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Molecular Orbital Study of Ionic Defects in Ice

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The potential energy for the diffusion of positive and negative defects in ice is calculated by a SCF-MO-LCAO procedure. The resulting height of the potential energy barrier for positive defects is much lower than for negative ones, thus explaining qualitatively the greater mobility of the H_3O^+ ions. It is also found that the potential-energy heights are very sensitive to the distance between the oxygens, the diffusion being greater when the oxygens are nearer. The results obtained suggest therefore that the diffusion of positive defects is correlated to the vibrations of the lattice.

1. INTRODUCTION

THE existence of ionic and valence defects in ice was postulated by Bjerrum¹ to explain the electrical conductivity of the crystal. The ionic defects are responsible for the direct-current conductivity of ice,² and to explain their mobility it is important to know the potential-energy curve for the motion of the proton. When the proton moves along a $\text{O}_1\text{-O}_2$ line (see Fig. 1),

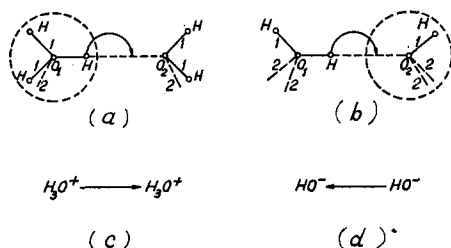


FIG. 1. Diffusion of positive and negative defects. The numbers on the bonds indicate the occupation of the corresponding hybrids.

the ionic defect is transferred to a neighbor water molecule.

We consider positively and negatively charged defects as the units H_3O^+ and HO^- , respectively, preserving the tetrahedral symmetry of ice. While the protons move as shown in Figs. 1(a) and 1(b), the defects diffuse as shown in Figs. 1(c) and 1(d), respectively. The notation is the same as in the previous paper,³ and similar assumptions are made: a system of four electrons in a closed-shell configuration is considered, with the same set of basic orbitals. The assumptions

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¹ N. Bjerrum, Kgl. Danske Videnskab. Selskab Mat. Fys. Medd. **27**, 56 (1951).

² H. Gränicher, Physik Kondensierten Materie **1**, 1 (1963); C. Jaccard, Helv. Phys. Acta **32**, 89 (1959).

³ M. Weissmann and N. V. Cohan, J. Chem. Phys. **43**, 119 (1965).

regarding the "core" potential are also the same as in the previous paper, and the numbers in Figs. 1(a) and 1(b) indicate the occupation number of the corresponding hybrid.

Therefore, the potential due to the electrons not involved in the bond is given by Formulas (3) of the

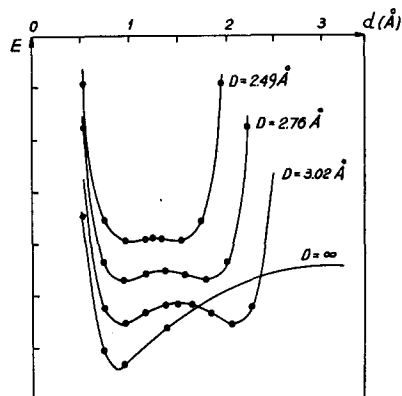


FIG. 2. Total energy E for positive defects as a function of d , for four values of D . The intervals on the energy scale are of 0.2 a.u. = 5.44 eV, and each curve is shifted vertically from the preceding one by exactly that amount.

preceding paper with $Q_1=Q_2=4$ for the H_3O^+ defect and with $Q_1=Q_2=5$ for the HO^- defect. The total energy E , calculated with the aid of Eqs. (1) and (2) of the preceding paper, represents the potential energy for the motion of the proton. It is symmetric in both cases, positive and negative defects. The same programs and integrals of the preceding paper were used.

2. RESULTS AND DISCUSSION

The results for the energies E are given in Table I and Fig. 2 for positive defects and in Table II and Fig. 3 for negative defects. The curve for $D=\infty$ for the negative defects coincides with that for the normal

TABLE I. Energies E for positive defects (in atomic units) for different values of D and d (in atomic units). The last line corresponds to the minimum value of E , fitted numerically. (1 a.u. of energy = 27.2 eV; 1 a.u. of length = 0.529 Å).

