

Computer-Simulation of Electron-Nuclear Double Resonance Spectra due to Hydrogen-Related Dangling Bonds in Hydrogenated Amorphous Silicon — Evidence for Existence of Hydrogen-Related Dangling Bonds in Hydrogenated Amorphous Silicon

by

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Abstract

Electron-nuclear double resonance (ENDOR) spectra due to hyperfine interaction of dangling bond electrons with hydrogen nuclei in hydrogenated amorphous silicon have been computer-simulated in terms of the local and matrix ENDOR. These spectra are in a semi-quantitative agreement with the ENDOR spectrum observed by Fehr et al. (Phys. Stat. Solidi A **207** (2010), 552).

Keywords: ESR; Electron-nuclear double resonance; Defect; Amorphous silicon; Amorphous network.

1 Introduction

We have proposed a model that there exist two types of silicon dangling bonds, i.e., normal dangling bonds and hydrogen-related dangling bonds (dangling bonds having hydrogen at a nearby site) in hydrogenated amorphous silicon (a-Si:H), as shown in Fig. 1, on the basis of the mechanism of light-induced defect creation in a-Si:H [1–3]. After then, evidence for existence of such two types of dangling bonds in a-Si:H has been obtained from electron-nuclear double resonance (ENDOR)

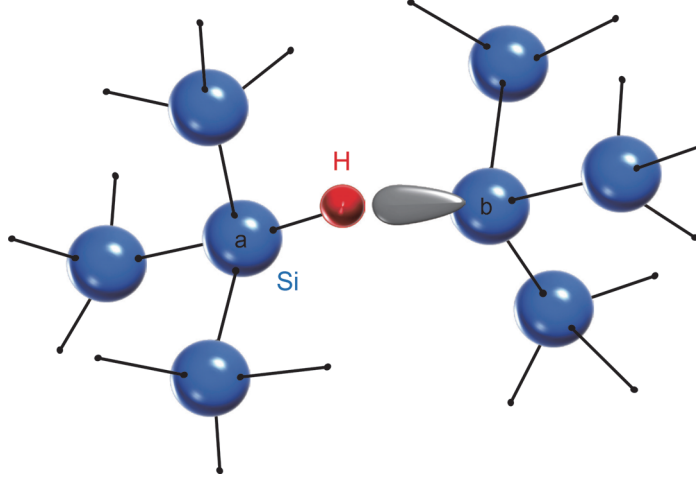


Figure 1: Schematic illustration of the hydrogen-related dangling bonds in a-Si:H [8].

measurements on a-Si:H and a-Si:D [4, 5]. The results of electron spin resonance (ESR) spectra on a-Si:H and a-Si:D have confirmed the existence of two types of dangling bonds from comparison between the observed ESR spectra and the computer-simulated ESR spectra obtained on the basis of two types of dangling bonds [6–8]. Recently, Fehr et al. [9] reported the results of ENDOR spectra observed in a-Si:H, using the pulse technique, which lead us to obtain detailed information about hyperfine interaction between hydrogen nuclei and dangling-bond electrons in a-Si:H. In this paper, we present computer-simulation of ENDOR spectra due to hydrogen-related dangling bonds in a-Si:H, furthermore taking into account those of matrix ENDOR spectra, i.e., ENDOR due to hydrogen atoms being situated not nearby the dangling bond site such as hydrogen-related dangling bonds, but within the distance from dangling bonds so that dipolar interaction operates between hydrogen nuclei and dangling-bond electrons. The computer simulated ENDOR spectra are compared with the ENDOR spectrum observed by Fehr et al. [9]. Such a comparison provides us with further evidence for existence of hydrogen-related dangling bonds in a-Si:H.

2 Electron-Nuclear Double Resonance Spectra

2.1 General aspects

Electron-nuclear double resonance (ENDOR) is generally classified by three classes: (1) distant ENDOR, (2) matrix ENDOR, and (3) local ENDOR. Here, we consider how nuclear transitions in hydrogen nuclei affect dangling bond electron spins.

(1) Distant ENDOR

Nuclear resonance of hydrogen nuclei being situated far from dangling bonds affects their electron spins through dipole-dipole interaction among neighboring hydrogen nuclei, i.e., this is called distant ENDOR. Such dipole-dipole interactions are so weak that ENDOR transition probability due to nuclear resonance of such hydrogen nuclei is very small, although the number of hydrogen nuclei participating in these interactions is large.

