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Abstract. Hydrogen and deuterium atoms are stabilized in a xenon matrix from the gas phase and investigated by electron spin resonance (ESR). It is shown that H and D atoms are trapped in substitutional positions of the matrix crystal lattice. The ESR linewidths of H and D show an isotope effect and are found to be greatly increased (up to 80%) by the zero-point vibrations of the atoms. The charge-transfer coefficient $\nu(r) \equiv \gamma \exp(-\eta r)$ between matrix atom and hydrogen atom is estimated. A comparison is carried out between experimental and theoretical values for the relative matrix shift of the H atom hyperfine constant.

1. Introduction

Hydrogen atoms stabilized in solid xenon were observed by Foner *et al* (1960) for the first time. The samples were prepared by a technique employing ultraviolet (UV) photolysis of a matrix containing HI molecules, as well as a method of simultaneous condensation on a cold substrate of rare-gas atoms and the products of an H_2 gas discharge. It was found in the photolysis experiment that each of the two H atom hyperfine (HF) lines split into at least 13 lines, and has an overall spread of the spectrum of 98.2 G. On the other hand, in the deposition experiment the HF components were two broad lines with peak-to-peak linewidth of the derivative of about 7 G. The existence of such a multicomponent spectrum in the case of the photolysis technique was explained (Foner *et al* 1960) by taking into account the Fermi isotropic hyperfine interaction of the electron spin of the H atom located at the octahedrally symmetric interstitial site (octahedral site) with magnetic nuclei of the surrounding isotopes ^{129}Xe and ^{131}Xe. In this paper it is supposed that the anisotropic hyperfine interaction, if present, would contribute to the widths of the registered lines. Then the authors came to the conclusion that the H atoms obtained in the deposition experiment were trapped in substitutional positions in solid xenon. The linewidth in this case was supposed to be a result of superhyperfine (SHF) interactions of atomic hydrogen with matrix nuclei (^{129}Xe and ^{131}Xe). But, because of a greater internuclear distance for the substitutional trapping site than for the octahedral one, the SHF splitting was much smaller than in the case of the octahedral site.

Jackel *et al* (1968) investigated the electron spin resonance (ESR) spectra of the hydrogen and deuterium atoms matrix-isolated in solid Xe. The samples were prepared by UV irradiation of Xe:NH$_3$, Xe:PH$_3$ and some other mixtures of xenon with molecules containing H or D atoms. The spectrum of H atoms was similar to the one reported previously by Foner *et al* (1960) (multicomponent spectrum). Additional evidence in support of the SHF

interaction responsible for the splitting of HF components has been found, in that the splitting was independent of the isotope used and the magnetic field value (the microwave frequency of the ESR spectrometer reported by Jackel *et al* (1968) was 24 GHz, while in the earlier work by Foner *et al* (1960) it was 9 GHz). The authors supposed that the ESR spectra recorded were due to the atoms trapped in octahedral positions.

The result obtained by Iwasaki *et al* (1979) is somewhat different from the results of the previous work. They reported the ESR spectrum of hydrogen atoms produced by UV photolysis of Xe:HI mixture at 4.2 K. The number of SHF lines was much more than 13, and each of the HF portions of the spectrum had overall spread of about 200 G, but the authors did not give data on the spin Hamiltonian.

The ESR spectrum of hydrogen atoms reported by Kinugawa *et al* (1978) also includes two multicomponent HF transitions, each of which extends over 214 G and contains about 80 lines. This result is similar to the one obtained by Iwasaki *et al* (1979). The samples were prepared by the UV photolysis of HI and HBr molecules trapped in solid xenon. It was suggested by the authors that, because of a low signal-to-noise ratio, the spectrum in previous work (Foner *et al* 1960) had had few SHF components and small overall spread. The multicomponent spectrum was supposed to be a result of the SHF interaction. The authors fitted the calculated ESR spectra of hydrogen atoms trapped in substitutional and two interstitial positions (octahedral and tetrahedral) to the experimental spectrum and decided that H atoms were stabilized in the substitutional site. The conclusion was in contradiction with the previous results.

