situation for $\vec{r} = \vec{r}_{min}$ is illustrated in Fig. 1.

The analysis of rotational motion, that is, the classification of the states Φ, may then be carried out in accordance with the approximation method given above by assuming the center of mass to be fixed at one of the positions $\vec{r}_{min}$. The symmetry group for which the Φ must form irreducible representations is evidently then C_{4v}. Consider now the situation if $V(\Omega:r = \vec{r}_{min})$ were to be of essentially two-dimensional harmonic-oscillator form with a single minimum for alignment of the O-H axis along the fourfold axis of C_{4v}, that

is [100]. The OH$^-$ ion would then perform librations in Ω about the single minimum and the only low-temperature spectral features associated with these motions would be those arising from transitions between the ground and excited states of a librator, that is, a confined OH$^-$ rotor. It follows from uncertainty-principle arguments that such confinement produces an energy splitting between the ground and first excited states greater than the 38 cm^{-1} for the free OH$^-$ rotor; one would expect this splitting in fact to become on the order of 100 cm^{-1} or more. Hence no spectral features other than those associated with center-of-mass motion would occur at frequencies below about 100 cm^{-1}. These latter have already been assigned to the levels lying within 0.3 cm^{-1} of the ground state, so that the 32-cm^{-1} doublet would not be present. However, the form of V predicted by a point-charge calculation of potential as a function of O-H axis alignment with the ion center of mass placed as shown in Fig. 1 is not as considered above. Taking the center of mass to be 0.4 Å off center on the [100] axis, the O-H distance to be 1.10 Å, and the effective charge on the H atom to be $0.3e$, giving the lattice parameters their known
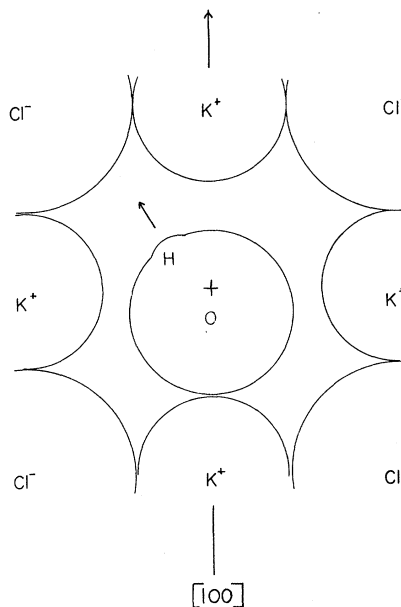

FIG. 1. Proposed configuration of minimum U for OH$^-$ in KCl, with $r = r_{min}$. The ion center of mass is on [100] with the oxygen atom in contact with K$^+$. The hydrogen atom, here shown on the [111] axis, moves in the potential V.

values for an undistorted KCl lattice, and sum-
ming over nearest- and next-nearest-neigh-
bor K^+ and nearest-neighbor Cl^- ions, we find[14]
that alignment of the O-H axis along [100] cor-
responds to a rather broad <u>maximum</u> in poten-
tial energy and that V decreases as the O-H
axis moves away from [100] in the two equiv-
alent (011) planes but tends to increase if the
deviation is in the (010) or (001) planes. The
situation is illustrated schematically in Fig. 2(a).
At sufficiently large deviation overlap repul-
sion causes V to increase and, although we
cannot state at what angle of deviation overlap
becomes significant, it appears likely that the
dominant feature in V is a shallow fourfold
minimum with lowest potential for positioning
of the H atom in a (011) plane off the [100] axis.
In terms of the potential cross section sketched
in Fig. 2(a), the angular motion of OH^- is that
of a librator in a harmonic well perturbed by
a potential barrier at the center, of height on
the order of 10^2 cm^{-1}. The height of this max-
imum is too small to give the motional states
Φ a true tunneling character; qualitatively the
main effect of the barrier will be to raise the
librator ground state in energy and diminish
the energy splitting between it and the first
excited state. Higher librational levels will
be much less affected, and their splittings should
lie in the range 100-150 cm^{-1} appropriate for
the equivalent approximate harmonic potential
of Fig. 2(a). The correct group-theoretical
labeling of these librational states under C_{4v}
is $^1A_1$, ^1E, $^1B_1$, $^1B_2$, $^2A_1$, ^2E, etc., in order
of increasing energy; this pattern is sketched
in Fig. 2(b). We propose that the 32-cm^{-1} fea-
ture is associated with the transition $^1A_1 \rightarrow {}^1E$
of the perturbed librator; the doublet charac-
ter of this feature is plausible since both lat-
tice distortion and higher Born-Oppenheimer
terms can split the ^1E states. Transitions from
$^1A_1$ to the triplet of states $(^1B_1, {}^1B_2, {}^2A_1)$ (which
would be degenerate if the potential were of
pure two-dimensional harmonic-oscillator form)
are electric-dipole forbidden. The transition
from $^1A_1$ to ^2E is again allowed; on the argu-
ments given above we expect energy splittings
$^1E \rightarrow (^1B_1, {}^1B_2, {}^2A_1)$ and $(^1B_1, {}^1B_2, {}^2A_1) \rightarrow {}^2E$ on or-
der of 100-150 cm^{-1}, and hence an energy of
230-330 cm^{-1} for the transition $^1A_1 \rightarrow {}^2E$. We
therefore assign the 293-cm^{-1} feature to this
transition.