(2) Matrix ENDOR

Although the Fermi-type contact hyperfine interaction does not operate between dangling-bond electrons and hydrogen nuclei, their mutual dipolar interaction works so that the ENDOR signal may be well observed compared to the distant ENDOR signal. This ENDOR line occupies the central part of the ENDOR spectrum that we are concerned with, as will be described later in detail.

(3) Local ENDOR

In the case of hydrogen-related dangling bonds, a hydrogen nucleus is located nearby the dangling bond site, so that the Fermi-type contact hyperfine interaction operates as well as the dipolar interaction, as will be shown below.

2.2 Zeeman energy and hyperfine interaction

The Hamiltonian responsible for ENDOR is given below:

$$\mathcal{H} = \mu_B \mathbf{S} g \mathbf{H} + g_n \mu_n \mathbf{I} \mathbf{H} + \mathbf{S} \mathbf{A} \mathbf{I}, \quad (1)$$

where μ_B , μ_n , $\mathbf{S}$, $\mathbf{I}$, $\mathbf{g}$, g_n , $\mathbf{H}$, and $\mathbf{A}$ are the Bohr magneton, the nuclear magneton, the electron spin, the nuclear spin (proton spin), the g tensor, the nuclear g factor, applied magnetic field, and the hyperfine interaction tensor, respectively. The first and second terms in eq. (1) represent the electronic and nuclear Zeeman energies, respectively, while the third term in eq. (1) expresses the hyperfine interaction. We consider the third term of eq. (1), i.e., hyperfine interaction with axial symmetry between electron spin and proton spin. When the static magnetic field is applied along the z -axis making an angle of θ with the axial symmetric axis of the hyperfine interaction tensor, A is given by its isotropic part, A_{iso} , and anisotropic part, A_{aniso} , as follows:

$$A = A_{iso} + A_{aniso}(3 \cos^2 \theta - 1). \quad (2)$$

Using $A_{//}$ ($A_{//}$ with $\theta = 0$) and $A_{\perp}$ ($A_{\perp}$ with $\theta = \pi/2$), A_{iso} and A_{aniso} are given by

$$A_{iso} = (A_{//} + 2A_{\perp})/3, \quad (3)$$

$$A_{aniso} = (A_{//} - A_{\perp})/3, \quad (4)$$

respectively. A_{iso} and A_{aniso} arise from the Fermi-type contact hyperfine interaction, whose constant is proportional to the electron density at the hydrogen nucleus, and from the dipolar interaction, respectively. A_{aniso} is given by

$$A_{aniso} = g_n \mu_n g \mu_B / R^3, \quad (5)$$

where R is the distance between the dangling bond site and a hydrogen nuclear spin.

A typical anisotropic hyperfine structure is illustrated in Fig. 2. The computer-simulation of hyperfine structure has been performed, using the program of FESRSDS (Fitting of Electron Spin Resonance Spectrum for Disordered System) [10].

In the following subsection, we consider the local ENDOR and the matrix ENDOR, using the hyperfine interaction described above.

2.3 ENDOR spectrum

(1) General aspects

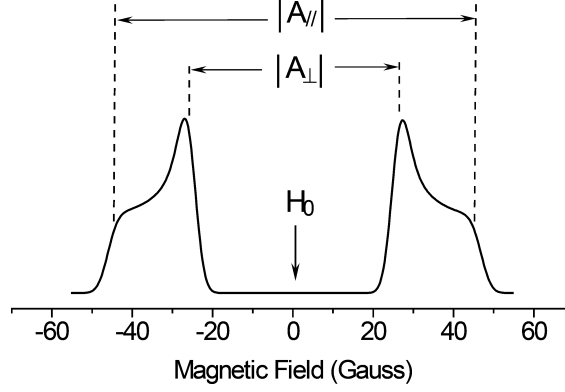


Figure 2: The computer-simulated hyperfine structure with the values of ESR parameters shown below: $g_{iso} = 2.004$, $A_{//} = 93$ G, $A_{\perp} = 51$ G, and $\sigma_{iso} = 2$ G. The isotropic g -value and the isotropic σ value are assumed for simplicity [8].