In the latest ESR work (Morton *et al* 1979) on the H and D atoms matrix-isolated in solid Xe, the samples were prepared by *in situ* photolysis of HI and DI molecules trapped in Xe matrix enriched to 37% in the isotope ^{129}Xe and containing a small amount of ^{131}Xe (1.7%). This permitted simplification of the ESR spectra of H and D atoms. It was found that each of the HF components of the hydrogen and deuterium ESR spectra contained a large number of lines and extended over approximately 200 G. The results obtained are in general agreement with observations reported by Iwasaki *et al* (1979) and Kinugawa *et al* (1978). However, contrary to the conclusions of the previous work, Morton *et al* (1979) found the SHF interaction to be anisotropic. Analysis of the SHF structure showed that the H and D atoms were trapped in the octahedrally symmetric interstitial site of the Xe matrix. This result is different from what was reported by Kinugawa *et al* (1978).

Thus, the investigations of H atoms trapped in solid Xe have been mostly performed using UV photolysis and only one deposition experiment has been carried out (Foner *et al* 1960). Hence, it is of interest to make deposition experiments with H and D in Xe and compare their ESR spectra in order to assess possible isotope effects. Finally, there have been no attempts to calculate the parameters of the ESR spectrum of the H atomic matrix isolated from the gas phase in solid xenon.

2. Experimental details

The essential features of the apparatus have already been described (Dmitriev and Zhitnikov 1987, Zhitnikov *et al* 1991). Xenon of 99.990% stated purity was purchased and used without further purification, but hydrogen and deuterium were purified by the known method of gas diffusion through a thin palladium wall. A typical matrix deposition experiment for trapping H and D atoms lasted about 30 min. Routinely, the concentration of H_2 and D_2 molecules in solid Xe was within the limits of 10^{-2} to 10^{-1} per cent. The molecular gases to be dissociated (H_2 and D_2) were passed through the gas discharge in a

mixture with xenon. In this way we recorded both the hydrogen and deuterium ESR spectra in every experiment.

3. Results

Figure 1 illustrates the ESR line of the high-field transition of H in Xe recorded in the experiment. The magnetic constants of H and D in Xe are given in table 1 along with the earlier data. The table also shows the relative matrix shifts of the hyperfine structure constants $\Delta A/A_f$ and g-factor matrix shifts Δg, where $\Delta A = A - A_f$, $\Delta g = g - g_f$, and A_f and g_f are the parameters of the free atom. The resonance lines have average peak-to-peak widths of 5.80 G and 5.25 G for H and D atoms, respectively. On the other hand, a small ($\leqslant 0.25$ G) variation among the values obtained in various experiments was observed. However, the ratio $\kappa_1 = (\Delta H)^{\mathrm{H}}/(\Delta H)^{\mathrm{D}}$ remained constant: $\kappa_1 = 1.10(4)$. So, the deposited H and D atoms exhibit an isotope effect in the ESR linewidths. We assign these spectra as the ESR spectra of H and D atoms trapped in the substitutional site in the Xe crystal lattice. This conclusion is based on results of the previous work by Foner *et al* (1960) and Morton *et al* (1979). In this case (see section 1) the ESR line broadening is due to the unresolved SHF interaction of the electron spin of a stabilized atom with the nuclear magnetic moments of the surrounding matrix atoms. Hydrogen and deuterium atoms, with their small masses compared with matrix atoms, perform large localized vibrations, which increase the SHF interaction (Spaeth 1969) and, therefore, lead to an increase in the ESR linewidths in the particular case of H and D atoms deposited in Xe. The isotope effect is connected with the difference in the vibrational amplitudes of the H and D atoms, which is due to the difference in their masses. It should be noted that the isotope effect in the SHF constants $a_\perp$ and $a_\parallel$ has been reported by Morton *et al* (1979) for octahedral H and D atoms trapped in solid Xe. At the same time no isotope effect was observed in the HF constant matrix shift and g-factor matrix shift within the error limits in our experiments, while it was detected for the case of octahedral H and D atoms (Morton *et al* 1979).
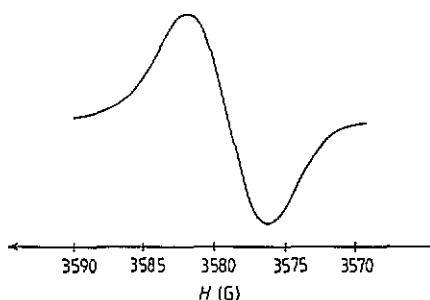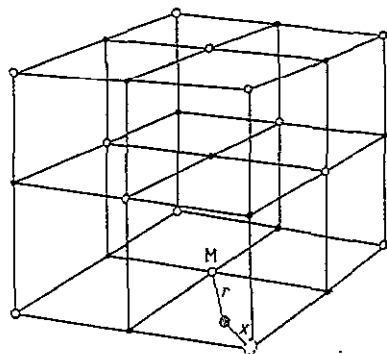

