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Influence of Zero-Point Vibration on the Superhyperfine Interactions of Hydrogen and Deuterium Centres in KCl

By

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The superhyperfine (shf) interactions of D_i^0 centres were measured by ENDOR and compared with those of H_i^0 centres (H_i^0 = H atom on interstitial lattice position). The isotropic shf constants of the nearest K and Cl neighbours are smaller for D_i^0 centres than for H_i^0 centres: $a_H(K)/a_D(K) = 1.165$ and $a_H(Cl)/a_D(Cl) = 1.026$. In a model calculation it is shown that the large difference in isotope effect of the K and Cl neighbours can be understood as a consequence of the overlaps of their ion cores. At least 30% of $a_H(K)$ and 10% of $a_H(Cl)$ are only due to zero-point vibrations of the H atom.

Mit ENDOR wurden die Superhyperfein (shf)-Wechselwirkungen von D_i^0-Zentren gemessen und mit denen von H_i^0-Zentren verglichen (H_i^0 = H-Atome auf Zwischengitterplatz). Die isotropen shf-Konstanten der nächsten K- und Cl-Nachbarn sind bei D_i^0-Zentren kleiner als bei H_i^0-Zentren: $a_H(K)/a_D(K) = 1.165$ und $a_H(Cl)/a_D(Cl) = 1.026$. Anhand einer Modellrechnung wird gezeigt, daß der große unterschiedliche Isotopeneffekt der K- und Cl-Nachbarn als Folge ihrer gegenseitigen Überlappung verstanden werden kann. Es ergibt sich, daß mindestens 30% von $a_H(K)$ und 10% von $a_H(Cl)$ nur durch die Nullpunktschwingungen des H-Atoms zustande kommen.

1. Introduction

Hydrogen atoms in interstitial lattice positions can be produced in alkali halides by photodissociation of OH^- or SH^- centres at low temperatures [1, 2, 3]. The ESR spectrum of these H_i^0 centres shows two proton hyperfine (hf) lines separated by approximately the hf constant of the free hydrogen atom. Each has a further structure due to the superhyperfine (shf) interactions with the neighbouring lattice nuclei. In most cases the ESR spectrum resolves only the shf interaction with the four nearest halogen nuclei [2, 4]. With ENDOR measurements on H_i^0 centres in KCl and RbCl the shf and quadrupole interactions with two shells of alkali nuclei and three shells of halogen nuclei could be determined with high precision [5, 18]. From the isotropic hf constants the density of the centre electron at the sites of the neighbouring nuclei can be calculated. Various attempts have been made to interpret theoretically the measured electron densities [5, 6, 7, 8, 9, 10]. The calculations were based on a static model for the H_i^0 centre. However, the light mass of the proton with the correspondingly large amplitude of the zero-point vibration can have an appreciable effect on the shf interactions. The measured electron density contains then a dynamical part which must be taken into account in theoretical calculations. This was first pointed out for H_i^0 in KCl by Mimura and Uemura [6], who had, however, no experimental data to compare with their calculations.

The influence of the zero-point vibration on the shf constants can be studied experimentally by investigating also D_i^0 centres, for which the amplitude of the zero-point vibration is smaller than for H_i^0 assuming the same potential for the motion. D_i^0 centres in KCl were studied with ESR by Hausmann [11]. We have investigated them with ENDOR and compared the shf interactions with those of H_i^0 centres.

2. Experimental

2.1 *Production of D_i^0 centres*

The D_i^0 centres were produced by photodecomposition of SD^- centres at 77 °K. To obtain SD^- centres, single crystals were grown by the Kyropoulos method from well dried KCl material in an atmosphere of 7 Torr D_2S and 15 Torr Ar. It was necessary to add some D_2O to the melt in order to avoid strong contamination with hydrogen from the growing apparatus. The crystals used contained about 80% SD^- and 20% SH^- centres.

2.2 *ESR and ENDOR measurements*

The measurements were done at X-band frequency with a superheterodyne spectrometer. For ENDOR the stationary method developed by Seidel [12] was used. The apparatus is described in [13]. ENDOR signals of H_i^0 centres could be obtained at 77 °K [5], whereas for the D_i^0 centres the temperature had to be lowered to about 60 °K. Related to the same number of centres the ENDOR effect was weaker in the case of D_i^0 compared to H_i^0.

