

Hydrogen atoms stabilized in neon and nitrogen matrices

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Hydrogen atoms obtained from a gaseous discharge were stabilized for the first time in neon and nitrogen matrices. Their ESR spectra were recorded. The hyperfine structure constants A , the matrix shifts $\Delta A / A_f$, and the g factors of these atoms are determined. In the case of hydrogen atoms in neon we found that the matrix shift was -0.13% , which was less than for all the other matrices. The ESR lines of the hydrogen atoms in neon were unusually narrow with a width less than 90 mG. It was established that these hydrogen atoms were stabilized at substitutional positions in the neon crystal lattice. In the case of hydrogen in nitrogen it was found that the ESR lines of the hydrogen atoms were considerably broadened by cooling the substrate during the deposition.

INTRODUCTION

Formation and investigations of stabilized (matrix-isolated) atoms have recently become popular.¹⁻³ Investigation of such atoms by the ESR method is particularly fruitful. The greatest interest lies in the formation and study of stabilized hydrogen atoms because they are the simplest and lightest. For example, hydrogen atoms in the H_2 matrix represent a quantum impurity in a quantum crystal. Studies of this system are reported in many papers.

Detailed investigations have also been made of hydrogen atoms stabilized in solid matrices consisting of heavy rare gases Ar, Kr, and Xe (Refs. 3–5). However, reliable data have not yet been obtained on the properties of hydrogen atoms stabilized in neon. This is unfortunate because neon is the most interesting matrix in the rare-gas series because its characteristics (polarizability, lattice constant, binding energy, crystallization temperature, etc.) distinguish solid neon from the other rare gases and make it closest to quantum crystals of hydrogen and helium.⁶ Moreover, there is no information on stabilization of hydrogen atoms in such a simple matrix as solid nitrogen.

We shall report the development of new apparatus and method for stabilization of atoms in solidified gases, describe the capture from a gas discharge and stabilization of hydrogen atoms in neon and nitrogen crystals, and give the results of studies of such stabilized atoms by the ESR method.

HYDROGEN ATOMS IN NEON

At present the neon matrix is the only one among solid rare gases in which it has not been possible to stabilize hydrogen atoms by capture from the gaseous phase.³ Only one report gave the results on the stabilization of hydrogen atoms in neon.⁴ These stabilized atoms were obtained by photolysis of HI molecules at 4.2 K in a neon matrix. The ESR spectrum of hydrogen then exhibited a matrix shift of the hyperfine structure constant $\Delta A / A_f$, which was 0.43% and this was in serious conflict with the theoretical prediction⁵ which gave the value -0.09% (Ref. 4), so that it could not be explained satisfactorily. However, in the case of hydrogen atoms in other matrices the agreement between the theory and experiment is fully satisfactory. Nevertheless, the authors of Ref. 4 ascribed the spectrum obtained to hydrogen atoms at substitutional positions in the strongly

distorted neon lattice. This conclusion was drawn because the hypothesis that the observed hydrogen atoms were located at various interstitial positions in the neon lattice gave rise to an even greater discrepancy between the observed matrix shift $\Delta A / A_f$ and its theoretical values. Attempts to obtain the same stabilized atoms by capture from a gaseous discharge were unsuccessful, in spite of the fact that the authors were able to use the same method to capture H atoms in H_2 , Ar, Kr, Xe, and CH_4 matrices.^{1,4} Cooling of the substrate during deposition to 2 K and also the replacement of H with D in order to improve the stabilization did not give rise to ESR signals of hydrogen or deuterium atoms captured in neon. This unexpected failure to observe the ESR spectra of hydrogen atoms, stabilized in neon by capture from a gaseous discharge, was described in Ref. 4 as surprising and it was pointed out that there were no clear reasons why the H atom should require an excess energy in order to occupy a substitutional position in the neon lattice.