The ENDOR spectrum is first assumed to consist of the local ENDOR spectrum due to hydrogen-related dangling bonds and the matrix ENDOR spectrum due to hydrogen nuclear spins (proton spins) being situated around the normal dangling bond. The distant ENDOR spectrum is neglected. The ENDOR spectrum is composed of hyperfine structure associated with the ENDOR transition, whose spin-packet lineshape is assumed to be Gaussian with the standard deviation of $\sigma_{//}$ and $\sigma_{\perp}$, that is, the components parallel and perpendicular to the axial symmetric axis, respectively.

(2) Local ENDOR spectrum

The local ENDOR spectrum is due to the hyperfine interaction of the hydrogen-related dangling bond, in which its electron spin and a hydrogen nuclear spin (proton spin) nearby the dangling bond site participate. We attempt to simulate the ENDOR spectrum with several choices of the values of the parameters $A_{//}$ and $A_{\perp}$, $\sigma_{//}$ and $\sigma_{\perp}$ in order to fit the ENDOR spectrum observed by Fehr et al. [9], i.e., called the Fehr ENDOR spectrum, particularly its shoulder part in the lower frequency side from the central frequency, 0. As a best fitted spectrum, a computer-simulated ENDOR spectrum (designated by HDB) is shown in Fig. 3 as well as in Fig. 5, using the following values of the parameters: $g_{//} = 2.0050$ and $g_{\perp} = 2.0056$, $A_{//} = 19.6$ MHz and $A_{\perp} = 2.80$ MHz, $\sigma_{//} = 2.24$ MHz and $\sigma_{\perp} = 3.36$ MHz. These values almost correspond to those for hydrogen-related dangling bonds with $R \cong 2.5$ Å (see eq. (5)). As seen in Fig. 3, the shoulder part of the Fehr ENDOR spectrum in the lower frequency side from the central frequency, 0, is realized in the computer-simulated ENDOR spectrum. The other computer-simulated ENDOR spectra shown in Fig. 3 correspond to the matrix ENDOR spectra, as will be discussed below.

(3) Matrix ENDOR spectrum

The spatial positions of hydrogen in a-Si:H have been investigated by Bellissent et al. [11], using the neutron scattering technique. A normal dangling bond is assumed to be located on a silicon site a in Fig. 4, i.e., a neighboring hydrogen atom is removed, and then a normal dangling bond is left behind. The distance between a normal dangling bond site and hydrogen is designated by r corresponding to R in eq. (5). According to their results, the second neighboring hydrogen is