3. Results

In Fig. 1 the ESR spectrum is shown for $\boldsymbol{B}_0$ in [100]. The two outer line groups are due to H_i^0 centres ($I_H = 1/2\ \hbar$), the three inner line groups are due to the D_i^0 centres ($I_D = 1\ \hbar$). The splitting into 13 equidistant lines of each group is

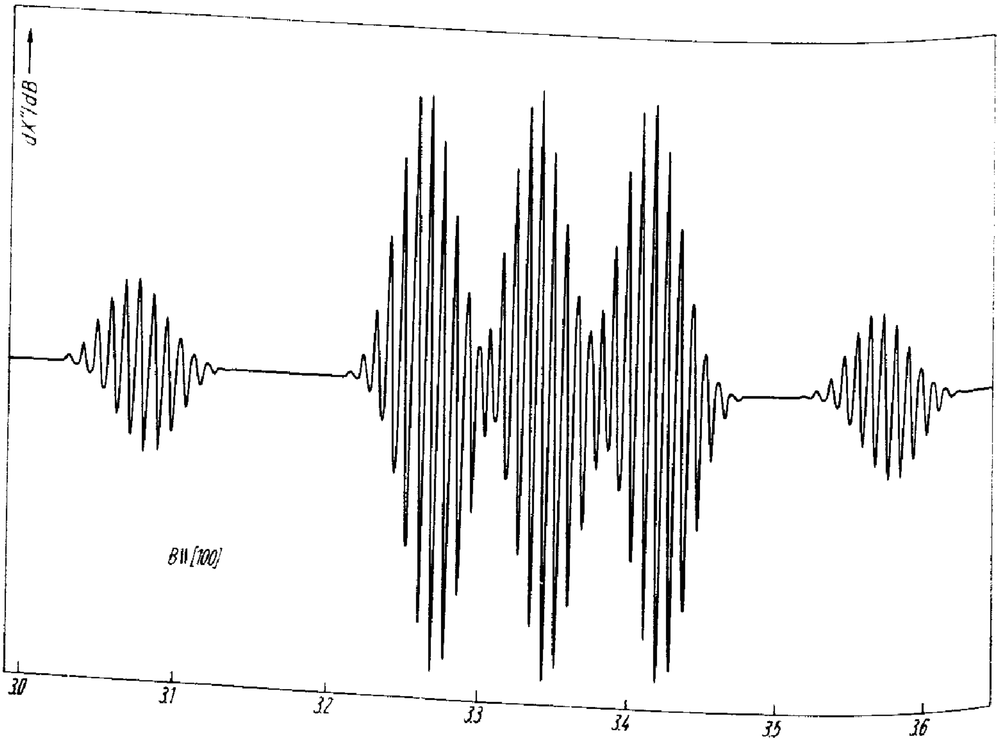

Fig. 1. ESR spectrum of H_i^0 and D_i^0 centres in KCl at 77 °K. $\boldsymbol{B}_0 \parallel [100]$, $\nu_{ESR} = 9.38$ GHz

Table 1

g-value and hf constants

	g	a (G)
H	$2.0030 \pm 1.2 \times 10^{-4}$	491.4 ± 0.2
D	$2.0030 \pm 1.0 \times 10^{-4}$	75.62 ± 0.10

due to the shf interaction with the 4 nearest Cl nuclei ($I_{\text{Cl}} = 3/2\ \hbar$). In Table 1 the g-values and the proton and deuterium hf constants are listed. g and a were determined taking into account the second-order shifts due to hf and shf interactions. The electron densities at the proton and deuterium are nearly equal:

$$\frac{\psi_{\text{H}}^2(0)}{\psi_{\text{D}}^2(0)} = (0.9974 \pm 0.0015)\,.$$

The ENDOR spectra are very similar to those obtained for H_i^0 centres. Their analysis proceeds along the same lines and is described in detail in [5].

In Table 2 the shf and quadrupole interaction constants of the 4 nearest Cl and K nuclei (first shell: Cl^{I}, K^{I}) are given in terms of a, b, and q.

$$a = \frac{2\,\mu_0}{3}\, g_e\, \mu_{\text{B}}\, g_{\text{I}}\, \mu_{\text{N}}\, |\psi(\boldsymbol{r}_\alpha)|^2 \tag{1}$$

is the isotropic part of the shf tensor, which is proportional to the centre electron density $|\psi(\boldsymbol{r}_\alpha)|^2$ at the site of nucleus α. b is related to the principal value of the anisotropic part of the shf tensor by $b = 1/2\ B_{zz}$, and similarly q to the quadrupole tensor by $q = 1/2\ Q_{zz}$. The z-direction was chosen as the axis with the largest principal value. The principal axes of the shf and quadrupole tensors of the K^{I} and Cl^{I} nuclei are the [111] directions, because they are threefold symmetry axes. For comparison the results are also given for H_i^0 centres. They