Figure 1. High-field transition of ESR spectrum of deposited hydrogen atoms in xenon matrix at 4.2 K; ESR resonance frequency $f = 9373.61$ MHz.

4. Superhyperfine interaction

In the paper of Morton *et al* (1979) it is pointed out that the highly symmetric environment of the trapped H atoms may result from a dynamical averaging over a set of potential

o Matrix atom
● Octahedral site
◌ Equilibrium position of H(D) atom trapped at
  substitutional site
◎ Instantaneous position of H (D) atom performing
  zero-point vibrations

Figure 2. Substitutional hydrogen (deuterium) atom and trapping sites in a face-centred cubic lattice of solid Xe.

Table 1. Hyperfine constants, g-factors and their matrix shifts for H and D atoms in solid xenon. The sample preparation is denoted by: dep., deposition; phot., photolysis; and γ, γ-irradiation. References: F, Foner *et al* (1960); P, present work; J, Jackel *et al* (1968); M, Morton *et al* (1979).

Atom	A (MHz)	$\Delta A/A_f$ (%)	g	$-\Delta g \times 10^4$	Prep.	Ref.
H	1404.99(28)	−1.09	2.00170(8)	5.6	dep.	F
H	1405.57(34)	−1.04	2.00057(8)	16.9	phot.	F
H	1405.55(38)	−1.05	2.00172(12)	5.4	dep.	P
D	215.88(22)	−1.09	2.00175(12)	5.1	dep.	P
H	—	−1.02	—	22.7	γ	J
H	1405.70(5)	−1.035	2.00070(5)	16.2	phot.	M
D	216.15(5)	−0.965	2.00107(5)	12.5	phot.	M

wells somewhat displaced from the centre of the trapping site. We have calculated the potential created by matrix Xe atoms surrounding the substitutional H atom and found that the potential wells displaced from the cage centre could not be deeper than 0.1 meV. This has been found by summing over pair interactions between a given H atom and Xe atoms located inside a sphere with radius $3R_0$ and centre at the H atom position. Here R_0 is the distance between nearest neighbours in the Xe crystal lattice. The H–Xe pair interaction was taken in the form of the Lennard-Jones potential:

$$f(r) = E_{\min}[(r_{\min}/r)^{12} - 2(r_{\min}/r)^6]$$

where $E_{\min} = 7.1$ meV and $r_{\min} = 7.2a_0$ are from the reference book by Radzig and Smirnov (1986), a_0 being the Bohr radius. So, the set of such 'shallow' potential wells cannot essentially influence the spatial wavefunction of the stabilized H atom because of the lack of binding energies in these displaced wells.

For an H atom trapped in a substitutional position, we calculate the ESR parameters assuming an approximation of a spherically symmetric well potential. The calculation shows that the potential well has a rather flat bottom. Therefore we use the approximation of a

spherically symmetric square-well (SW) potential besides the usually employed spherically symmetric harmonic well (HW) potential model.

