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ATOMIC HYDROGEN AND MUONIUM IN ALKALI HALIDES

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Atomic hydrogen can be trapped at interstitial and substitutional cation and anion sites in alkali halides. The geometrical structure of these defects was established by electron nuclear double resonance (ENDOR). From the analysis of the ENDOR spectra also detailed information was obtained on the electronic structure. In this article the major experimental and theoretical results for atomic hydrogen in several alkali halides are briefly reviewed. Special emphasis is given to the isotope effects upon replacing hydrogen by deuterium. The nature of the dynamical hyperfine and superhyperfine interactions is discussed. Its magnitude to be expected for muonium is estimated. Recent results on muonium centres are discussed on the basis of the knowledge about the hydrogen centres.

1. INTRODUCTION

Muonium atoms are often considered as 'light' hydrogen atoms and one should therefore expect to be able to understand their properties in solids on the basis of the knowledge on atomic hydrogen centres. In alkali halides the centres should have a particularly simple structure due to the purely ionic host crystal. They can therefore be regarded as model centres, the understanding of which should help to understand them in covalent crystals and other more complicated hosts.

Atomic hydrogen and muonium have the same electronic structure to first approximation, their dynamical behaviour is expected to be different due to the mass difference of approximately a factor of 9. Therefore, important differences in muonium and hydrogen centres are expected where vibrations are involved. Since the hyperfine (hf) and superhyperfine (shf) interactions of atomic hydrogen centres are influenced appreciably by zero point vibrations and thermally activated vibrations, such an effect should a forteriori also be expected for muonium centres.

In this article the major experimental results on the ground state of atomic hydrogen centres in alkali halides and some features of optically excited states are briefly reviewed. Then the simple theoretical models used to describe their electronic structure are discussed and a comparison between theoretical and experimental shf data is given for some selected cases. Following this a simple treatment of the dynamical part of the hf and shf interaction is discussed and some extrapolations to muonium centres are presented.

Finally, we discuss some recent results on muonium centres using the knowledge on the hydrogen centres.

2. EXPERIMENTAL RESULTS ON HYDROGEN CENTRES

2.1 Production of Centres

Fig. 1 shows the models of the 3 types of atomic hydrogen centres, which were identified by electron nuclear double resonance (ENDOR) (see section 2.3). These are interstitial atomic hydrogen centres (H_i^o-centres), substitutional centres on anion sites ($H_{s,a}^o$-centres) and cation sites ($H_{s,c}^o$-centres). The older names U_2-centres for interstitial centres and U_3-centres for anion site centres should be avoided and replaced by the notation used above.

H_i^o-centres are produced by photodecomposition of OH_s^-- or SH_s^--centres below 80 K. H_i^o-centres are stable up to approximately 100-110 K /1-3/. $H_{s,a}^o$-centres are generated by X-irradiation of crystals containing H_s^--centres /4/. They are stable in KCl up to 145 K /5/. To produce $H_{s,c}^o$-centres one lets H_i^o-centres diffuse into cation vacancies provided by doping divalent cations like Ca^{++} /4/. They are stable up to 165 K in KCl. The divalent cation is next along [110] /6,7/. $H_{s,a}^o$-centres and $H_{s,c}^o$-centres were studied only in KCl and RbCl.

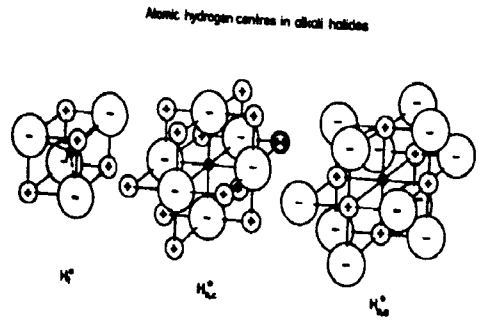

Fig. 1. Models of atomic hydrogen centres in alkali halides. After /36/.

2.2. ESR Investigations

Fig. 2 shows the ESR spectra for all 3 centres in KCl /8/. Characteristic is the isotropic doublet splitting of approximately 50 mT (500 G) due to the hf interaction of the unpaired electron with the proton ($I = 1/2$ ħ). Only for the interstitial centres the shf interactions with 4 nearest halogen ions are resolved. The ESR spectra of the other two centres differ markedly in the line width indicating that their shf interactions are very different. The spectra are described by the Spin Hamiltonian

$$H = g_e \mu_B \underset{\sim}{B}_o \underset{\sim}{S} + \sum_l \left(\underset{\sim}{I}_l \tilde{A}_l \underset{\sim}{S} - g_{I,l} \mu_n \underset{\sim}{B}_o \underset{\sim}{I}_l + \underset{\sim}{I}_l \tilde{Q}_l \underset{\sim}{I}_l \right) \qquad (1)$$

The electronic g-factor g_e is isotropic. The sum runs over the central proton and all neighbour nuclei. The second term in qu.(1) describes the hf and shf interactions, respectively, the last term

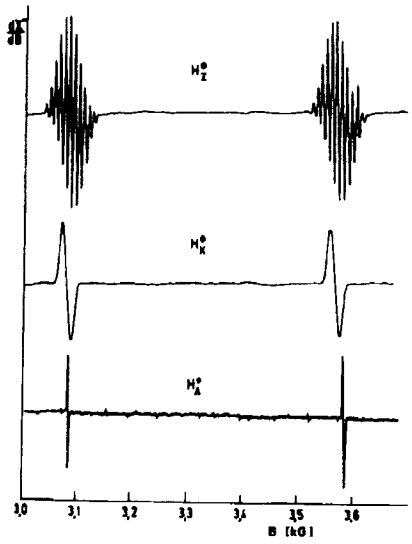

Fig. 2. ESR spectra of three atomic hydrogen centres in KCl. $B_o \| [100]$. After /8/.

the quadrupole interactions. g_I is the nuclear g-factor, μ_n the nuclear magneton, B_o the external static magnetic field, $\tilde{A}_I$ and $\tilde{Q}_I$ the hf (shf) and quadrupole tensors, respectively.