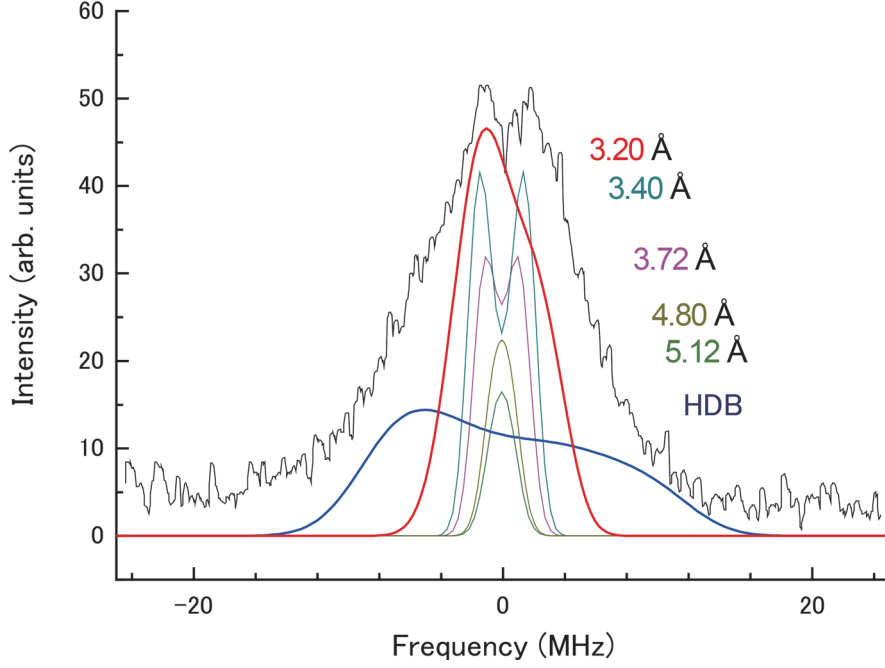


Figure 3: The computer-simulated ENDOR spectra in a-Si:H. HDB(blue): The values of the parameters are given below: $g_{//} = 2.0050$ and $g_{\perp} = 2.0056$, $A_{//} = 19.6$ MHz and $A_{\perp} = 2.80$ MHz, $\sigma_{//} = 2.24$ MHz and $\sigma_{\perp} = 3.36$ MHz. The matrix ENDOR spectra for various distance between the dangling bond site and the hydrogen, r , are shown as follows: $r = 3.20$ Å (red). The values of the parameters are given below: $g_{//} = 2.0050$ and $g_{\perp} = 2.0056$, $A_{//} = 4.68$ MHz and $A_{\perp} = 2.34$ MHz, $\sigma_{//} = 1.12$ MHz and $\sigma_{\perp} = 1.68$ MHz. $r = 3.40$ Å (sky blue), $r = 3.72$ Å (magenta), $r = 4.80$ Å (yellow brown), $r = 5.12$ Å (olive): The values of the parameters for these r are given in Table 1. The Fehr ENDOR spectrum [9] is also shown.

apart from the silicon site a with 3.2 Å (ℓ_2 in Fig. 4), while the third neighboring hydrogen is separated from the silicon site a in the range of 3.72 Å to 5.12 Å (ℓ_3 in Fig. 4). These hydrogen atoms contribute to the matrix ENDOR, so that $A_{//}$ and $A_{\perp}$ are estimated from dipolar interaction between a dangling bond electron spin and hydrogen nuclear spins, as follows: For $r = 3.2$ Å, we obtain $A_{//} = 4.68$ MHz and $A_{\perp} = 2.34$ MHz. Further, for $r = 3.2$ Å, it is assumed that the values of $g_{//}$ and $g_{\perp}$ are those for hydrogen-related dangling bonds, as mentioned above, and that $\sigma_{//}$ and $\sigma_{\perp}$ are half values compared to those for hydrogen-related dangling bonds. Thus, the matrix ENDOR spectrum for $r = 3.2$ Å is computer-simulated, as shown in Fig. 3. For the values of r , i.e., 3.4 , 3.72 , 4.8 , and 5.12 Å, the isotropic g -value of 2.0054 , i.e., that of normal dangling bonds, and half values of $\sigma_{//}$ and $\sigma_{\perp}$ compared to those for the case of $r = 3.2$ Å, as mentioned above, are assumed. Although normal dangling bonds have anisotropic g -values, their anisotropy is small [3], so that the g -value measured by ESR is taken here. Furthermore, hydrogen atom affects the g -value of normal dangling bonds when it is located close to the dangling bond like HDB. However, the case of $r \geq 3.4$ Å is not like the case of HDB, so that anisotropy of the dangling bond should be small. The value of σ arises from spatial variation of g -values and hyperfine interaction constants. When r becomes large, the influence of hydrogen atoms on the g -value and the hyperfine interaction

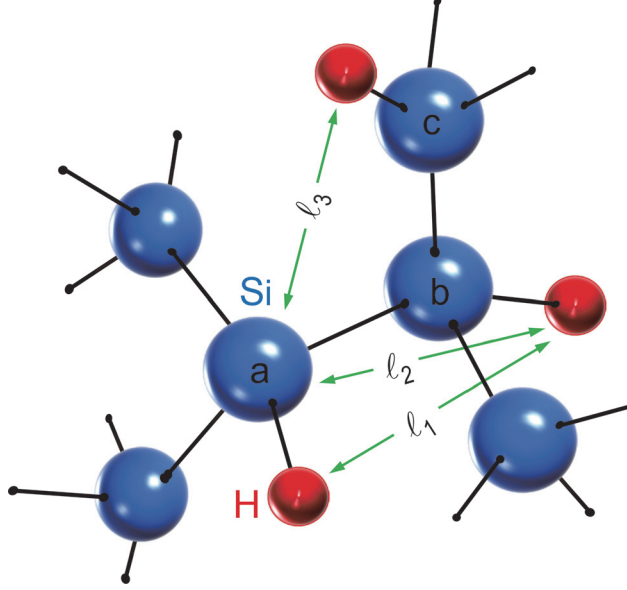


Figure 4: Schematic illustration of the local structure being composed of silicon atoms and hydrogen atoms. The distances ℓ_1 , ℓ_2 , and ℓ_3 are cited from Bellissent et al. [11] as follows: $\ell_1 = 3.3 - 4.3$ Å, $\ell_2 = 3.2$ Å, and $\ell_3 = 3.72 - 5.12$ Å.