In the case of an ESR polycrystalline spectrum associated with an unresolved SHF interaction the second moment of the lineshape function is given by the expression (Lefebvre and Maruani 1965):

$$M_2 = \tfrac{1}{3} \sum_i s_i [(c_i^x)^2 + (c_i^y)^2 + (c_i^z)^2]$$

s_i being $\tfrac{1}{4}$, $\tfrac{1}{3}$ or $\tfrac{5}{4}$ according to whether nucleus i has a spin $\tfrac{1}{2}$, 1 or $\tfrac{3}{2}$; c_i^x, c_i^y and c_i^z are diagonal components (in frequency units) of the SHF tensor denoted in its principal axes. This tensor is related to the SHF interaction between the Xe nucleus and the electron spin of a hydrogen atom. If this SHF interaction is cylindrically symmetric, we may use the term $a_\perp$ instead of c^x and c^y and $a_\parallel$ instead of c^z. The following expression is deduced for the H atom trapped in the substitutional position of crystalline natural Xe containing two isotopes (^{129}Xe, ^{131}Xe) with non-zero spins:

$$M_2 = 1.09(a_\parallel^2 + 2a_\perp^2). \tag{1}$$

The isotope ^{129}Xe has nuclear spin $I = \tfrac{1}{2}$, nuclear magnetic moment $\mu_I = -0.778\mu_N$ and a natural abundance $C = 26\%$. The corresponding quantities for ^{131}Xe are $I = \tfrac{3}{2}$, $\mu_I = 0.692\mu_N$ and $C = 21\%$. Here μ_N is the nuclear magneton; and $a_\parallel$ and $a_\perp$, the parallel and perpendicular ^{129}Xe SHF constants measured in frequency units. The contribution of isotope ^{131}Xe is taken into account by the coefficient 1.09 in expression (1), since $a_\parallel$ and $a_\perp$ for ^{129}Xe are proportional to the corresponding components for ^{131}Xe.

It is found that the shape of ESR lines of H and D atoms is close to Gaussian. Therefore the second moment M_2 in magnetic field units is $\tfrac{1}{4}(\Delta H)^2$, where ΔH is the linewidth measured between the extrema of the first derivative. Hence, the linewidth is

$$\Delta H = 0.746(a_\parallel^2 + 2a_\perp^2)^{1/2}.$$

Here ΔH is measured in magnetic field units; $a_\parallel$ and $a_\perp$ are measured in frequency units.

Morton *et al* (1979) have obtained the formulae for the isotropic and anisotropic (a and $B_\parallel$, respectively) SHF constants of the interaction between the H atom and Xe nucleus. In the case of an admixture with the coefficient $\nu \equiv (1 - \chi^2)^{1/2}$ of a small component of the ionic structure $Xe^+ \cdots H^-$ with the normal covalent component $Xe \cdots H$, the SHF constants are given by

$$a(^{129}Xe) = N^2(^2\Sigma)[\chi^2 a_1 + 2\chi(1 - \chi^2)^{1/2}a_2 + (1 - \chi^2)a_3] \tag{2}$$

$$B_\parallel(^{129}Xe) = N^2(^2\Sigma)[\chi^2 b_1 + 2\chi(1 - \chi^2)^{1/2}b_2 + (1 - \chi^2)b_3] \tag{3}$$

where

$$N(^2\Sigma) = [1 + 2\chi(1 - \chi^2)^{1/2}O^{Xe^0}O^{H^0}S']^{1/2}$$

is a normalization constant, S' is the overlap integral $S' = \langle \Psi_{1s}^{H^0} | \Psi_{5p_z}^{Xe^0} \rangle$, and $O^{H^0} = 0.949$ and $O^{Xe^0} = 0.985$ are small correction factors.

The wavefunction describing the interaction between the H atom and one of the Xe atoms is given by

$$\Psi(\text{Xe} \cdots \text{H}; {}^{2}\Sigma) = N({}^{2}\Sigma)[\chi A \Phi^{\text{Xe}^{0}} \Phi^{\text{H}^{0}}(1s) - (1 - \chi^{2})^{1/2} A \Phi^{\text{Xe}^{+}}(5p_{z}) \Phi^{\text{H}^{-}}]$$

where A is the antisymmetrization and renormalization operator, $\Phi^{\text{Xe}^{0}} \Phi^{\text{H}^{0}}$ (1s) denotes a product of atomic orbitals appropriate to the valence bond (VB) structure Xe$\cdots$H, and $\Phi^{\text{Xe}^{+}}(5p_{z}) \Phi^{\text{H}^{-}}$ denotes a product of atomic orbitals appropriate to the VB structure Xe$^{+} \cdots$H^{-}.