From the ESR spectra alone it cannot be decided, where the hydrogen atoms are trapped. A comparison of the ESR spectra in several alkali halides for the interstitial centres made the site assignment very probable, however, the two substitutional sites cannot be assigned from the ESR spectra. Their structure was revealed by ENDOR investigations.

The fact, that really hydrogen is involved, can be proved by substituting hydrogen by deuterium with nuclear spin $I(D^o) = 1$ resulting in a triplet spectrum with a reduced splitting according to $g_I(D) = 0.1535\ g_I(H)$.

H_I^o-centres were observed in almost all alkali halides. In table 1 the hf interaction constants are given relative to the hf interaction constant of the free H-atom ($a_{HO} = 1420.4$ (MHz)) as well as the deviation of their isotropic g-factors from the value of the free electron g_e /10,11,12/. For a comparison recent observations of the relative central hf interaction of muonium-centres are also included /13/.

Within the temperature range of the centre stability no shifts were detectable in the proton hf constants nor in g-factors in contrast to the observations made for Mu-centres in KCl /14/. In spite of intensive search no interstitial hydrogen centres could be observed in LiF. Paramagnetic atomic hydrogen was observed in γ-irradiated LiF containing OH^- ions. However, the ESR spectra did not show a large ^{19}F shf interaction nor a ^7Li shf interaction as should be expected when extrapolating from the results of KF and NaF /15/. ENDOR experiments on those crystals revealed, that the atomic hydrogen occupies larger cavities in these crystals, which were probably formed as a result of the radiation damage introduced by the γ-irradiation /16/. It seems that the interstitial site is already too small to accomodate a hydrogen atom.

Table 1
g-factors and hf interactions of interstitial hydrogen centres and low temperature hf interactions of Mu-centres in alkali halides

	$\frac{a(H_i^o)}{a_{free\ H^o}}$	$\frac{a(Mu^o)}{a_{free\ Mu^o}}$	$\Delta g(H_i^o)$ (10^{-4})
NaF	1.058	1.041	-2.5 ±5
KF	1.048	--	-2.8 ±1.8
RbF	1.153	--	-1.9 ±5
NaCl	0.952	0.937	+1.3 ±1.2
KCl	0.970	0.959	+7.0 ±1.2
RbCl	0.974	0.958	+14.6 ±2.4
NaBr	0.917	--	+16.5 ±3.6
KBr	0.941	0.905	+38.9 ±2.1
RbBr	0.950	0.930	+52.3 ±1.8
NaI	--	0.845	--
KI	0.905	0.875	+221 ±10
RbI	--	0.863	--

$\Delta g = g_{H_i^o} - g_e$. The uncertainty in $a(H_i^o)/a_{free\ H^o}$ is $\pm\ 5\cdot10^{-4}$ in all crystals, except in RbCl and NaBr, where it is $\pm\ 2\cdot10^{-3}$ and $3\cdot10^{-3}$, respectively. Results on hydrogen centres after /10-12/, on Mu-centres after /13/.

Substitutional centres were studied in KCl and RbCl /5,6,7,17, 18,19/. In table 2 the proton hf interaction of interstitial and the two substitutional centres are compared in KCl. It is seen, that the reduction of the proton hf constant is largest for interstitial centres and smallest for the anion site centres. This observation correlates with the ESR line widths. The reduction is smallest for the narrowest ESR lines, that is for the smallest shf interactions.

Table 2
Relative hf interactions and isotope effects for three atomic hydrogen centres in KCl

centre	H_i^o	$H_{s,c}^o$	$H_{s,a}^o$
$\frac{a}{a_{free\ H^o}}$	0.970	0.986	0.993
$\frac{a(H)/g_I(H)}{a(D)/g_I(D)}$	0.9974 ±0.0005	--	0.9964 ±0.0015

The hf splitting does not exactly scale as the nuclear moments of protons and deuterons (table 2). There is a small isotope effect, which indicates that the electron density at the central nucleus is slightly bigger for the deuterium centres. This effect is due to the

influence of the zero point vibrations on the hf structure (see below).

2.3. ENDOR Investigations

The shf interactions can be resolved by performing ENDOR experiments. In this method the nuclear magnetic resonance (NMR) transitions between the nuclear Zeeman sublevels are detected via the change of the signal intensity of a partially saturated ESR signal /20,21/. An ENDOR line is measured as an increase of the partially saturated ESR line, when an NMR transition involving a shf coupled neighbour nucleus is induced. The ENDOR frequencies are given by

$$h\nu^{\mp}_{ENDOR} = \left|\frac{1}{2}W_{shf} \pm g_I\mu_n B_o \mp m_q W_q\right| \qquad (2)$$

The signs refer to the m_s-quantum number ($\pm 1/2$), W_{shf} and W_q are the shf and quadrupole interactions, respectively. $m_q = (m_I + m_I')/2$, the average of the two nuclear quantum numbers between which the NMR transitions take place. For I = 3/2 there are three ENDOR lines for each m_s-value due to the quadrupole interaction. If $W_q = 0$, there is only one for each m_s.

