

Electron Spin Resonance of Free Radicals Produced by Gamma Irradiation of Various Substances at 4.2°K*

HARVEY N. REXROAD† AND WALTER GORDY

Department of Physics, Duke University, Durham, North Carolina

(Received July 6, 1961)

Hydrogen atoms and other free radicals have been produced by gamma irradiation of a number of substances at 4.2°K. Electron spin resonance was employed for detection and study of the free radicals within the solids at this temperature. It was found that strong electron spin resonance signals of H atoms could then be produced by dosages of 10^6 r or less in H_2O , HF, H_2 , and CH_4 , but no H atom signals could thus be produced in HCl, H_2S , NH_3 , NaH, or LiH. The spacing of the hyperfine doublet was approximately 504 gauss for the H signals observed. An anomaly in the relative intensities of the H doublet for irradiated H_2O was detected and attributed to spin-spin interaction with a second free radical. It is concluded that in HF and H_2O the H atoms are formed from electron capture by the essentially ionic hydrogens rather than by removal of an electron from the molecule (ionization). Because this process does not require displacement of the atoms from their original sites in the lattice, it can take place in hard-frozen, rigid solids. In H_2 , CH_4 , and similar substances the production of H atoms requires the breaking of covalent bonds. This process, although initiated by ionization, appears to require also the displacement of the H from its original site in the lattice.

INTRODUCTION

THE electron spin resonance of atomic hydrogen produced by irradiation was first detected at liquid air temperature by Livingston, Zeldes and Taylor.¹ The spacing of the hyperfine doublet for the Paschen-Back case was found to be 504 gauss, very close to that for the free hydrogen atom in the gaseous state. The solid state perturbations of the doublet spacing were found to be less than one percent. Thus electron spin resonance provides a means for identification and study of hydrogen atoms trapped, or produced, within various solids.

The original detection of the hydrogen atom by Livingston, Zeldes, and Taylor was found only in certain strong acids, and this observation was not followed by detection of hydrogen atoms in various other solids at this temperature. It now appears that the choice of the strong acids was a fortunate one. Negative results on a number of hydrogen compounds at 77°K in our laboratory suggest that hydrogen atoms are not produced by ionizing irradiation of most substances containing hydrogen or that they cannot be trapped and detected in most solids at 77°K.

The production of the free radicals which are observed when certain amino acids such as glycylglycine, certain proteins such as silk and certain synthetic polymers such as polyethylene are irradiated at room temperature, seems to require the breaking of the C—H bond and the consequent loss of hydrogen from the parent molecule. Although no hydrogen atoms are detected by electron spin resonance study of these substances, it is reasonable to suppose that such atoms, if produced by the irradiation, might escape too rapidly for detection

through the lattice at room temperature, and perhaps even at the temperature of liquid air. Partly for these reasons we have designed a system for the production of atomic hydrogen and other free radicals at low temperatures by gamma irradiation of substances directly within the microwave cavity used for observation of the electron spin resonance of the free radicals at the low temperature.

EXPERIMENTAL PROCEDURE

The substance to be irradiated is placed, or trapped, directly on the metallic walls of the microwave resonant cavity which is inserted in the cryostat and cooled to liquid helium temperatures. The portion of the cryostat containing the cavity is then inserted within a kilocurie cobalt 60 gamma-ray source. Dosages of the order of 10^6 r are then given by irradiation directly through the walls of the liquid helium flask and the microwave cavity. No detectable signals were thus produced in the metallic walls of the cavity; and since no other container was used for the sample, detectable free radicals were produced only in the sample under irradiation. After irradiation the cryostat was removed from the irradiation source and immediately placed between the poles of the electromagnet of the electron spin resonance spectrometer.

All the electron spin resonances were observed at the frequency of 25 kMc/sec. The rectangular waveguide cavity which resonates at this frequency is sufficiently small to fit easily within the cylindrical tip of a liquid helium flask of such size that it could be conveniently inserted within the cobalt source and between the poles of our electromagnet. The microwave cavity was of the reflection type, connected to the microwave source and to the microwave detector through a common waveguide, a section of which was made of stainless steel to reduce heat conduction. The usual "magic tee" was employed for separation of the input and output power from the cavity.

* This work was supported by the Air Force Office of Scientific Research.

† Now at the Department of Physics, West Virginia University, Morgantown, West Virginia.

¹ R. Livingston, H. Zeldes, and E. H. Taylor, Phys. Rev. **94**, 725 (1954).

When the sample to be observed was a solid at room temperature, it was placed in the cavity, and the cavity and connecting waveguide were thoroughly pumped before the system was cooled. When the sample was gaseous at room temperature, the cavity and waveguide were thoroughly evacuated before the gaseous substance was admitted, trapped, and frozen into the cavity.

The cryostat was so designed that a single filling with liquid helium would suffice for several hours. Thus after irradiation of the sample for 2 to 3 hr, observation on the resulting free radicals could be made for 3 to 4 hr.