The authors have computed a_{n}, b_{n} and S' as functions of the distance r from the matrix atom to the trapped hydrogen atom (see figure 2).

Taking into account the following relations (Morton *et al* 1979)

$$a_{\perp} = a - \tfrac{1}{2} B_{\parallel} \qquad a_{\parallel} = a + B_{\parallel}$$

we calculate the theoretical ESR linewidth of an H atom located at the substitutional position in solid xenon:

$$(\Delta H)_{\text{theor}} = 2.83 \text{ G.} \tag{4}$$

For the values a and $B_{\parallel}$ theory gives $a = 113$ MHz, $B_{\parallel} = 49$ MHz (for the octahedral H atom), in satisfactory agreement with the experimental results $a = 90$ MHz, $B_{\parallel} = 46$ MHz. On the other hand, in the case under consideration (the substitutional atom), there is a much greater discrepancy between theory and experiment: $(\Delta H)_{\text{exp}}/(\Delta H)_{\text{theor}} = 2.05$. At the same time, it is clear from the shape of the H atom potential well that trapped atoms have to 'spread' over the matrix cage and, if there is a considerably strong dependence of the SHF constants on the distance r, the linewidth should increase due to this 'spreading'.

Let us consider this effect in detail based on the work by Heder *et al* (1980) and Jette *et al* (1982). If the condition

$$\hbar \omega \gg kT \gg hf \tag{5}$$

is satisfied, that is the resonance frequency f of the ESR transition is far smaller than the frequency ω of the zero-point vibration of the trapped atom, and the observed temperature T is sufficiently low to suppose that only the zero-point vibration is predominant, the static SHF constants (equations (2) and (3)) must be averaged over the probability distribution of the hydrogen locations to obtain the theoretical ESR linewidth:

$$\bar{a} = \int a(r) \phi(x)^{2} \, dV \left(\int \phi(x)^{2} \, dV \right)^{-1}$$

$$\bar{B}_{\parallel} = \int B_{\parallel}(r) \phi(x)^{2} \, dV \left(\int \phi(x)^{2} \, dV \right)^{-1}.$$

The coordinate x and the coordinate r related to a nearest-neighbour Xe atom denoted by M are shown in figure 2. Here x is the distance from the instantaneous position of a hydrogen atom to its equilibrium substitutional position; r is the instantaneous distance of the vibrating H atom from the matrix atom M; and $\phi(x)$ is the probability distribution for the zero-point vibrations. The calculation proceeds by fitting the theoretical linewidths taken in the harmonic oscillator model to the corresponding experimental quantities in order

to obtain $(x_{0.5})_H$ and $(x_{0.5})_D$, the vibration amplitudes measured between the equilibrium position of hydrogen atom and the point where the probability is one half of the probability at $x = 0$:

$$(x_{0.5})_H = 1.02a_0$$

$$(x_{0.5})_D = 0.95a_0.$$

The ratio κ_3 is then

$$\kappa_3 \equiv (x_{0.5})_H/(x_{0.5})_D = 1.07.$$

If the HW potential model were suitable for the system under consideration, the constant κ_3 would be 1.2. In turn the SW potential would give $\kappa_3 = 1.0$, if it were an exact approximation. Thus, a more real approximation for the substitutional H atom seems to lie between these two. Repeating the above procedure we compute the SW potential radius α:

$$\alpha = 2.9a_0.$$

The condition (5) is really satisfied, because both approximations give the following values:

$$kT = 0.36 \text{ meV} \qquad hf = 0.038 \text{ meV} \qquad \hbar\omega = 10 \text{ meV}.$$

Thus, we find uncommonly large contributions to the hydrogen and deuterium ESR linewidths from zero-point vibrations of these atoms if the required vibrational amplitudes do not appear too large to be reasonable. In reality, the calculated amplitudes are quite reasonable, since they are nearly equal to those obtained by Baldini (1964) for the substitutional H and D atoms stabilized in the Ar matrix, which is even tighter than the Xe one.