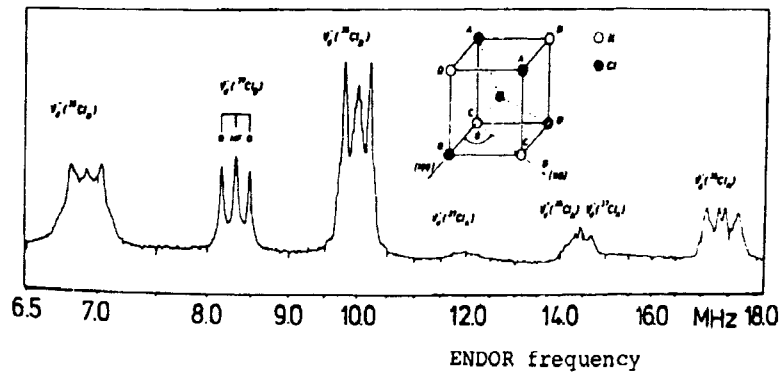

Fig. 3. ENDOR spectrum of nearest halogen neighbours for H_i^o-centres in KCl. $B_o \| [110]$. After /22/.

Fig. 3 shows the ENDOR lines due to the nearest Cl-neighbours for H_i^o-centres in KCl for $B_o \| [110]$ /22/. Because of symmetry the shf and quadrupole interaction tensors of the nearest neighbours are oriented along [111]-axes, which are threefold symmetry axes. The interaction tensors are also axially symmetric. Clearly, the interactions with the two isotopes ^{35}Cl and ^{37}Cl (I = 3/2 ħ for both) are resolved. There are ENDOR lines from $m_s = +1/2$ and $m_s = -1/2$, the frequencies of which differ by approximately $2/h\ g_I\nu_n B_o$ (see equ. (2). The ENDOR lines are grouped into triplets due to a small quadrupole interaction.

The geometrical structures of the hydrogen centres were determined by measuring the dependence of the ENDOR spectra on the crystal orientation with respect to the magnetic field B_o. The angular dependence can be calculated from the Spin Hamiltonian for a given -

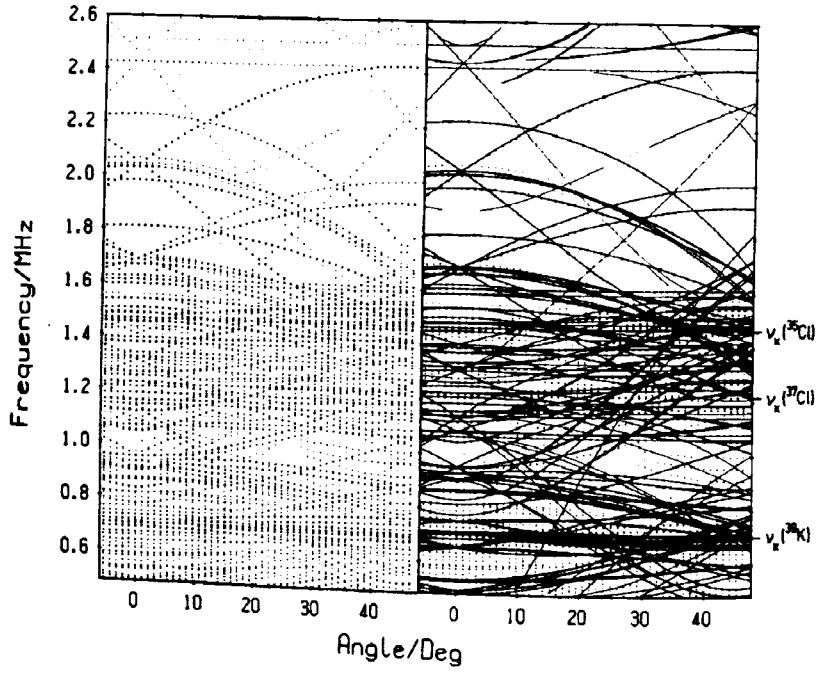

Fig. 4. Angular dependence of the ENDOR lines of $H^O_{s,a}$ - centres in KCl. B_o was rotated in a (100)-plane, $O^O \triangleq B_o \| [100]$, T = 40 K, B_o = 3514 G. a) Experimental results, b) calculated with the Spin Hamiltonian parameters and comparison to the experimental results. After /5/.

or assumed - centre configuration and compared with experiment. If agreement is found, the centre model is determined with very high accuracy and beyond doubt. There is a great deal of redundancy. Of a particular neighbour nucleus the tensor orientation and its principal values can be determined from a small number of ENDOR lines, that is a small number of angles. Since mostly one measures the angular dependence in small angular steps of 1^O or less, there are so many lines that they are either all explained well or not at all. Therefore, structural analysis is usually very safe.

Although in principle the ENDOR analysis is straightforward, in actual practice it can be quite difficult and tedious. For $H^O_{s,a}$- centres there are many ENDOR lines in a very narrow frequency range. The angular dependence (Fig. 4a) is very complicated. It is not easy to recognise the expected simple angular patterns for the neighbours /5/. Such a case requires the measurement of many angles and the determination of all the ENDOR frequencies. This is only feasible with a computer-controlled ENDOR spectrometer. Such an apparatus was developed in our group. The angular dependence can be measured automatically, typically in a continuous experiment of 2-3 weeks duration. The spectra are digitally filtered to enhance the resolution /24/ and the line positions are determined with a computer-aided peak-search algorithm, sometimes after application of special deconvolution algorithms /25/. Fig. 4b shows the experimental and theoretically calculated angular dependence after

determining the shf and quadrupole interaction tensors using the Spin Hamiltonian of equ.(1). The ENDOR spectrum contains also weak 'forbidden' ENDOR transitions, in which $|\Delta m_I| > 1$ (between 2.2 and 2.6 MHz).