It would therefore be of considerable interest to stabilize hydrogen atoms in neon by capture from a gaseous discharge. Such an experiment was carried out by us but we improved considerably the experimental conditions for the capture of hydrogen atoms in a matrix by employing a gaseous discharge in an H_2 -Ne mixture and using an additional matrix gas (Ne) which was supplied to the substrate along a separate tube cooled with liquid nitrogen.

We recorded the ESR spectrum of the hydrogen atoms in neon, shown in Fig. 1. We can see that this figure includes two spectra: a doublet of narrow lines (1) with a large hyperfine splitting and a doublet of wider lines with a smaller hyperfine splitting (2). The narrow lines had an unusually small width (~ 90 mG). Usually the ESR lines of hydrogen and other atoms stabilized in various matrices have widths of the order of 1 G or more. Only in one case⁷ was it reported that hydrogen atoms stabilized in parahydrogen had lines of width 100 mG. Moreover, hydrogen atoms in neon could have lines with even smaller widths than that given above, since the width of 90 mG obtained in our study was distorted by homogeneous broadening due to inhomogeneities of the magnetic field. This inhomogeneous broadening of the lines was confirmed by the observation that an increase in the power of a microwave resonance field altered only the amplitudes of the ESR lines of hydrogen without broadening

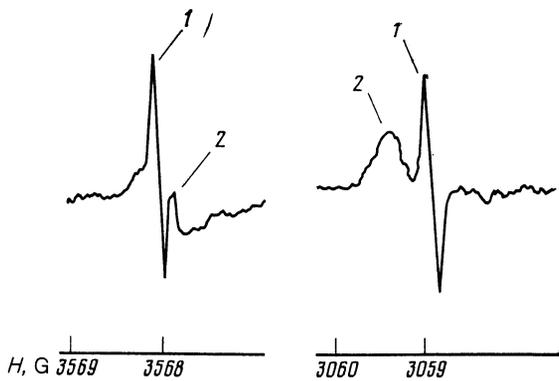


FIG. 1. High- and low-field lines in the ESR spectrum of hydrogen atoms stabilized in neon and deposited on a substrate at $T_{\text{dep}} = 4.2$ K. The spectrum was recorded at $T_{\text{rec}} = 4.2$ K. The concentration of hydrogen in neon was $[\text{H}_2]/[\text{Ne}] \approx 2 \times 10^{-3}$ and the resonance frequency was $f_{\text{res}} = 9339.22$ MHz.

them. It was known that in the case of such very dilute paramagnetic systems as those employed in the present study the only cause of noninstrumental broadening of the ESR lines could be the inhomogeneity of the surrounding matrix.^{2,5} Therefore, our spectra indicated that the hydrogen atoms responsible for these spectra were in an unusually regular (for matrix experiments) environment in the neon lattice. This was probably due to the very low crystallization temperature of neon (24.5 K), so that when the substrate was kept at 4.2 K and the heat of crystallization was evolved, neon was annealed and recrystallized at the moment of deposition so that high-quality crystals were formed. It was important to note also that 99.7% of the natural neon consisted of even isotopes with the nuclear spin and magnetic moment of zero, which avoided the superhyperfine broadening of the ESR lines of the atoms stabilized in neon. We found that the hydrogen atoms stabilized in neon had a hyperfine structure constant $A = 1418.5(3)$ MHz; the matrix shift was $\Delta A / A_f = -0.13(2)\%$ [$\Delta A = A - A_f$; the hyperfine structure constant of a free hydrogen atom was $A_f = 1420.40573(5)$ MHz] and the g factor was [$g_f = 2.00211(8)$]. These values together with other results (for the sake of comparison) are given in Table I. The measured matrix shift was in good agreement with the theoretically predicted⁵ value $(\Delta A / A_f)_{\text{theor}} = -0.09\%$ (Ref. 4) for the hydrogen atom located in a substitutional position in the neon lattice. Therefore, the matrix shift $\Delta A / A_f$ and the very small width of the ESR lines demonstrated that the narrow lines in Fig. 1 were due to the hydrogen atoms stabilized at the substitutional position in the regular lattice of neon crystals.