5. The g-factor

The g-factor of a trapped atom is influenced by the trapping medium, which shifts it by $\Delta g = g - g_f$, where g_f is the free-state value. The theoretical prediction of the shift in the g-factor for the case of an H atom trapped in solid xenon is given by Morton *et al* (1979):

$$\Delta g = (4N_M/3)N^2(^2\Sigma)\{[(1 - \chi^2)\lambda_{5p}^{Xe^+} + 2\chi(1 - \chi^2)^{1/2}O^{Xe^0}O^{H^0}S'(\lambda_{5p}^{Xe^+}\lambda_{5p}^{Xe^0})^{1/2}](E^{Xe^-})^{-1}$$

$$- \langle\Psi_{1s}^{H^0}|\Psi_{5p_z}^{Xe^0}\rangle^2[\chi^2\lambda_{5p}^{Xe^0} + 2\chi(1 - \chi^2)O^{Xe^0}O^{H^0}S'(\lambda_{5p}^{Xe^+}\lambda_{5p}^{Xe^0})^{1/2}](E^{H^0})^{-1}\}.$$

Here N_M is the number of nearest-neighbour matrix atoms; $\lambda_{5p}^{Xe^0}$ and $\lambda_{5p}^{Xe^+}$ are the spin–orbit interaction constants of an Xe 5p and Xe$^+$ 5p electron; E^{H^0} is an average excitation energy of the H atom orbital, which is estimated as the average of the first excited state and the ionization energy of the H atom; and E^{Xe} is, approximately, the energy of the ionic state.

The positive terms arise from the ionic contribution to Δg, while the negative terms come from both the overlap and the ionic contribution.

In the absence of the admixture of the ionic structure ($\chi = 1$) the vibrationally averaged g-factor shifts are

$$\overline{(\Delta g)}_{HW} = -9.0 \times 10^{-4}$$
$$\overline{(\Delta g)}_{SW} = -9.1 \times 10^{-4}$$

for the HW and SW potentials respectively, and considerably exceed the experimental value. The difference between theoretical and experimental g-factor shifts means that one must correct for the contribution of the ionic structure, since this has the positive resulting sign. Therefore, based on the experimental data, the charge-transfer coefficient can be estimated as follows.

The charge-transfer coefficient v is a function of the distance r between hydrogen atom and xenon atom: $v \equiv (1 - \chi^2)^{1/2} = \gamma \exp(-\eta r)$, where γ and η are constants to be defined. We have three known experimental quantities: the octahedral v from the paper by Morton *et al* (1979), and the substitutional ΔH and Δg measured in our experiment. These provide the possibility to determine three unknown quantities: the coefficients γ and η, and the zero-point vibrational amplitude $x_{0.5}$, which now changes its value, because, according to equations (2) and (3), the SHF constants increase when $\chi \neq 1$. For $r = R_0 = 5.76a_0$, which is the nearest-neighbour distance in the octahedrally symmetric interstitial site, the values of χ and v are $\chi(5.76) = 0.99982$, $v(5.76) = 0.0190$ (Morton *et al* 1979). Averaging the theoretical a, $B_{\parallel}$ and Δg over the probability of hydrogen locations and fitting the vibrationally averaged theoretical linewidth ΔH and g-factor shift Δg, the former being obtained with averaged a and $B_{\parallel}$, to the corresponding experimental quantities, we get

$$(x_{0.5})_H = 0.93a_0 \qquad \text{HW approximation}$$
$$\alpha = 2.65a_0 \qquad \text{SW approximation}$$
$$\gamma = 25.707 \qquad \eta = 1.252 \qquad \text{for both approximations.}$$

Hence, the charge-transfer coefficient is independent of the approximation used:

$$v(8.20) = 8.9 \times 10^{-4}. \tag{6}$$

Here $8.20a_0$ is the nearest-neighbour distance in the substitutional site.

Thus, the substitutional v is only one-twentieth of the octahedral value. Performing no vibrations, the substitutional hydrogen atoms would have an ESR linewidth of only 3.05 G. This value differs from the quantity calculated before (equation (4)) owing to the contribution of ionic structure to the SHF constants.