As a result of the ENDOR analysis one obtains the geometrical structure of the centres. In the case of $H^o_{s,c}$-centre the lowering of the symmetry due to the presence of the divalent cation in [110] is clearly established: there are 3 (slightly) different non-equivalent nearest Cl-neighbours of the hydrogen atom /7/. Also one obtains detailed information on the electronic structure of the centre from the shf and quadrupole interaction constants. The shf interactions are given in terms of the isotropic shf constant a and the anisotropic shf constants b and b', which are related to the shf tensor $\tilde{A}$ in its principal axis system by /26/

$$\tilde{A} = a + \tilde{B} \tag{3}$$

and

$$b = \frac{1}{2} B_{zz}, \quad b' = \frac{1}{2} (B_{xx} - B_{yy}) \tag{4}$$

Correspondingly the quadrupole constants q and q' are defined by

$$q = \frac{1}{2} Q_{zz}, \quad q' = \frac{1}{2} (Q_{xx} - Q_{yy}) \tag{5}$$

The shf interactions of H^o_i-centres were determined in KF, NaCl, KCl, RbCl, NaBr, KBr, RbBr and KI for 3 shells of halogen and alkali neighbours /10,28/. As an example for quantitative results, the interaction constants are reproduced for $H^o_{s,a}$- and $D^o_{s,a}$-centres in KCl in table 6 /5/.

There is a pronounced isotope effect, which was also found for cation site /18/ and interstitial centres /27/. The shf interactions are smaller for deuterium centres. The isotope effect is smaller for the anisotropic compared to the isotropic shf constants, while it is almost zero for the quadrupole interactions. In table 6 the isotope effect $I_{a,b}$ is defined by

$$I(a,b) = (a,b/g_I(H^o) - a,b/g_I(D^o))/a,b/g_I(D^o) \tag{6}$$

The isotope effect clearly shows the influence of the atomic vibrations on the shf interactions.

For H^o_i-centres no temperature shift of the shf interactions could be detected within the temperature range of their stability. It must be added, however, that ENDOR measurements were only possible up to approx. 80 K. However, a clear temperature dependence was observed for both substitutional centres. With increasing temperature the ENDOR frequencies and thus the shf interaction increase. The temperature shift of the ENDOR frequencies is quite large compared to the position of ±2 kHz with which the frequency of the ENDOR lines can be determined. For Cl_{II}-neighbours of $H^o_{s,a}$-centres in KCl it increases by 110 kHz between 30 K and 130 K. The temperature shift is due to a thermally activated process. It is due to thermally activated localized hydrogen vibrations. Similar observations were made for the $H^o_{s,c}$-centres in KCl /6/.

2.4. Interstitial Atomic Hydrogen in Mixed Alkali Halides

The hydrogen atoms experience a weak covalent bonding to the nearest halogen ions. The covalency increases from F^- to Br^-, the halogen ions with lower electronegativity having a stronger tendency to loose an electron to form H^- leaving a hole in the halogens. The covalency can be seen directly when creating H_i^o-centres in mixed crystals like $KCl:Br^-$, $KCl:I^-$ or $KBr:I^-$. The doping level of the heavier halogen is of the order of $2 \cdot 10^{-2}$ parts per mole in the melt, of which approximately 1/2 or 1/3 is built into the crystal. After low temperature generation of H_i^o-centres only a few 'mixed' H_i^o-centres are formed according to statistics. However, upon warming the crystal to approximately 80-100 K, where the hydrogen atoms can diffuse, they are formed preferentially. In KCl:KI, e.g. 80% of the H_i^o-centres are transformed into the mixed configuration $H_i^o(I)$. The structure model was derived from ESR. The hydrogen atom is surrounded by 3 host halogen ions and one (doped) heavier halogen ion. The hf and shf structure is changed markedly compared to the normal H_i^o-centres. The symmetry is now C_{3v} about the connection line hydrogen-heavier halogen, the g-tensor anisotropic. Also the proton hf interaction is slightly anisotropic. The isotropic hf term is clearly reduced compared to the value of the normal centre. The shf interaction with the doped halogen is dominating /29/ (Table 3).

Table 3. Spin Hamiltonian parameters for normal and mixed H_i^o-centres in KCl.

H_i^o in	KCl	$KCl:Br^-$	$KCl:I^-$	Accuracy
$g_{\parallel}$	2.0030	1.995	1.994	± 0.004
$g_{\perp}$	± 0.0001	2.008	2.006	
a_p[mT]	49.14 $\pm$ 0.02	48.7	46.6	± 0.3
b_p[mT]		<0.1	<0.2	
$a_{Br,I}$[mT]		6.6	15.6	± 0.2
$b_{Br,I}$[mT]		2.0	3.4	

2.5. Optical Properties of Interstitial Hydrogen Centres

H_i^o-centres have absorption bands in the UV. In the chlorides only one band is observed (KCl: at 5.27 eV), whereas in the bromides and iodides 3 bands are measured, which are best resolved in iodides /2,3/. The observed optical absorption bands are not due to a hydrogen 1s-2p transition expected to be at 10 eV in the UV. The optical absorption is due to charge transfer transitions, in which an electron from the outer halogen p-band is transferred to the hydrogen forming an H_i^--ion. This is seen most clearly in the mixed configuration, e.g. for KCl doped with I^-. There the optical absorption bands are determined mainly by a charge transfer from the I^- to H_i^o-atom. There are 'iodine' bands at lower energy between 4-5 eV

compared to the composite 'chlorine' band centered at 5.5 eV. The lower electronegativity of I^- compared to Cl^- causes the lower energy of the transitions /30/. This nature of the absorption bands was confirmed by magneto-optical studies and calculations /31,33/. In the mixed halides the lower energy bands due to the heavier ion can be well understood by considering crystal field and spin orbit effects /30/.