Table 2

Shf constants of D_i^0 and H_i^0 centres in KCl (in MHz)

	a/h	b/h	$3\,q/h$
$^{39}\text{K}^{\text{I}}$(D)	0.844	0.443	+0.050
$^{39}\text{K}^{\text{I}}$(H)	0.983	0.457	+0.045
$^{35}\text{Cl}^{\text{I}}$(D)	23.13	6.64	−0.172
$^{35}\text{Cl}^{\text{I}}$(H)	23.74	6.71	−0.174
X (K)	1.165	1.032	0.90
	± 0.005	±0.005	±0.06
X (Cl)	1.026	1.010	1.00
	± 0.002	±0.002	

The values of H_i^0 centres are taken from [5]. The last given figure is uncertain in 1 or 2 units. The temperature for D_i^0 is 60 °K, for H_i^0 77 °K. X is the ratio of the hydrogen and deuterium constants (e.g., $a_{\text{H}}(\text{K})/a_{\text{D}}(\text{K})$).

were taken from [5]. In the last two rows of Table 2 we list the ratios of the hydrogen and deuterium interaction constants, which are denoted by X. The shf constants of the deuterium centre are lower than those of the hydrogen centre, demonstrating the influence of the vibrational amplitude. The effect is larger in the isotropic than in the anisotropic constant, and much larger for the K^I nuclei than for the Cl^I nuclei. The magnitude of the reduction of $a(K^I)$ for deuterium indicates that here indeed a very large portion of the measured isotropic shf constant is due to hydrogen vibrations, i.e., is purely dynamical in nature.

The quadrupole interaction showed within experimental error no change for the Cl^I nuclei, whereas it increases for K^I in contrast to the hf values in the deuterated centre.

Like in the case of H_i^0 centres the interactions of a second shell of K nuclei, which are immediate neighbours to the Cl^I nuclei, could be determined. Within the experimental error of ±2% the shf and quadrupole constants are the same for D_i^0 and H_i^0 centres (see also [5]).

4. Model Calculation

4.1 *Qualitative considerations*

The aim of the following theoretical considerations is to explain (i) the observed reduction of the isotropic shf constants of the K^I and Cl^I nuclei and (ii) the fact that for the K^I nuclei the isotope effect is much larger than for the Cl^I nuclei.

We assume a static lattice in which only the hydrogen and deuterium atoms vibrate which is justified approximately considering the much larger masses of the K and Cl nuclei. Further we assume that

$$h\,\nu_0 \gg kT \gg h\,\nu_{\text{shf}}\,,$$

where ν_0 is the vibration frequency of the centre atom and ν_{shf} is the frequency of the fluctuation of the local magnetic field due to the shf interaction. For ν_0 a frequency of the order of $10^{13}\,\text{s}^{-1}$ is to be expected judging from IR data on U_1-centres (H_i^- centres) in alkali halides [14] or IR data on H^0 centres in CaF_2 [15]. The results we obtain below justify the assumption that the condition $h\,\nu_0 \gg kT$ is satisfied, and thus we assume that we have to consider only zero-point vibrations. $\nu_0 \gg \nu_{\text{shf}}$ means that we observe only an average effect of the vibrations on the shf structure. H_i^0 and D_i^0 shall move in the same potential, i.e. the lattice shall not be affected differently by introducing H_i^0 and D_i^0 atoms. For simplicity it is supposed to be undistorted.

According to equation (1) the wave function of the centre electron must be known to calculate the isotropic shf constant. The most simple wave function for the ground state which explains the observed order of magnitude of $a(K^I)$ and $a(Cl^I)$ is obtained by orthogonalizing the hydrogen 1s function Φ_H to the ion cores of the 8 neighbouring ions [5, 16]. This leads to admixtures of core orbitals into Φ_H. Since only s-admixtures contribute to a, one obtains with this wave function for, e.g., Cl^I [5]

$$a^{Cl^I} = \frac{2\,\mu_0}{3}\, g_e\, \mu_B\, g_I\, \mu_N\, N^2 \left|\Phi_H(Cl^I) - \sum_{j=1}^{3} \langle \Phi_H | \psi_{js}^{Cl^I}\rangle\, \psi_{js}^{Cl^I}(0)\right|^2 . \qquad (2)$$

The admixture coefficients are the overlap integrals of Φ_H with the ion core s-orbitals. The contribution of Φ_H to a is only very small. a is mainly due to the ion core s-admixtures. A similar relation holds for the K^I nuclei.