In the case of the spectrum of wide lines (2) we also

determined the hyperfine structure constant $A = 1417.4(2)$ MHz, the matrix shift $\Delta A / A_f = -0.21(2)\%$, and the g factor [$g_f = 2.00213(8)$]. It was pointed out in Refs. 8 and 9 that when a mixture of gases is precipitated on a cold surface, microcrystals of the impurity gas may form in the main matrix. In this case there is a possibility that some of the atoms will become stabilized in these microcrystals. This was the hypothesis put forward in Ref. 8 to account for the identical nature of the ESR spectra of nitrogen atoms in H_2 , Ne, Xe, and N_2 matrices. It was concluded there that in all these matrices there were molecular nitrogen microcrystals which stabilized N atoms. Therefore, we carried out experiments in which hydrogen atoms were stabilized in an H_2 matrix and compared the results with the spectrum 2. We found that in the case of H in the H_2 matrix the relevant parameters were as follows: $A = 1416.9(2)$ MHz, $\Delta A / A_f = -0.24(2)\%$, and $g_f = 2.00221(8)$, which are included also in Table I and are close to those reported in Ref. 1. Clearly, the parameters of the spectrum 2 were practically identical with those of the H atoms in the H_2 matrix. Hence, we concluded that the spectrum 2 representing the wider lines (Fig. 1) was due to those hydrogen atoms which were stabilized in microcrystals of molecular hydrogen formed during precipitation of a hydrogen–neon mixture. However, in contrast to the case of nitrogen atoms in Ref. 8, we observed simultaneously the ESR spectra of the hydrogen atoms in the main matrix (neon) and in impurity microcrystals (H_2).

When the temperature of the substrate at the moment of deposition was $T_{\text{dep}} = 1.5$ K, we found that the H_2 :Ne system exhibited clearly the spectrum 2. However, the spectrum 1 either decreased strongly in amplitude relative to the spectrum 2 or it was not observed at all. This could be explained partly by the fact that at $T = 1.5$ K the narrow lines were saturated much more strongly by the microwave resonance field. In fact, when a sample was prepared at $T = 4.2$ K and then the substrate temperature was lowered, the spectrum 1 decreased considerably in intensity relative to the spectrum 2, and to observe it we had to reduce still further the microwave power. Heating of a sample prepared at $T_{\text{dep}} = 1.5$ K to 4.2 K resulted in the appearance of the spectrum 1 in some cases, but this spectrum was much weaker than the spectrum 2. It was established in Ref. 4 that the hydrogen atoms stabilized by precipitation from a gaseous discharge in Ar, Kr, and Xe gave rise to just one ESR spectrum for each of these matrices and such spectra corresponded to the substitutional positions in the lattice of the matrix. Hydrogen atoms formed by photolysis of HI in the same matrices gave rise to multiplet spectra corresponding both to substitutional positions and positions in octahedral

TABLE I. Characteristics of hydrogen atoms stabilized in neon, hydrogen, and nitrogen matrices.

Matrix	Polarizability of matrix particles, \AA^3	Substrate temperature T_{dep} , K	A , MHz	$\Delta A / A_f$, %	g Factor	Line width ΔH , G
Free atom (gaseous phase)	—	—	1420.40573(5)	—	2.002256(24)	0.06
Ne	0.40	4.2	1418.5(3)	-0.13	2.00211(8)	0.09
H_2	0.77	4.2	1416.9(2)	-0.24	2.00221(8)	0.5
N_2	1.74	1.6	1415.1(3)	-0.38	2.00207(9)	4.0