Fluorescence was observed in the mixed configuration for H_i^o-centres. It comes from two charge transfer type relaxed excited states, one of which is a spin quartet and responsible for a long lifetime of 720 ns at 4 K in KCl /34/. In the normal configuration in most alkali halides no emission was found, except in KI, RbI and KBr, where a very weak fluorescence emission was found in the IR (at 0.87 eV in KI) /35,36/.

It should be noted that in competition to the emission the interstitial hydrogen centres decay upon optical excitation forming H_s^--centres and 'H-centres' (halogen$_{2s}^-$-centres) /37,38/ in a process analogous to the fundamental process of F- and H-centre formation from a relaxed excited state of the self-trapped exciton /39/.

2.6. Magnetic Resonance in the Relaxed Excited State of Interstitial Atomic Hydrogen Centres

In the mixed configuration in KCl and RbCl doped with I^- the ESR of relaxed excited states could be observed by optical detection (ODESR). Table 4 shows for KCl the proton hf constant a_p and the shf constants a and b for the I^- neighbour for both the ground state and the relaxed excited state /40/. The proton hf constant is reduced by 35% in the relaxed excited state compared to the ground state. The properties of the relaxed excited state, which is a spin quartet state, can be reasonably well understood for an electronic structure, which consists of a configuration mixing between the ground state configuration (H_i^o + lattice) and the charge transfer configuration (H_i^- and a p-hole in I^-), whereby the fraction of the hole in the I_{5p} orbital is 2/3. The reduced central hf interaction is due to the admixture of the 'diamagnetic' H^--configuration /40/. In the case of KBr doped with I^- a metastable nonradiating relaxed excited state was found with an ODESR spectrum due to a hole at the I^--neighbour interacting with 2 Br-neighbours along [110], which tunnels back into the H_i^o(I)-centre /41/.

Table 4
Hf and shf interactions for the ground state and relaxed excited quartet state of H_i^o(I)-centres in KCl

	ground state	relaxed excited state
a_p (mT)	46.6 ±0.3	30.6 ±0.3
a_I (mT)	15.9 ±0.2	16.2 ±0.2
b_I (mT)	3.9 ±0.1	3.2 ±0.1

3. Theoretical Interpretation of the hf and shf Interactions of Atomic Hydrogen Centres

3.1. Static Models

The isotropic shf constant a_1 is proportional to the density $|\psi(r)|^2$ of the unpaired electron at site r_1.

$$a_1 = \frac{2}{3}\mu_o g_e \mu_B g_I \mu_n \mid \psi(r_1) \mid^2 \tag{7}$$

The anisotropic shf constant b is the expectation value of the magnetic dipole-dipole interaction between the unpaired electron and the neighbouring nucleus:

$$b_1 = \frac{\mu_o}{8\pi} g_e \mu_B g_I \mu_n \int \frac{3\cos^2\theta - 1}{r^3} |\psi(r)|^2 \, dV \tag{8}$$

Equ. (7) and (8) hold, if the wave function can be approximated by a one-particle wave function.

$\psi(r)$ is the wave function of the defect. It is tempting to approximate it by the atomic hydrogen function $\psi_{1s}^{H^o}$. However, assuming this the shf interaction cannot be explained. The isotropic shf constants calculated with $\psi_{1s}^{H^o}$ are too small by several orders of magnitude.

The Pauli principle must be considered, which is conveniently done by orthogonalising the hydrogen 1s function as envelope function to the ion cores by the Löwdin procedure /42/. It proved necessary to introduce a weak covalency to the outer halogen p-orbitals (X_{mp}^-) with the z nearest neighbours leading to the following defect wave function:

$$\phi_H^\lambda = \frac{N}{(1+z\lambda^2)^{1/2}} \left\{ \psi_{1s}^{H^o} - \sum_{i \neq X_{mp}^-} c_i \psi_i - \sum_{j=1}^{z} \left(\frac{\lambda}{N} + c_{mp}^{X^- j} \right) \psi_{mp}^{X^- j} \right\} \tag{9}$$

with

$$N^\lambda = (1 + z\lambda^2)^{1/2} \tag{10}$$

and N an normalisation constant for the orthogonalisation.

ψ_i are the occupied ion core orbitals, c_i admixture coefficients, involving overlap integrals (for details see ref. /43/). λ is the covalency parameter. The covalency model is suggested by the relative small electron affinity of the halide ions, which allows a partial charge transfer from the anions to the hydrogen atom. One has to add the configuration $H^- - X^o$ to the ground state $H^o - X^-$. In equ. (9) the difference between H^- and H^o orbitals and between X^o and X^- orbitals is neglected. Then the hydrogen centres can still be treated in a one-particle approach /44/. Since an ab initio calculation of the covalency parameter is difficult, it was fitted to one of the experimental shf constants, in the case of the H_I^o-centres to the anisotropic shf interaction constants of the nearest halogen neighbours. The covalency model explains the experiments rather well and much better than the pure orthogonalisation

model /44/. The covalency parameter is ∿0.1.