$D=4.7$		$D=5.2154$		$D=5.7$		$D=\infty$	
d	E	d	E	d	E	d	E
1.0029	-4.282	1.0029	-4.247	1.4116	-4.752	1.0029	-4.190
1.4116	-4.811	1.4116	-4.774	1.8103	-4.808	1.4116	-4.716
1.8103	-4.887	1.8103	-4.838	2.2090	-4.771	1.8103	-4.761
2.2090	-4.883	2.2090	-4.816	2.6077	-4.737	2.6077	-4.623
2.3500	-4.882	2.6077	-4.802	2.8500	-4.731	∞	-4.374
1.9278	-4.889	1.8347	-4.838	1.7827	-4.808	1.6570	-4.775

hydrogen bond for $D = \infty$, given in the preceding paper [see Fig. 1(b)].

For each value of D , the optimum value of d is larger than in the neutral case and we also find that the optimum value of d increases as D decreases, the effect being more pronounced than in the neutral case.

We have not attempted to calculate the optimum value of D in the case of the ionic defects because it is much more complicated than in the case of a normal hydrogen bond. In fact, any departure from the normal distance in ice implies deformation of the surrounding hydrogen bonds which should properly be taken into account in the calculations. On the other hand, the experimental value of D for the ionic defects is not known exactly as some deformation of the lattice near the defect is likely to occur. We assume that this distortion is zero, thus considering the experimental value of D for the ionic defects the same as in a normal hydrogen bond, that is, 2.76 Å. As in our previous paper and for similar reasons all the following results are given for the experimental value of D .

The proton affinity of the water molecule in ice is calculated as the difference in energy for a positive defect between the values for the optimum value of d (H_3O^+) and $d = \infty$ ($\text{H}_2\text{O} + \text{H}^+$), both for $D = \infty$. The result obtained of 10.9 eV agrees well with Rosenfeld's⁴ calculated value of 11.4 eV and with the experimental one of 8.0 ± 0.7 .

Table III gives the height of the potential barriers for the motion of the protons, as a function of D , and this increases almost linearly with D , the effect being more pronounced for positive defects.

If we try to make up the potential-energy curves for the diffusion of the proton just by superposing symmetrically at $D = 2.76$ Å (5.2154 a.u.) two identical curves for $D = \infty$ as suggested by Baker⁵ we obtain a barrier of 4.1 eV (0.151 a.u.) for a positive defect (see Fig. 4) and of 7.4 eV for a negative one. Configuration interaction with the next energetically closed-shell configuration was done for the case $D = \infty$. It lowered the height of the barrier for the negative defect by 0.9 eV and for the positive defect by only 0.1 eV. This result is to be expected as configuration interaction changes the dissociation products in the case of a neutral molecule from $\text{HO}^- + \text{H}^+$ to the energetically lower $\text{HO} + \text{H}$, but for the positive ion both calculations yield $\text{H}_2\text{O} + \text{H}^+$. Comparison of the height of these barriers with those given in Table III shows that the effect of the neighbor molecule (hydrogen bonding) in the case of the ionic defects is important, as in the case of neutral molecules.

3. MOBILITY OF IONIC DEFECTS

Our results indicate a much lower barrier for the diffusion of positive defects than for the diffusion of

 TABLE II. Energies E for negative defects (in atomic units) for different values of D and d (in atomic units). The last line corresponds to the minimum value of E , fitted numerically. (1 a.u. of energy = 27.2 eV; 1 a.u. of length = 0.529 Å).

$D=4.7$		$D=5.2154$		$D=5.7$		$D=\infty$	
d	E	d	E	d	E	d	E
1.0029	-2.114	1.0029	-2.076	1.4116	-2.486	1.0029	-2.006
1.4116	-2.558	1.4116	-2.513	1.8103	-2.491	1.4116	-2.435
1.8103	-2.593	1.8103	-2.530	2.2090	-2.427	1.8103	-2.419
2.2090	-2.574	2.2090	-2.486	2.6077	-2.382	2.6077	-2.189
2.3500	-2.571	2.6077	-2.466	2.8500	-2.374	∞	-1.299
1.7578	-2.594	1.6674	-2.536	1.6156	-2.503	1.5676	-2.461

⁴ J. L. J. Rosenfeld, J. Chem. Phys. **40**, 384 (1964).

⁵ A. N. Baker, J. Chem Phys. **22**, 1625 (1954); **25**, 381 (1956).