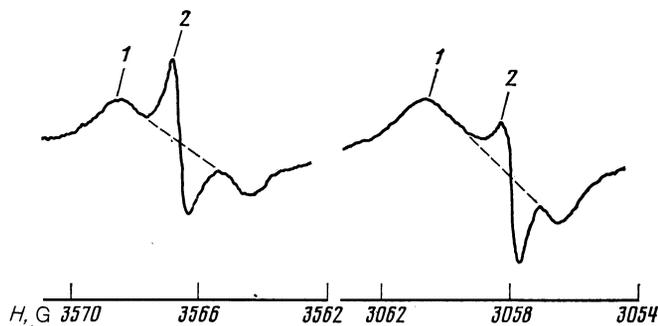


FIG. 2. High- and low-field lines in the ESR spectrum of hydrogen atoms stabilized in nitrogen and deposited on a substrate at $T_{\text{dep}} = 1.6$ K when the concentration of hydrogen was $[H_2]/[N_2] \approx 2 \times 10^{-2}$; the spectrum was recorded at $T_{\text{rec}} = 1.6$ K at a frequency $f_{\text{res}} = 9335.44$ MHz.

and tetrahedral interstices. The above results demonstrated that the hydrogen atoms captured from a gaseous discharge by the neon matrix were also stabilized at one position, which in the neon crystal was the regular site.

HYDROGEN ATOMS IN NITROGEN

Solid nitrogen has been investigated intensively in many cryogenic laboratories.⁶ Studies of the ESR spectra of matrix-isolated hydrogen atoms in solid N_2 can contribute to our knowledge of the crystal structure of solidified nitrogen and of the interactions of impurity atoms with the matrix environment. From the point of view of the matrix isolation method, crystals of solid nitrogen represent a more "rigid" matrix than hydrogen and neon, because in the case of nitrogen the crystallization temperature is $T_{\text{cr}} = 63$ K, which is much higher than $T_{\text{dep}} = 4.2$ K. Hence, at 4.2 K we can expect nitrogen crystals with more defects and lattice distortions, and this in turn may broaden considerably the ESR lines of stabilized atoms compared with the lines of the same atoms in hydrogen and in neon, because the crystallization temperatures of the last two elements are $T_{\text{cr}} = 13.8$ and 24.5 K.

We recorded for the first time the ESR spectra of hydrogen atoms stabilized in a molecular nitrogen matrix. These atoms were formed because a gaseous discharge in hydrogen, from which the hydrogen atoms were captured, and the matrix gas (nitrogen supplied to the substrate along a separate tube) were cooled in our experiments with liquid nitrogen. We found that this improved considerably the conditions for the stabilization of atoms. One of the ESR spectra obtained after deposition at $T_{\text{dep}} = 1.6$ K is reproduced in Fig. 2. It is clear from this figure that high- and low-field signals of the captured hydrogen atoms are doublets, each consisting of a wide line 1 and a narrow line 2. For clarity, the wide line 1 is continued by a dashed curve to the region where it is overlapped by the line 2. We recorded the spectrum at a low microwave power, because an increase in the power resulted in saturation of the narrow ($\Delta H \approx 550$ mG) lines 2 so that the spectra 1 and 2 were poorly resolved. The spectrum 1 consisted of two wide ($\Delta H \approx 4$ G) lines and had the following parameters: $A = 1415.1(3)$ MHz, $\Delta A/A_f = -0.38(2)\%$, $g_J = 2.00207(9)$. The corresponding parameters for the spectrum 2 were: $A = 1417.0(3)$ MHz, $\Delta A/A_f = -0.24(2)\%$, $g_J = 2.00213(9)$, which were practically identical with the parameters of the spectrum of the hydrogen atoms in an H_2 matrix. Hence, we concluded that

the spectrum 2 was due to the hydrogen atoms stabilized in microcrystals of solid molecular hydrogen formed in the process of deposition of the hydrogen–nitrogen mixture. The spectrum 1 differed strongly from the spectrum 2 in respect of its parameters, particularly in respect of the matrix shift $\Delta A/A_f$. The considerable width of the lines denoted by 1 was due to a large number of defects in the lattice of the nitrogen matrix, which—as mentioned at the beginning of this section—was determined by the nature of the matrix, i.e., by its "rigidity."