The overlap integrals depend on the distance between the proton (deuteron) and the neighbouring nuclei. In this static calculation the isotropic constant is exactly the same for H_i^0 and D_i^0 since both have the same distance from the neighbours. If one considers the vibration of the centre atom, however, then at each moment the overlap integral will be different and we will observe in the experiment an average effect of the motion on the overlap integrals and the isotropic constant, respectively. To discuss this further let us consider for simplicity only the 3s admixture which gives the largest contribution to a. We have then

$$a^{\mathrm{Cl^I}}(\varrho) = C\,|\langle \Phi_H | \psi_{3s}^{\mathrm{Cl^I}} \rangle (\varrho)|^2 \,.$$

C is a constant and ϱ the distance between the centre atom and the $\mathrm{Cl^I}$ nucleus. $C = \frac{2\,\mu_0}{3}\, g_e\, \mu_B\, g_1\, \mu_N\, N^2\, |\psi_{3s}^{\mathrm{Cl^I}}(0)|^2$ (the small dependence on ϱ of N^2 through the overlap integral can be neglected). We will assume that the electron wave function follows adiabatically the motion of the proton and deuteron, respectively.

In Fig. 2 the effect of the zero-point vibration on the square of the overlap integral is shown schematically. $S^2 = \langle \Phi_H | \psi_{3s}^{\mathrm{Cl}} \rangle^2$ is plotted as a function of ϱ. Centered around R, the equilibrium distance between the centre atom and the $\mathrm{Cl^I}$ nucleus, the probability $\chi_H^2\,(\varrho - R)$ to find the proton, and $\chi_D^2\,(\varrho - R)$ to find the deuteron, as a consequence of the zero-point vibrations are drawn. (Their difference is exaggerated somewhat to clarify the picture.)

Let us assume the proton hops infinitively fast between the two points H_1 and H_2 where χ_H^2 has its half value. One would then observe for S^2 the linear average between $S_{H_1}^2$ and $S_{H_2}^2$ (point A). Similarly for deuterium one would observe the linear average between $S_{D_1}^2$ and $S_{D_2}^2$ leading to a lower value for $\overline{S^2}$ (point B) and thus to a lower isotropic constant. The static value of S^2 (point C) is again lower. One observes thus an interaction constant a which contains a dynamical part which is the difference between A and C for the proton and B and C for the deuteron.

More accurately one must average $S^2(\varrho)$ with the probabilities χ_H^2 and χ_D^2 in order to determine the dynamical parts of the isotropic constants quantitatively. From Fig. 2 one can see that the magnitude of the dynamic part of a depends on the curvature of the function $S^2(\varrho)$.

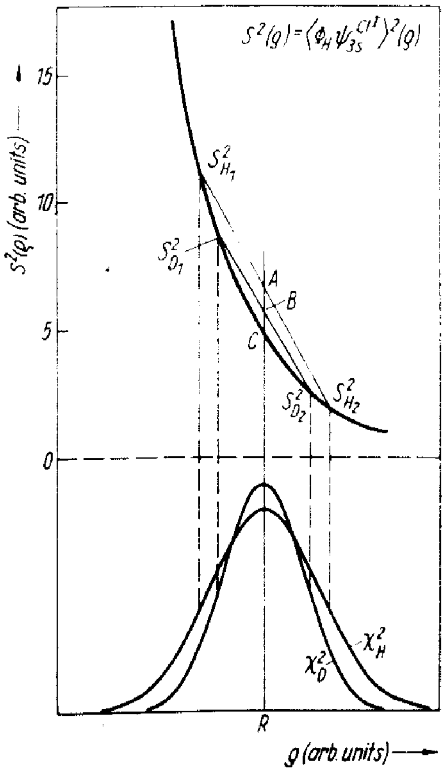

Fig. 2. Schematic representation of the influence of hydrogen and deuterium vibrations on $\langle \Phi_H | \psi_{3s}^{\mathrm{Cl^I}} \rangle\, (\varrho)$

4.2 *Quantitative treatment — Model I: Schmidt orthogonalization of hydrogen 1s to the ion cores*

Assuming a harmonic potential for the zero-point vibration, χ_H is given by

$$\chi(r) = \left(\frac{\alpha}{\pi}\right)^{3/4} e^{-\alpha/2\, r^2}\,, \tag{3}$$

where $\alpha = \frac{1}{\hbar}\sqrt{fM}$. f is the force constant of the potential and assumed equal for H_i^0 and D_i^0, M is the mass of the proton or deuteron. r is the distance as measured from the equilibrium position. In order to average $S^2(\varrho)$ with χ_H^2, χ_D^2 one needs an analytical expression for $S(\varrho)$. We have computed the overlap integrals $\langle \Phi_H | \psi_{ns}^{KI, ClI} \rangle$ and $\langle \Phi_H | \psi_{3p_\sigma}^{KI, ClI} \rangle$ as a function of ϱ and found that $S(\varrho)$ could be represented by

$$S(\varrho) = S_0\, e^{-\beta\varrho} \tag{4}$$

around the equilibrium distance R. β and S_0 are fitting parameters. The accuracy of (4) is lowest for the largest overlaps (3s and 3p), but for $\varrho = R$ ($= 5.14$ at. units) ± 1 at.unit the fit is accurate within 1 to 2%. It suffices to consider the above range of ϱ as the resulting value for α (or the amplitude of the vibration) will show. In Table 3 the obtained parameters S_0 and β are collected. The overlap integrals were calculated using the analytical Clementi functions of the free K^+ and Cl^- ions [17].