The proton hf constants are less well explained. According to equ.(9) it should be given by $(N \cdot N^{\lambda})^2$ times the atomic value (neglecting the very small amplitudes of np and ns neighbour ion admixtures at the proton).

$$(NN^{\lambda})^2 = (1 - \sum_i |\langle \psi_{1s}^{H^o} | \psi_i \rangle|^2 + \sum_j \lambda_j^2)^{-1} \qquad (11)$$

Due to the orthogonalisation the normalisation constant N becomes bigger than 1, which is reduced somewhat by the covalency (NN^{λ}). Table 5 shows the results for H_I^o-centres in 3 potassium halides. The covalency model cannot explain the observations satisfactorily. An improvement was achieved by taking into account the van der Waals interaction between the H^o-atom and its neighbouring ions (table 5). This effect of correlation between the hydrogen electron and the outer electrons of the neighbouring ions pulls electron density away from the proton into the outer region of the H^o-atom (for details see ref. 44). The van der Waals effect is of the right order of magnitude to cancel or overcompensate the positive shift due to the normalisation factor N. The van der Waals correction is very similar for the 3 potassium halides KF, KCl and KBr. The relative decrease in proton constants from KF to KBr is due to the increase in covalency from KF to KBr. (λ(KF) = 0.070, λ(KCl) = 0.090, λ(KBr) = 0.114 /44/).

Table 5
Relative proton hyperfine shifts $\frac{a_{H_i^o} - a_{H^o}}{a_{H^o}}$

cryst.	exp.	orthog. + covalency	van der Waals	
KF	+4.75	+12.72	-10.55	
KCl	-3.01	+ 9.27	- 9.73	$\times 10^{-2}$
KBr	-5.88	+ 7.51	-10.30	

The interpretation of the $H_{s,a}^o$-centre shf data in KCl require two further refinements of the theoretical model:

(i) distortion of the halogen orbitals by the positive charge of the anion vacancy
(ii) a configuration mixing in which the difference of H^- and H^o orbitals and those of X^o and X^- orbitals is now considered.

The simple covalency model has to be extended to a many particle approach /45,46/. The configurations considered are $\psi_A = H^o - Cl_{II}^- - K_I^+$ and the two charge transfer configurations $\psi_B = H^- - Cl_{II}^o - K_I^+$ and $\psi_C = H^- - Cl_{II}^- - K_I^{++}$, in which outer p-electrons are transferred to form H^-. The ground state is then

$$\psi = N \quad (\psi_A - \mu\psi_B - \varepsilon\psi_C) \qquad (12)$$

μ and ε are mixing parameters, which are also determined semi-imperically.

Table 6. Interpretation of the hyperfine and superhyperfine interactions of $H^o_{s,a}$-centres in KCl with different theoretical models. r_o = d(K-Cl) = 5.904 a.u.; α = 1.5 (a.u.)$^{-2}$; the values marked with asterisks were fitted to fix the covalency or configuration admixture coefficients.

	Experiment	Covalency	Distortion	Configuration
$H^o a_p$ (MHz)	1409.9	1429.7	1436.6	1417.1
K_I a(kHz)	253	230	227	225
b(kHz)	219	158	158	219*
I_a	0.205	0.212	0.219	0.230
I_b	0.048	0.043	0.044	0.048
Cl_{II} a(kHz)	257	78	217	260
b(kHz)	312	312*	312*	312*
I_a	0.108	0.174	0.129	0.105
I_b	0.047	0.044	0.040	0.030
Cl_{IV} a(kHz)	37	3	3	30
b(kHz)	54	36	36	47
I_a	0.06 ±0.03	0.115	0.111	0.062
I_b	0.02 ±0.03	0.009	0.007	0.012
K_V a(kHz)	4	5	5	5
b(kHz)	11	11	11	11
λ or $\mu/C^{Cl^-}_{3p}$		0.689	0.367	0.204
$\varepsilon/C^{K^+}_{3p}$				0.287

Table 6 shows the results obtained for the covalency model, the additional consideration of the distortion of the halogen orbitals ('distortion') and the configuration mixing ('configuration') /43/. In the calculation also the important influence of the hydrogen vibrations was taken into account, which will be discussed below. The overall agreement is very good, including for the isotope effects. The van der Waals interaction would again reduce the somewhat too large proton interaction. It seems that the $H^o_{s,a}$-centres are quantitatively well understood. The H^o_I-centres are fairly well understood /44/.

From the analysis of many hydrogen centres it was found, that the covalency parameter is approximately given by

$$\lambda \approx 0.5 \langle \psi^{H^o}_{1s} | \psi_{X\bar{m}p} \rangle \qquad (13)$$

3.2. Dynamical hf and shf Interactions

The hydrogen and deuterium vibrations have a marked influence on the shf interactions. In a good approximation one can represent the vibrations by localised vibrations in a static lattice because of the large mass difference between H(D) and the lattice ions. Further, it turned out that for interstitial centres $h\nu_o >> kT >> h\nu_{shf}$, where ν_o is the vibration frequency of the atoms and ν_{shf} frequency of the local magnetic field due to the shf interactions. Therefore for interstitial centres only zero point vibrations need to be considered. For substitutional centres $h\nu_o$ becomes of the order of kT, thus temperature activated vibrations cause a temperature dependence of the shf constants.