Table 1: The values of parameters used in the calculation

Normal DB					
$r(\text{\AA})$	g	$A_{//}(\text{MHz})$	$A_{\perp}(\text{MHz})$	$\sigma_{//}(\text{MHz})$	$\sigma_{\perp}(\text{MHz})$
3.20	2.0054*	4.68	2.34	0.56	0.84
3.40	2.0054	3.90	1.95	0.56	0.84
3.72	2.0054	2.98	1.49	0.56	0.84
4.80	2.0054	1.39	0.694	0.56	0.84
5.12	2.0054	1.14	0.571	0.56	0.84

σ : Standard deviation of the Gaussian spin-packet.

* Note that the isotropic g -value is used for $r = 3.20$ Å only in Fig. 5, while the anisotropic g -values are used for $r = 3.20$ Å in Fig. 3.

constant becomes weak, so that the value of σ becomes small. The values of the parameters are listed in Table 1, and then the matrix ENDOR spectra are computer-simulated, as shown in Fig. 3.

When the isotropic g -value of 2.0054 is used even for the case of $r = 3.2$ Å, as shown in Table 1, and the values of the other parameters are listed in Table 1, the computer-simulated matrix ENDOR spectra are shown in Fig. 5 as well as those for other values of r . The difference in the shape of matrix ENDOR spectra for $r = 3.2$ Å between the above two cases is significant, as seen in Figs. 3 and 5. As seen in Fig. 4, the distance between the normal dangling bond on the silicon site a and the second neighboring hydrogen is longer than that for hydrogen-related dangling bonds with

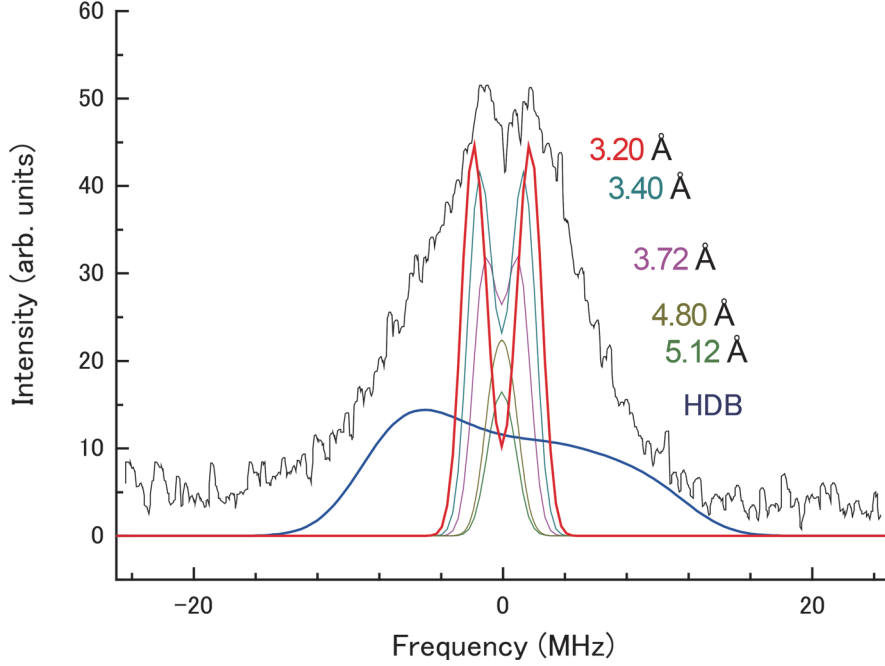


Figure 5: The computer-simulated ENDOR spectra in a-Si:H. HDB(blue): The values of the parameters are given below: $g_{//} = 2.0050$ and $g_{\perp} = 2.0056$, $A_{//} = 19.6$ MHz and $A_{\perp} = 2.80$ MHz, $\sigma_{//} = 2.24$ MHz and $\sigma_{\perp} = 3.36$ MHz. The matrix ENDOR spectra for various distance between the dangling bond site and the hydrogen, r : $r = 3.20$ Å (red), $r = 3.40$ Å (sky blue), $r = 3.72$ Å (magenta), $r = 4.80$ Å (yellow brown), $r = 5.12$ Å (olive): The values of the parameters for these r are given in Table 1. The Fehr ENDOR spectrum [9] is also shown.