Table 3

Overlap intergrals $\langle \Phi_H | \psi_{ns,3p}^{ClI, KI} \rangle$ as a function of ϱ represented in the form $S = S_0\, e^{-\beta\varrho}$ around the equilibrium distance R. β in at. units

		3 s	2 s	1 s	3 p
K^I	S_0	4.6113	0.8230	0.1038	4.4392
	β	0.9293	0.9945	1.0000	0.8403
Cl^I	S_0	4.9390	1.0255	0.1224	3.2236
	β	0.8283	0.9938	1.0000	0.5766

With the analytical expression (4) for $S(\varrho)$ we can calculate the average of $S^2(\varrho)$ with χ_H^2 (see Fig. 3):

$$\overline{S^2} = \left(\frac{\alpha}{\pi}\right)^{3/2} S_0^2 \iiint e^{-2\beta\varrho}\, e^{-\alpha r^2}\, \varrho^2\, d\varrho \sin\theta\, d\theta\, d\varphi\,,$$

$$\overline{S^2} = \left(\frac{\alpha}{\pi}\right)^{3/2} S_0^2 \iiint e^{-2\beta\varrho}\, e^{-\alpha(R^2+\varrho^2-2R\varrho\cos\theta)}\, \varrho^2\, d\varrho \sin\theta\, d\theta\, d\varphi\,.$$

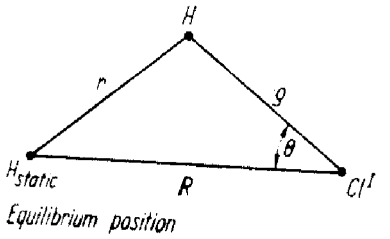

Fig. 3. Coordinates used in deriving equation (5)

The integral can be evaluated and one obtains

$$\overline{S^2} = S_0^2 \left[\frac{1}{2} \left(1 - \frac{\beta}{\alpha R}\right) e^{(\beta^2/\alpha) - 2\beta R} \left\{ 1 + \mathrm{erf} \left(\sqrt{\alpha} \left(R - \frac{\beta}{\alpha} \right) \right) \right\} + \right.$$

$$\left. + \frac{1}{2} \left(1 + \frac{\beta}{\alpha R}\right) e^{(\beta^2/\alpha) + 2\beta R} \left\{ 1 - \mathrm{erf} \left(\sqrt{\alpha} \left(R + \frac{\beta}{\alpha} \right) \right) \right\} \right], \tag{5}$$

where

$$\mathrm{erf}\,(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2}\, dx\,.$$

Since $\beta \approx 1$ at.unit, $R \approx 5$ at.units, this expression can be approximated for $\alpha \geqq 0.4$ at.units to better than 10^{-3} by

$$\overline{S^2} = S_0^2\, e^{-2\beta R} \left(1 - \frac{\beta}{\alpha R}\right) e^{\beta^2/\alpha}\,, \qquad \overline{S^2} = S^2_{\text{static}} \left(1 - \frac{\beta}{\alpha R}\right) e^{\beta^2/\alpha}\,. \tag{6}$$

This approximation is very good, since for $\nu_0 = 10^{13}\ \mathrm{s}^{-1}$ one has $\alpha = 2.8$ at.units.

Essentially the factor $e^{\beta^2/\alpha}$ determines the dynamical effect on S^2 or the isotropic constant. From this it is seen, what we discussed already qualitatively, that $\overline{S^2}$ is greater than S^2_{static}, that is the measured isotropic constant is higher than one would expect from static calculations. For a given potential α the dynamical effect depends on β^2, which determines the curvature of $S^2(\varrho)$. This dependence was already qualitatively seen. Hence one expects that for a given potential $a(\mathrm{K}^{\mathrm{I}})$ has a higher dynamical part than $a(\mathrm{Cl}^{\mathrm{I}})$ since, e.g., $\beta(\mathrm{K}^{\mathrm{I}}_{3s})$ is larger than $\beta(\mathrm{Cl}^{\mathrm{I}}_{3s})$. The value of β is, of course, related to the extension of the neighbour ion core orbitals. The orbital Cl^-_{3s} is more extended and consequently falls off more slowly in its far wing than the orbital K^+_{3s}. This leads to a lower value of β for Cl^-_{3s} compared to K^+_{3s}. The dynamical effect is smaller for extended orbitals like Cl^-_{3s} and Cl^-_{3p} than for more contracted ones.