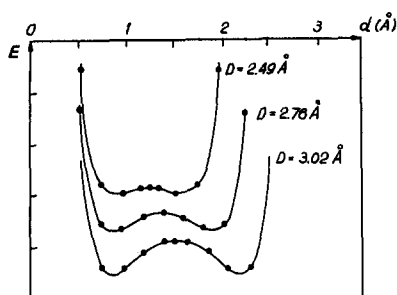


FIG. 3. Total energy E for negative defects as a function of d , for three values of D . The intervals on the energy scale are of 0.2 a.u. = 5.44 eV, and each curve is shifted vertically from the preceding one by exactly that amount.

negative ones. This result seems intuitively correct as in this case the proton, when in the middle of its motion, is between two approximately neutral groups, while in the negative case it is between two negatively charged groups, which produce a great attraction and a deeper well. The results also agree with the experimentally known fact of the greater mobility of the positive ion. In fact, Eigen and de Maeyer⁶ consider the ratio of both mobilities between 10 and 100.

Recently, Gosar⁷ developed a theory for the mobility of the positive defects. In this theory the mobility is proportional to the square of the separation between the first two proton levels in the symmetric potential-energy curve. This separation changes almost exponentially with the height of the barriers thus making the mobility very sensitive to it. Finally, it should be remembered that the height of the barrier depends almost linearly with D .

To obtain the experimental value of $0.075 \text{ cm}^2/\text{V}\cdot\text{sec}$,⁶ a separation of $1.24 \times 10^{-3} \text{ eV}$ is needed.

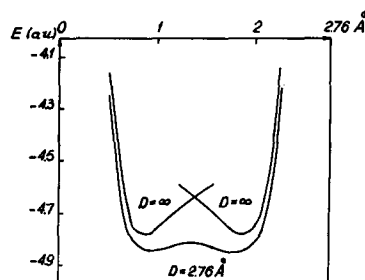


FIG. 4. Potential-energy barriers for positive ions.

⁶ M. Eigen and L. de Maeyer, Proc. Roy Soc. (London) **A247**, 505 (1958).

⁷ P. Gosar, Nuovo Cimento **30**, 931 (1963); P. Gosar and M. Pintar, Phys. Status Solidi **4**, 675 (1964).

TABLE III. Height of the potential barrier for the motion of positive and negative defects (in electron volts).

D (Å)	H_3O^+	HO^-
2.49	0.19	0.62
2.76	0.98	1.90
3.02	2.20	3.50

We find that this separation corresponds approximately to a barrier of 0.44 eV, almost independent of the shape of the potential barriers. This follows from the calculations due to Hornig and Somorjai⁸ and to Gerson.⁹ From our results of Table III, this potential-energy height would correspond to a value of $D = 2.58 \text{ Å}$. It seems reasonable that such a value can be obtained by the vibrations of the lattice, from its equilibrium position with $D = D_0 = 2.76 \text{ Å}$. In fact, a simple calculation supports this view. The mean quadratic displacement from the equilibrium distance D_0 is given by

$$\langle (D - D_0)^2 \rangle_{av} = \int_{-\infty}^{\infty} F(D) (D - D_0)^2 dD.$$

For low temperatures

$$F(D) = (\beta/\pi)^{1/2} \exp[-\beta(D - D_0)^2]$$

and $\beta = 2.69 \times 10^{17} \text{ cm}^{-2}$ according to Haas and Hornig.¹⁰ Then,

$$\langle (D - D_0)^2 \rangle_{av} = (1/2\beta)^{1/2} = 0.13 \text{ Å}.$$

This value agrees fairly well with the above results.

It should also be noted that when D decreases, the optimum value of d increases thus contributing also to the lowering of the height of the barrier.

For positive ions Gosar found that the motion of the protons is correlated and that the mean free path of the H_3O^+ ion is approximately $3D$. Our method of calculation neglects this correlation altogether, and it is by no means simple to include it.

We finally conclude that the potential energy for the diffusion of positive defects is definitely lower than for negative defects, and that both are extremely sensitive to the $\text{O}_1\text{-O}_2$ distance. Therefore, it is highly probable that the diffusion of the charged defects is correlated with the vibrations of the lattice.

⁸ R. L. Somorjai and D. F. Hornig, J. Chem. Phys. **36**, 1980 (1962).

⁹ F. Gerson, Helv. Chim. Acta **44**, 471 (1961).

¹⁰ C. Haas and D. F. Hornig, J. Chem. Phys. **32**, 1763 (1960).