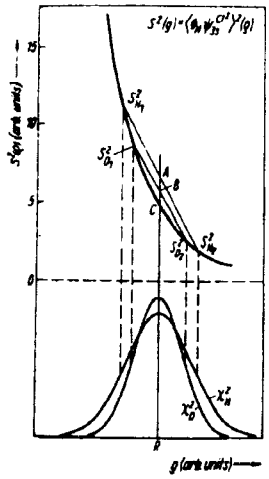

Fig. 5. Schematic representation of the influence of hydrogen and deuterium vibrations on the overlap integrals. After /27/.

The vibrations influence the shf interactions, since the overlap integrals depend on the distance between proton (deuterium) and the neighbouring nuclei and this distance dependence has to be averaged over the hydrogen (deuterium) motion. This is illustrated in Fig. 5 for the isotropic constant of nearest halogen neighbours for H_i^O-centres, which is approximately given by

$$a^{Cl^I}(\rho) = C\left|\langle\psi_{1s}^{H^O} \mid \psi_{3s}^{Cl^I}\rangle(\rho)\right|^2 \tag{14}$$

with

$$C = \frac{2}{3}\mu_o g_e \mu_B g_I \mu_n N^2 \left|\psi_{3s}^{Cl^I}(o)\right|^2 \tag{15}$$

The larger amplitude of hydrogen vibrations leads to a higher dynamical contribution to the shf interaction compared to the deuterium centres, and thus explains qualitatively the isotope effects observed. Assuming a harmonic potential for the vibrations, the nuclear wave function for H^O and D^O is given by

$$\chi_{(\rho)} = \left(\frac{\alpha}{\pi}\right)^{3/4} \exp\left(-\frac{\alpha}{2}(\rho-\rho_o)^2\right). \tag{16}$$

with $\frac{\alpha}{\hbar} = (fM)^{1/2}$, where f is the force constant and M the mass. f is assumed equal for D^O and H^O. Since the overlap integrals follow very well a distance dependence given by

$$S(\rho) = S_o e^{-\beta(\rho-\rho_o)} \tag{17}$$

one can analytically calculate the average over the overlap integrals. ρ_o is the equilibrium distance $H^O(D^O)$ - nearest neighbour. The average $\bar{S}^2$ is approximately (for $\beta \sim 1$, $\rho_o = 5$ a.u., $\alpha \geq 0.4$)

$$\bar{S}^2 = S^2_{static}\left(1-\beta/\alpha\rho_o\right)e^{\beta^2/\alpha} \tag{18}$$

and the isotope effect for a becomes according to equ.(14)

$$I_a = \frac{a(H)}{a(D)} = \frac{(1 - \beta/\alpha\rho_o)\, e^{\beta^2/\alpha}}{(a - \frac{\beta}{\sqrt{2}\alpha\rho_o})\, e^{\beta/2\sqrt{2\alpha}}} \qquad (19)$$

From equs. (18) and (19) it is qualitatively seen that the vibrational influence and thus the isotope effect depends stronly on β. Since β for s-overlaps is bigger than for those p_σ-orbitals, the dynamical influence is bigger for isotropic constants than for anisotropic constants, which is also found experimentally. (E.g. $\beta = 0.8283$ for Cl^-_{3s} and 0.5766 for $Cl^-_{p\sigma}$ for H^o_i-centres in KCl) /27/.

The estimate above is an oversimplification. In general one must calculate the average shf constants

$$\bar{a},\bar{b} = (\frac{\alpha}{\pi})^{3/2} \int a,b(\rho)\, \exp[-\alpha(\rho-\rho_o)]^2\, dV \qquad (20)$$

by numerical integration.

For the substitutional centres in KCl the vibration frequency could be determined from the temperature dependence of the shf interactions. For $H^o_s,_c$-centres $\tilde{\nu} = (199 \pm 16)$ cm^{-1} /7/ and for $H^o_s,_a$-centres $\tilde{\nu} = (177 \pm 8)$ cm^{-1} /6/. Using this, the theoretical shf parameters and isotope effects of $H^o_s,_a$-centres (table 6) were calculated. It turned out that half of the isotropic nearest neighbour interactions is dynamical in nature /43/.

For interstitial centres the potential parameters could not be determined from a temperature dependence, since none was detectable. It was determined from the interpretation of the isotope effect of the anisotropic shf constant of the nearest halogen neighbours in KCl assuming that the covalency parameter would average as the overlap integrals with halogen p_σ-orbitals. The vibrational frequncy $\tilde{\nu} = 420$ cm^{-1} thus obtained agrees well with that determined from IR measurements (437 cm^{-1}) /47/ and Raman measurements (441 cm^{-1}) /48/.

Also the hf interaction is influenced by the vibrations via equ. (11), since both the overlap integrals and the covalency parameters must be averaged. Qualitatively, the hf of D-centres is bigger than that of H^o-centres, since less spin density moves in the neighbours due to the smaller dynamical contributions. This is also found experimentally.

4. DISCUSSION: HYDROGEN AND MUONIUM CENTRES

The major difference in the hydrogen and Mu-centres is expected to be the mass difference. $M(Mu) = 0.1126\, M(H^o)$. Therefore, the influence of vibrations on the hf and shf structure of Mu-centres should be even more pronounced than for hydrogen centres. In Fig. 6 the effect is calculated for overlaps with $Cl^-_{3p\sigma}$-orbitals ($R = 5.10$ a.u.) according to equ. (18). For the potential of the interstitial centres in KCl the dynamical contributions for Mu-centres is 20% compared to 6% for hydrogen centres. The dynamical contribution will be even more pronounced for the s-overlaps.