The ratio of the isotropic constant for H_i^0 and D_i^0 centres becomes

$$X = \frac{a(\mathrm{H})}{a(\mathrm{D})} = \frac{\left(1 - \dfrac{\beta}{\alpha R}\right) e^{\beta^2/\alpha}}{\left(1 - \dfrac{\beta}{\sqrt{2}\,\alpha R}\right) e^{\beta^2/\sqrt{2}\,\alpha}}\,. \tag{7}$$

This relation holds for the case that the overlap with only one orbital is considered. It is known, however, that all three s-orbitals must be taken into account (cf. equation (2)). This leads to a sum of expressions similar to equation (6) and consequently to an expression for X somewhat more complicated than equation (7).

So far the potential parameter α is not known. We have calculated $X(\mathrm{K}^{\mathrm{I}})$ and $X(\mathrm{Cl}^{\mathrm{I}})$ as a function of α including 3s, 2s, and 1s admixtures. If one fits $X(\mathrm{Cl}^{\mathrm{I}})$ to the experimental value, one gets a potential parameter $\alpha = 5.44$ at.units which corresponds to a frequency for the hydrogen vibration of $\nu_0 = 1.95 \times \times 10^{13}\ \mathrm{s}^{-1}$.

This is in agreement with the expected order of magnitude. For the same α one obtains for the K^{I} nuclei $X(\mathrm{K}^{\mathrm{I}}) = 1.036$. Although this result describes the right tendency that $X(\mathrm{K}^{\mathrm{I}}) > X(\mathrm{Cl}^{\mathrm{I}})$, it cannot explain the observation that the isotope effect for K^{I} is about 6 times that of Cl^{I}.

The fit to determine α was made to $X(\mathrm{Cl^I})$, because in the static calculation of equation (2) the observed isotropic constant of $\mathrm{Cl^I}$ could be much better explained than that of the $\mathrm{K^I}$ nuclei. With (2) one obtains $a(\mathrm{Cl^I})_{\mathrm{theor}} = 0.8\, a(\mathrm{Cl^I})_{\mathrm{exp}}$ and $a(\mathrm{K^I})_{\mathrm{theor}} = 4.6\, a(\mathrm{K^I})_{\mathrm{exp}}$ (for details see [5]). The values for $Y = a(\mathrm{H})/a_{\mathrm{static}}$ for $\mathrm{K^I}$ and $\mathrm{Cl^I}$ according to Table 4 show that the dynamical effects are of the order of 10% for both ions.

Table 4
Results of model calculation

	Model I	Model II	Experiment
$X\ (\mathrm{Cl^I})$	(1.026)*)	(1.026)*)	1.026
$X\ (\mathrm{K^I})$	1.036	1.091	1.165
$Y\ (\mathrm{Cl^I})$	1.090	1.093	
$Y\ (\mathrm{K^I})$	1.13	1.37	
α	5.44 a. u.	5.6 a. u.	
ν_0	$1.95 \times 10^{13}\ \mathrm{s^{-1}}$	$2.01 \times 10^{13}\ \mathrm{s^{-1}}$	
x_0	0.227 Å	0.223 Å	

*) These values were fitted to the experimental result. $X = \bar{a}(\mathrm{H})/\bar{a}(\mathrm{D})$; $Y = \bar{a}(\mathrm{H})/a_{\mathrm{static}}$; α potential parameter, ν_0 hydrogen frequency, x_0 amplitude of hydrogen vibration for which $\chi_{\mathrm{H}}^2(x_0) = 1/e$.

4.3 *Model II: Consideration of the mutual overlap of neighbouring ion cores*

It was shown in [5] that the theoretical static value for $a(\mathrm{K^I})$ could be greatly improved by taking into account the fact that the ion core orbitals of neighbouring lattice ions are mutually not orthogonal. It was tacitly assumed in deriving equation (2) that the ion cores were orthogonal on each other. Consideration of their nonorthogonality leads to changes in the admixture coefficients of core orbitals into Φ_{H}. For the admixture coefficient of, e.g., $\psi_{3s}^{\mathrm{K^I}}$ one obtains instead of $\langle \Phi_{\mathrm{H}} | \psi_{3s}^{\mathrm{K^I}} \rangle$ the following coefficient:

$$\langle \Phi_{\mathrm{H}} | \psi_{3s}^{\mathrm{K^I}} \rangle'(\varrho) \approx \left\{ \langle \Phi_{\mathrm{H}} | \psi_{3s}^{\mathrm{K^I}} \rangle - \frac{3}{\sqrt{3}} \langle \Phi_{\mathrm{H}} | \psi_{3p\sigma}^{\mathrm{Cl^I}} \rangle (\varrho) \langle \psi_{3p\sigma}^{\mathrm{Cl^I}} | \psi_{3s}^{\mathrm{K^I}} \rangle \right\}. \tag{8}$$