Thus, the zero-point vibrations of hydrogen atoms trapped in substitutional sites in solid xenon increase the width of the ESR lines of these atoms by 80% (or 90% with respect to the SHF constants). This is a very big vibrational (or dynamical) contribution, but an even bigger ($\simeq 100\%$) dynamical contribution to the isotropic SHF constants has been found by Heder *et al* (1980) in the case of atomic hydrogen at the anion site in KCl crystal.

6. Hyperfine interaction

Hyperfine interaction of the unpaired electron with the hydrogen nucleus is given in terms of the isotropic hyperfine constant A, which is influenced by the matrix surroundings. The

theory of the HF constant matrix shift has been developed by Adrian (1960). The relative shift is

$$\Delta A/A_f = N_M\left([2/E^{H^0} + (E^{H^0} + E^{Xe^0})^{-1}]E_v + \sum_{nl}|\langle\Psi^{H^0}_{1s}|\Psi^{Xe^0}_{nl}\rangle|^2\right).$$

Here E^{H^0} and E^{Xe^0} are the average energies for the excited states of H and Xe atoms, respectively; E_v is the van der Waals interaction energy between the H and Xe atoms; the functions $\Psi^{Xe^0}_{nl}$ are the one-electron orbitals of the neighbouring Xe atoms. The coefficient N_M reflects the fact that only nearest-neighbour matrix atoms are taken into account.

The overlap integrals $\langle\Psi^{H^0}_{1s}|\Psi^{Xe^0}_{nl}\rangle$ fall off rapidly with decrease in the quantum numbers n and l. As an example, we obtained with the orbitals used in the calculations

$$\langle\Psi^{H^0}_{1s}|\Psi^{Xe^0}_{5p_z}\rangle = 0.0225$$

$$\langle\Psi^{H^0}_{1s}|\Psi^{Xe^0}_{5s}\rangle = 0.0053.$$

Therefore, for the calculation of the HF constant matrix shift we can use the approximation

$$\langle\Psi_{H,1s}|\Psi_{Xe,nl}\rangle \simeq 0$$

for all the Xe orbitals except the 5p orbital.

As a result, for the substitutional H atom the theory gives

$$(\Delta A/A_f)_{\text{theor 1}} = -0.60\%.$$

The interaction between the stabilized atom and the matrix atoms outside the first coordination sphere could remove much of the difference between theory and experiment, because the positive contributions from the overlap integrals fall off more rapidly with increasing distance from the H atom does than the contribution from the van der Waals interaction, leading to a reduction in the HF splitting. In this way we obtain the following result

$$(\Delta A/A_f) = -0.91\%.$$

The admixture of ionic structure contributes the additional negative term to $\Delta A/A_f$. Heder *et al* (1980) have derived a formula for the unpaired spin density in the case of a system including covalent and ionic structures. Using this formula and the above value (equation (6)) for v we therefore get approximately

$$(\Delta A/A_f)_{\text{is}} \simeq -0.07\%$$

for the contribution from the ionic structure to the HF constant matrix shift.

Finally,

$$(\Delta A/A)_{\text{theor}} = -0.98\%.$$

This result is in satisfactory agreement with experiment.

7. Conclusions

Thus, in this work deuterium atoms in solid xenon are stabilized by deposition from the gas phase and investigated by ESR for the first time. This permits the isotope effect in the ESR linewidth of trapped H and D atoms to be detected. The comparison of experimental values for ΔH with corresponding theoretical quantities led to the conclusion that the dynamical broadening of ESR lines, which is due to the zero-point vibrations of the trapped atoms, is nearly equal to the static one. We show that substitutional H and D atoms trapped in solid xenon perform measurably anharmonic vibrations. It should be noted that the optical investigation of octahedral H and D atoms in the Xe matrix (Creuzburg *et al* 1989) also shows anharmonic vibrations of these atoms. In the present work a comparison is carried out between experimental and theoretical values for the g-factor and relative matrix shift of the hyperfine constant of a trapped H atom, and it is found that experimental and theoretical quantities are in satisfactory agreement. It would be of interest to compute the charge-transfer coefficient and compare it with the above experimental value.

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