The available data seem consistent with these
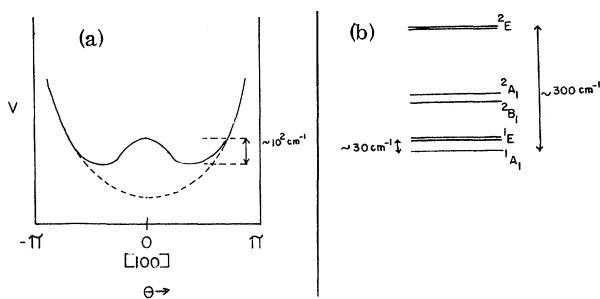assignments. At the temperatures used in Ref.

FIG. 2. (a) Schematic diagram of potential V as func-
tion of polar angle θ for fixed $r = r_{min}$, in (011) plane.
Solid line: actual potential with barrier at $\theta = 0$.
Dashed line: equivalent approximate harmonic poten-
tial; the barrier is considered a perturbation on this
potential. (b) Proposed energy-level diagram for
states Φ of OH^- in KCl.

5 thermal population of excited librational states
would be insufficient to provide any intensity
in the $^1E \rightarrow {}^1B$ or higher transitions. The merg-
ing of the lines of the 32-cm^{-1} doublet at high-
er temperatures[5] is consistent with the prob-
able effect of phonon broadening on the ^1E com-
ponents. Our interpretation is in agreement
with the remark[5] that the rms angular displace-
ment associated with the 32-cm^{-1} feature is
large. The observed mass dependence of both
the 32- and 293-cm^{-1} features[5] is consistent
with librational motion.[15] The low oscillator
strengths reported in Ref. 5 are consistent
with the observation that the dipole moments
of the $^1A_1 \rightarrow E$ transitions are not parallel to
the average orientation of the O-H axis, along
which the dipole of the O-H stretch is aligned,
and with the distribution of the available oscil-
lator strength among several transitions.

The proposed model can be tested experimen-
tally. Only light with polarization perpendic-
ular to the $\langle 100 \rangle$ axis on which the center of
mass resides can induce the $A_1 \rightarrow E$ transitions,
so that if a sample is oriented and a strong
electric field along a $\langle 100 \rangle$ axis is provided
to give preferential center-of-mass alignment
of the OH^- ions, the 32- and 293-cm^{-1} features
should be weaker in the absorption spectrum
obtained using light polarized in the field direc-
tion than in that obtained for polarization per-
pendicular to the field direction. Such an ex-
periment has been carried out[16] but the temper-
atures chosen were so high as to produce con-
siderable thermal broadening and no conclusion
can be reached from the data given. It would

be worthwhile to repeat this experiment at lower temperatures. In addition, we predict that the 32- and 293-cm^{-1} features should shift as (reduced mass)$^{1/2}$ upon isotopic substitution of oxygen in OH^-. We predict that in a Raman absorption experiment on OH^--KCl, the transition $^1A_1 \rightarrow {}^1B_1$ would appear at a frequency in the range 130-180 cm^{-1}. Finally, on the proposed model the splittings in the 0.3-cm^{-1} manifold, here associated with center-of-mass motion, should be sensitive to total mass rather than hydrogen isotope mass specifically. Thermodynamic or microwave absorption experiments may clarify this point.

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[9]M. E. Baur and W. R. Salzman, Phys. Rev. 151, 710 (1966).

[10]M. E. Baur and W. R. Salzman, Phys. Rev. Letters 16, 701 (1966).

[11]The moment of inertia referred to here and elsewhere in this note is the moment of inertia of the OH^- ion taken with respect to an axis perpendicular to the O-H bond and passing through the center of mass. This moment of inertia is assumed independent of both the position of the center of mass and the ion orientation.

[12]See, for example, L. I. Schiff, Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1949), p. 289.

[13]In writing the Hamiltonian in this form, we assume the OH^- rotor to be strictly rigid; that is, we neglect effects due to centrifugal distortion.

[14]A point-charge calculation should be at least qualitatively accurate for a calculation like the present one in which the only species whose position is being varied is, in essence, a hydrogen atom.

[15]Note that the central barrier in the libration potential V proposed here is not so high as to impose the much stronger dependence on mass characteristic of large barrier tunneling situations.

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COLLISION IONIZATION OF SINGLET EXCITONS IN MOLECULAR CRYSTALS

Amalia Bergman, Menahem Levine, and Joshua Jortner
Departments of Chemistry and Physics, Tel-Aviv University, Tel-Aviv, Israel
(Received 21 June 1966)

This Letter is concerned with the electronic relaxation mechanisms of singlet-exciton states in crystalline anthracene. At low exciton densities the lifetime of singlet and triplet excitons in molecular crystals is determined by unimolecular radiative decay and nonradiative internal-conversion processes, while at high exciton densities exciton-exciton interactions may play an important role in the exciton decay processes. From recent experimental and theoretical studies, the following conclusions were drawn:

(a) Triplet-triplet exciton collisions were observed in crystalline anthracene and other molecular crystals, inferred by delay fluorescence, arising from the radiative decay of singlet excitons produced by triplet-triplet exciton annihilation.[1-3]

(b) Collision ionization of singlet excitons in crystalline anthracene[4-6] was studied theoretically.[5,6] The transition of a pair of singlet excitons to a state involving an electron-hole pair is analogous to an Auger-type autoionization process. Experimental evidence for photoconductivity arising from exciton collision-ionization processes in anthracene was presented,[7,8] and seemed to confirm the theoretical value[5] of $\gamma_S = 2.5 \times 10^{-12}$ cm^3 sec^{-1} for the singlet-singlet exciton-annihilation rate constant.

We have been able to provide a direct evidence for bimolecular annihilation of singlet excitons in crystalline anthracene by the study of the radiative decay of two-photon excited states.[2,3,9]