For simplicity only the overlap of the Cl 3p orbital with the K 3s orbital along [100] directions connecting $\mathrm{K^I}$ and $\mathrm{Cl^I}$ is considered, which gives the largest contribution. The corresponding expression for $\langle \Phi_{\mathrm{H}} | \psi_{3s}^{\mathrm{Cl^I}} \rangle'$ is obtained by interchanging $\mathrm{K^I}$ and $\mathrm{Cl^I}$ orbitals in (8) (for details see [5]). The effect of the nonorthogonality of the ion cores is to reduce the admixture coefficients. Both terms in (8) are of the same order of magnitude. One obtains for $\mathrm{K^I}$: $\langle \Phi_{\mathrm{H}} | \psi_{3s}^{\mathrm{K^I}} \rangle' \approx$ $\approx 0.5 \langle \Phi_{\mathrm{H}} | \psi_{3s}^{\mathrm{K^I}} \rangle$. In order to calculate the dynamical effect on the reduced admixture coefficient of $\psi_{3s}^{\mathrm{K^I}}$, we have to square equation (8) and to average with χ_{H}^2 or χ_{D}^2. Since the ϱ-dependence of the second term in equation (8) is

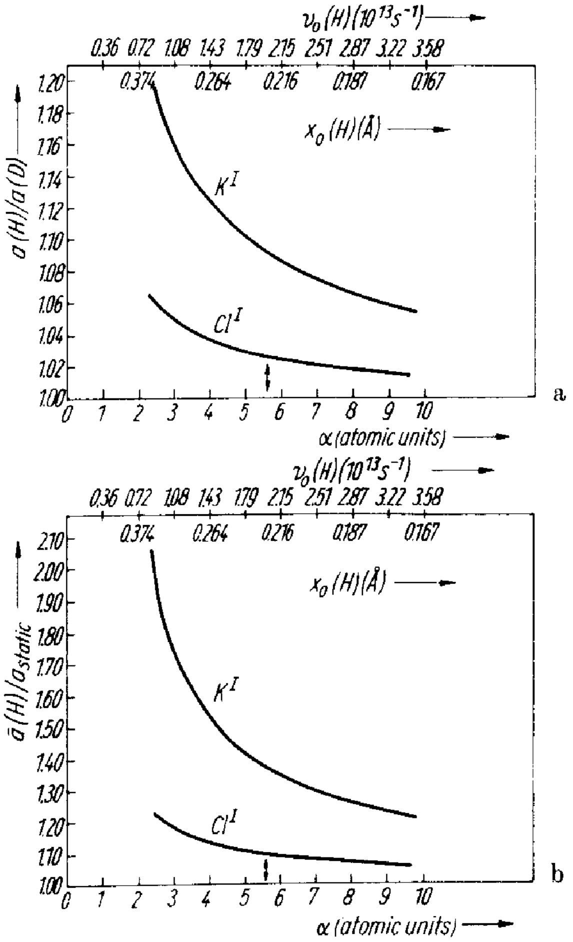

Fig. 4. Isotope effect and $\bar{a}(\mathrm{H})/a_{\mathrm{static}}$ as function of the potential parameter α according to model II. ν_0 is the hydrogen vibration frequency and x_0 the hydrogen amplitude for which $\chi^2_{\mathrm{H}}(x_0) = 1/e$. a) Isotope effect; b) $a(\mathrm{H})/a_{\mathrm{static}}$

much smaller (as seen from the much smaller value of β for $\langle \Phi_{\mathrm{H}} | \psi^{\mathrm{Cl}}_{3\mathrm{p}\sigma} \rangle$; Table 3) than that of the first term and consequently the influence of the vibration on it also ($\propto e^{\beta^2/\alpha}$), the vibration affects mainly the first term. That means that the relative dynamical effect $\langle \Phi_{\mathrm{H}} | \psi^{\mathrm{K}}_{3\mathrm{s}} \rangle'^2 / \langle \Phi_{\mathrm{H}} | \psi^{\mathrm{K}}_{3\mathrm{s}} \rangle^2_{\mathrm{static}}$ (or $\bar{a}/a_{\mathrm{static}}$) is increased compared with the unreduced admixture coefficient. For the $\mathrm{Cl^I}$ 3s admixture the same consideration brings practically no changes because the nonorthogonality affects the admixture coefficient only very little [5].