With μSR so far only the shift of the central hf interaction could be measured. The question arises whether the Mu-centres observed /13,14/ are indeed interstitial centres analogous to the H^o_i-centres. The shift of the central hf interaction compared to the free μ^+-value is consistantly approx. 1% bigger than that observed for H^o_i-centres (table 1). Qualitatively, due to the bigger amplitude of the zero point vibrations one should expect this. Quantitatively for KCl, only about half of the difference can be explained

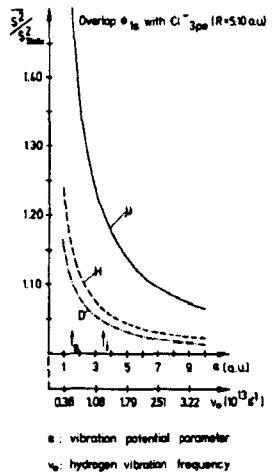

Fig. 6. Dynamical to static ratio of the square of overlap integrals between ψ_{1s} (H, D and Mu) and $Cl^-_{3p\sigma}$ neighbours.

assuming the same potentitial and covalency for both centres and calculating $a/a_{free\ atom}$ considering only N^λ of equ.(9), which in the different alkali halides qualitatively determines the hf shifts (table 7). Inclusion of the orthogonalisation normalisation factor N gives the wrong answer. It is not clear how a dynamical influence on the van der Waals interaction would be able to repair this.

Table 7. Theoretical estimate of the hyperfine shift $a/a_{free\ atom}$ of H_i^O- and Mu^O-centres in KCl

Theory	Static	H_i^O	dynamic Mu^O
$(N^\lambda)^2$	0.972	0.970	0.966
$(N^\lambda N)^2$	1.125	1.137	1.165
Experiment		0.970	0.959

The hf shift of the substitutional centres seems too small to account for the Mu-results. However, the dynamical effects are bigger due to the lower vibrational frequencies.

Problems arise, however, for the identification of the Mu-centres with interstitial centres, when looking at the temperature dependence of the hf shift. It was found by Kiefl et al. /14/ in KCl that a/a_{free} decreases clearly when increasing the temperature already as from approx. 20 K, while no temperature shift was observed for H_i^O due to the high frequency of $\tilde{\nu}$ = 440 cm^{-1}. For Mu-centres $\tilde{\nu}$ would be expected to be approx. 3 times as large and no thermal activation is expected at 20 K. Possibly, due to the high zero point energy of 660 cm^{-1} expected for the Mu-centres (compared to 220 cm^{-1} for H_i^O), which is equal to the energy of the thermally first excited state of H_i^O-centres, the Mu-centres are not trapped anymore in the interstitial site, but diffuse through the lattice. This diffusion is perhaps thermally activated at low temperatures and thus responsible for the temperature decrease of a/a_{free}.

It should be added, that the thermal stability of H_i^0-centres is about the same for KCl and RbCl ($\sim$ 100 K) and not so different as reported in ref. /13/. In LiF no interstitial Mu-centres are expected to have space to be trapped, since no H_i^0-centres could be created.

It is suggested to study the Mu-centres in the mixed alkali halides. If interstitial Mu-centres are formed and trapped then the hf interaction should shift more and become anisotropic ('anomalous') analogous to the observations made for the H_i^0-centres. Also cation vacancies can be introduced into the crystal and provided as Mu traps. Then the hf shift should be smaller due to the smaller shf interactions.

During the cooling process of the μ^+ particles a lot of crystal damage is created and enough energy present to cause excitations. It is conceivable that Mu-atoms are formed also in an excited state, which may have an analogous configuration as the excited hydrogen centres : (Mu^- + hole in the halogen band) mixed with the (Mu + lattice) configuration, which results in a strong reduction of the hf interactions. Since the lifetime of the relaxed excited hydrogen quartet state is of the order of µs, such a state could well be observed in µSR.

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DISCUSSION

Roduner: With your calculations you can reproduce small effects in coupling constants. Is the Born-Oppenheimer approximation for Mu at this level of accuracy still valid?

Spaeth: For atomic hydrogen centers the answer seems to be yes. For Mu the answer is: this is a very good question!

Hedegård: How large is the lattice relaxation and how do you calculate it?

Spaeth: For H_i^0 centres in KCl about 3 % outwards. This was calculated from the second shell K-quadrupole interactions. For H_I^0 centre (anion substitutional site) the distortion was calculated with the HADES programme of Harwell. The n-neighbours are displaced outwards due to the point charge of the anion vacancy by about 8 %. Similar results were obtained for the cation site centre.

Bucci: From time-resolved optical spectroscopy in alkali halides one knows that light impurities have long-lived excited states (electronic as well as vibrational). The time scale (10^{-8}-10^{-6}sec) is relevant to μSR data and a comparison with ESR and ENDOR experiments should take this situation into account. Could excited vibrational Mu-states account for the hyperfine frequencies and dampings so far observed?

Spaeth: We have measured with optically detected magnetic resonance (ODMR) the optically excited states of atomic interstitial hydrogen centres in mixed alkali halides (H_I^0(I,Br) centres in KCl). We find that the relaxed excited state is a superposition of the H_I^0-lattice) and (H_I-hole in the halide lattice) configurations. In this state the proton hf interaction is relaxed appreciably. I could imagine, that an excited Mu state could be formed similarly.