These observations indicated that the spectrum 1 was due to the hydrogen atoms that were stabilized in the matrix of solid N_2 . We concluded that these atoms were at the substitutional positions in the crystal lattice of nitrogen, because penetration to interstitial positions would require a kinetic energy considerably higher than stabilization at the regular sites. The thermal energy of the particles of the deposited gases, especially when cooled to liquid nitrogen temperature, was clearly insufficient for the penetration to the interstices of the crystal lattice of the matrix. All the experiments reported so far on the stabilization of atoms³ confirmed the conclusion reached sometime ago⁴ that hydrogen atoms captured by deposition from a gaseous discharge are stabilized in the lattice of the matrix in just one position and this position is substitutional (regular site).

We found that the substrate temperature during deposition T_{dep} affected the width of the lines in the spectrum of the hydrogen atoms stabilized in nitrogen. When a sample was prepared at $T_{\text{dep}} = 4.2$ K, the lines denoted by 1 were considerably narrower than in Fig. 2. Their width ΔH was then ~ 1.2 G. The width of the lines 2 decreased in this case only slightly to 400–450 mG. Heating or cooling of the samples prepared at $T_{\text{dep}} = 1.6$ and 4.2 K did not alter the initial nature of these spectra. These investigations of the influence of temperature confirmed that the width of the ESR lines of hydrogen atoms in nitrogen was governed by the structure of the matrix and by the number of defects in this matrix, which increased on reduction in T_{dep} and was no longer affected by a further change in the temperature of the solid matrix.

CONCLUSIONS

We obtained for the first time and investigated the ESR spectra of hydrogen atoms stabilized at the substitutional positions in an undistorted crystal lattice of neon. The unusually small width of the ESR lines of atoms, compared with other matrices, indicated a high regularity of the matrix environment. The matrix shift of the hyperfine structure constant of these atoms (Table I) was less than for all the other matrices and it agreed well with the theoretically predicted shift for the hydrogen atoms stabilized at the substitutional positions in the regular lattice of a neon crystal. The hypothesis⁴ that a hydrogen atom stabilized at a substitutional position in the neon lattice has a matrix shift $\Delta A/A_f = 0.43\%$ and is responsible for the compression of the immediate environment in this lattice by 8% was in conflict with our results, which showed that the hydrogen atoms stabilized at the substitutional position in the neon lattice did not distort this lattice and were characterized by a matrix shift $\Delta A/A_f = -0.13\%$, which was close to the value -0.09% predicted theoretically for the undistorted neon lattice.

We also recorded for the first time the ESR spectrum of hydrogen atoms which were stabilized in a matrix of N_2 . We determined the hyperfine structure constant, the matrix shift, and the g factor of these atoms. We observed a considerable increase in the number of defects in the crystal lattice of nitrogen when the temperature of the substrate on which a sample was deposited was reduced from 4.2 to 1.6 K, which was attributed to a considerable increase in the width of the ESR lines of the stabilized hydrogen atoms.

In the case of hydrogen atoms in neon and nitrogen matrices we recorded second ESR spectra differing from the above by the values of the hyperfine structure constants. These spectra could be explained by stabilization of some of the hydrogen atoms in microcrystals of solid H_2 formed in Ne and N_2 matrices.

Our results, like those reported in Ref. 4, confirmed one of the conclusions of Ref. 5 that the polarizability of the matrix particles influenced the nature of the ESR spectra of stabilized hydrogen atoms. This influence is reflected in Table I, which shows that the matrix shift of the hyperfine structure constant of a stabilized hydrogen atom increases in a regular manner on transition from an Ne matrix to an N_2 matrix, i.e., in accordance with an increase in the polarizability of the matrix particles. This is due to an increase in the strength of the van der Waals interaction of a stabilized hydrogen atom with particles in the matrix as the polarizability of these particles increases. According to the theory of Ref.

5, this van der Waals interaction reduces the spin density at the nucleus of the hydrogen atom and is responsible for a negative matrix shift of the hyperfine structure constant. Higher values of the polarizability correspond to larger widths of the ESR lines. In the case of hydrogen atoms in an H_2 matrix the line width of 0.5 G is mainly due to the broadening by the dipole interaction of the hydrogen atoms with the surrounding hydrogen orthomolecules.

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