$r \cong 2.5$ Å. Thus, the anisotropy of the g -value used for the computer-simulated ENDOR spectrum in Fig. 3 seems to be emphasized compared to the computer-simulated ENDOR spectrum with the isotropic g -value of 2.0054. This is one of the reasons of why the difference in the shape of the matrix ENDOR spectra between the above two cases is significant. The other reason is the difference in the values of $\sigma_{//}$ and $\sigma_{\perp}$ between the above two cases.

As seen in the figures, the computer-simulated matrix ENDOR spectra occupy the central part of the total ENDOR spectrum. A dip in the central part of the Fehr ENDOR spectrum is also seen in the computer-simulated matrix ENDOR spectra for $r = 3.2, 3.4$, and 3.72 Å. In the figure, the intensity of each computer-simulated matrix ENDOR is arbitrary, because it is difficult to estimate the number of hydrogen involved in the matrix ENDOR and the transition probability of the matrix ENDOR. Thus, it is impossible to sum up the intensity of each computer-simulated matrix ENDOR to construct the total ENDOR spectrum, and then, it is also impossible to compare the total intensity of computer-simulated matrix ENDOR with that of the Fehr ENDOR spectrum. However, as has already been pointed out above, the shoulder of the left side of the Fehr ENDOR spectrum seems to be fitted by the computer-simulated local ENDOR spectrum due to hydrogen-related dangling bonds, as shown in the figures. A question of how many hydrogen-related dangling bonds participate in the local ENDOR spectrum is unknown, because we have no information about the number of hydrogen-related dangling bonds in Fehr's sample. However, it may be

supposed that the principal part of dangling bonds is the normal dangling bond, judging from the preparation temperature of Fehr’s sample.

Accordingly, a quantitative comparison between the experiment and the calculation has not been made, but we can say that the experimental and calculated spectra are semi-quantitatively similar to each other.

Finally, we point out that the area of the computer-simulated local ENDOR spectrum due to hydrogen-related dangling bonds is 44% compared to the area of the Fehr ENDOR spectrum, and that the remaining area of 56% may come from the matrix ENDOR spectra due to hydrogen nuclei. As mentioned above, the number of hydrogen-related dangling bonds is smaller than that of normal dangling bonds in Fehr’s sample, but the transition probability of the local ENDOR is very higher than those of the matrix and distant ENDOR, so that even if the number of hydrogen-related dangling bonds is only several percentage for the total number of dangling bonds, the local ENDOR intensity of hydrogen-related dangling bonds may be such as seen in Figs. 3 and 5. For a quantitative comparison between the experiment and the calculation, it is required to show that this is the case for the computer-simulated local ENDOR spectrum.

(4) Summary

We have computer-simulated the local and matrix ENDOR spectra, but for the matrix ENDOR, we have taken several cases of distance between a central normal dangling bond site and hydrogen being located around it. From these considerations, we have been able to account for typical features of the Fehr ENDOR spectrum, as mentioned above.

3 Conclusion

In summary, we have considered the Fehr ENDOR in terms of the local and matrix ENDOR. The local ENDOR spectrum due to hyperfine interaction between an electron in the hydrogen-related dangling bond and a hydrogen nucleus (proton) being located nearby the dangling bond is computer-simulated. Further, matrix ENDOR spectra have been computer-simulated on the basis of the dipolar interaction between an electron in the normal dangling bond and hydrogen nuclei being located around it, in which several hydrogen atoms being separated from the dangling bond are taken into account. We have obtained a semi-quantitative agreement between the Fehr ENDOR spectrum and the computer-simulated ENDOR spectra. A quantitative comparison between the experiment and the calculation is a future problem, taking into account the amorphous silicon network and the ENDOR intensity calculated from the transition probability of the matrix ENDOR and the distribution of hydrogen around a dangling bond, i.e., a normal dangling bond or a hydrogen-related dangling bond.

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