We have calculated the influence of the zero-point vibrations taking into account the overlaps with the 3p and 3s orbitals along the [100] directions between $\mathrm{K^I}$ and $\mathrm{Cl^I}$ and considering 3s, 2s, and 1s admixtures into Φ_{H}. The integration over χ^2_{H} leads to a number of three-centre integrals, which cannot be evaluated exactly. We have evaluated them by means of an expansion of the integrand around the equilibrium position of the proton to an accuracy of better than 5%. The quantities $\bar{a}(\mathrm{H})/\bar{a}(\mathrm{D})$ and $\bar{a}(\mathrm{H})/a_{\mathrm{static}}$ were then calculated as function of α on the computer TR 4 of the Stuttgart University computing centre. The result is plotted in Figs. 4a and b. Note that the vertical scale in Fig. 4a is extended by a factor of 5 compared to the one in Fig. 4b. On the upper scale the frequency for the hydrogen vibration ν_0 and the hydrogen amplitude x_0 (measured from R), for which $\chi^2_{\mathrm{H}}(x_0) = 1/e$, are given.

Fitting again to the experimental value $X(\mathrm{Cl^I})$, one obtains the results listed in the second column of Table 4. With nearly the same α and ν_0, $X(\mathrm{K^I})$ comes out much larger, although still somewhat smaller than the experimental value.

The consideration of the overlap of the neighbouring ion core gives thus a better description not only of the static model, but also of the dynamical effect. With an amplitude of the zero-point vibration, which is $\approx 8\%$ of the equilibrium distance H-$\mathrm{Cl^I}$ or H-$\mathrm{K^I}$ ($d = 2.72$ Å), about 30% of $a(\mathrm{K^I})$ and 10% of $a(\mathrm{Cl^I})$ turn out to be of dynamical nature.

5. Conclusions

It is not surprising that our simple theory does not fully explain the observations. The wave function of the $\mathrm{H_i^0}$ centre is not yet known very well. Even the consideration of the ion core overlaps yields a value for $a(\mathrm{K^I})$ which is still too high $(a(K^I)_{theor} = 1.7\, a(K^I)_{exp}$ [5]). If with a better wave function $a(K^I)$ would be "statically" reduced, then with a similar calculation as above the observed isotope effect could possibly be quantitatively explained. In view of this we assume that more than the 30% of $a(K^I)$ derived above are dynamical: probably at least half of the measured isotropic constant is due to the vibrations. This must be taken into account in theoretical calculations of the shf constants, and enhances the present discrepancies between theory and experiment by a factor of two.

From the theoretical results obtained in Sections 4.2 and 4.3 we conclude that the influence of the vibrations on an isotropic constant for H_i^0 centres in alkali halides is large in such cases where admixtures of core orbitals from one neighbour ion (e.g., halogen) are much larger than those of the other neighbour ion (e.g., alkali), that is in cases where the extensions of the ion core orbitals are much different. It would be interesting to check this experimentally in other alkali halides. In [5] and [18] the consideration of the mutual ion overlaps improved the theoretical (static) isotropic constants for the first-shell neighbours considerably and explained the observed transferred shf interaction of the second-shell K nuclei. It is interesting to see that these overlaps explain here a different experimental result.

From the result that the quadrupole constants of the second-shell K nuclei are the same for H_i^0 and D_i^0 centres the assumption made above seems justified that the lattice distortion around the centre atom is the same for H_i^0 and D_i^0. This quadrupole constant is due to an electrical field gradient which arises because of a lattice distortion around the centre atom (otherwise it would be practically zero; see [5]). If D_i^0 caused a different distortion this should show up in $q(K^{II})$.

The obtained vibration frequency of $\nu_0 = 2.01 \times 10^{13}\, s^{-1}$ or $\lambda_0 = 15.0\, \mu m$ can be compared with a measured IR absorption at 9 μm of KCl crystals containing H_i^0 centres. It is, however, not quite clear yet whether this observed IR absorption is due to undistorted H_i^0 centres [19]. The IR absorption of H_i^- centres (U_1-centres) in KCl is observed in the same region at 11.75 μm [14]. H_0 centres in CaF_2 show an absorption at 15.5 μm [15]. In view of the approximate character of our calculations the indirectly derived frequency seems to be quite reasonable. The assumption of an harmonic potential is certainly only approximately right. There are, however, no other data on the potential available.

For H^0 and D^0 centres in CaF_2 it was observed that for the 8 nearest F^- neighbours $a(H)/a(D) \approx 1.01$ [20]. In comparison it should be interesting to derive for this isotope effect the vibrational potential and compare it with the experimental IR absorption.

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