The electron spin resonance spectrometer is the usual one employing magnetic modulation of the resonance at an audio frequency with a phase-sensitive, lock-in detector tuned to the second harmonic of the modulation frequency. For a line shape $S(H)$ and a modulation amplitude A , this type of detection records the Fourier coefficient of $\cos(2\omega t)$ in the expansion of $S(H+A\sin\omega t)$, which is equivalent to the second derivative of the resonance curve when A is small. For the usual absorption curve with a gaussian shape, one thus obtains a symmetrical signal with a maximum at the peak of absorption and with minima at the half-power points on either side of the absorption curve. With a cavity of the reflector type employing a magic-tee bridge it is difficult to observe a pure absorption curve without distortion effects of the anomalous dispersion which arises from an imbalance in the microwave bridge. Some of our signals show such distortions. Magnetic field measurements were made with a proton resonance probe.

H₂O AND D₂O

Radiation effects on H₂O are of considerable interest partly because of the presence of high concentrations of water in all forms of life. The first study of radiation effects on H₂O with electron spin resonance was made by Matheson and Smaller.² They observed a doublet with a spacing of only 40 gauss which they explained as possibly arising from H atoms greatly perturbed by the solid medium. After the detection of electron spin resonance of H atoms by Livingston, Zeldes, and Taylor,¹ it was evident that the effects of internal fields of solids on the H doublet are much less drastic, and are, in fact, generally much less than one percent. The doublet found by Matheson and Smaller is now thought to arise from OH radicals.³ So far as we know, H atoms have not yet been detected in ice irradiated at 77°K. However, observations of the electron spin resonance of H atoms produced by bombardment of ice at 4.2°K with high-energy electrons⁴ and with gamma rays⁵ have recently been reported.

² M. S. Matheson and B. Smaller, *J. Chem. Phys.* **23**, 521 (1955).
³ J. A. McMillan, M. S. Matheson, and B. Smaller, *J. Chem. Phys.* **33**, 609 (1960).

⁴ L. H. Piette, R. C. Rempel, and H. E. Weaver, *J. Chem. Phys.* **30**, 1623 (1959).

⁵ S. Siegel, J. M. Flournoy, and L. H. Baum, *J. Chem. Phys.* **34**, 1782 (1961).

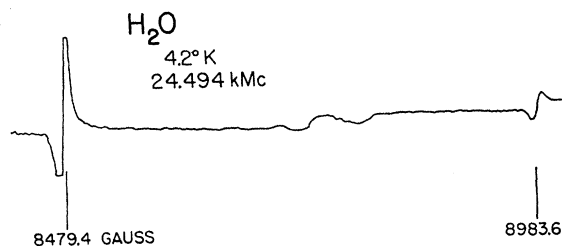


Fig. 1. Electron spin resonance of gamma-irradiated H₂O at 4.2°K. The outer components separated by 504 gauss arise from H atoms. The broad central doublet of about 40 gauss spacing probably arises from OH radicals. The signals are distorted by the modulation and represent a mixture of first and second derivatives of the actual resonance contour.

We have examined⁶ the electron spin resonance at 24 kMc/sec of H atoms in gamma-irradiated H₂O at 4.2°K. The doublet spacing which we observed, 504 gauss, agrees satisfactorily with that found by others.^{4,5} We, however, observed an anomaly in the relative intensities of the lines which they did not report. We observed the lower field component to be several times the strength of the upper field component. This anomaly is illustrated in Fig. 1. Interestingly, it is not observed for the D lines of D₂O but is observed for the H lines in the D₂O mixture. See Fig. 2.

Under normal circumstances the two components of the H doublet are, of course, expected to be of equal intensity within the accuracy of observation. The slight difference in intensity caused by the small difference in population of the upper and the lower spin state, $+\frac{1}{2}$ and $-\frac{1}{2}$, of the proton at thermal equilibrium would not be detectable under the conditions of our experiment. If the large difference observed in intensities should be ascribed to difference in the population of the two nuclear orientation states, an absurdly large nuclear polarization would be required. The most reasonable explanation, we think, is a more rapid electronic spin relaxation of the lower frequency component. If T_h represents the electronic spin lattice relaxation time of the higher field component and T_l that of the lower, then we must assume that T_h is greater by a factor of 10 or more than is T_l . We must also assume that to observe the intensity difference we were operating under conditions of power saturation, i.e., the rate of absorption of energy by the electronic spin system was limited by the rate of dissipation of the power of the spin system. The phenomena were evident at all power levels which we employed, always, however, above 1 μ w. Siegel, Floumoy, and Baum⁶ observed power saturation of the H lines in gamma-irradiated H₂O at 4.2°K down to 0.1 μ w, the lowest power level available in their experiments. Surprisingly, however, they did not observe the intensity anomaly, a fact which we think is due to the frequency which they employed, 9.5 kMc/sec, as contrasted with 25 kMc/sec

⁶ H. N. Rexroad and W. Gordy, *Bull. Am. Phys. Soc.* **6**, 257 (1961).

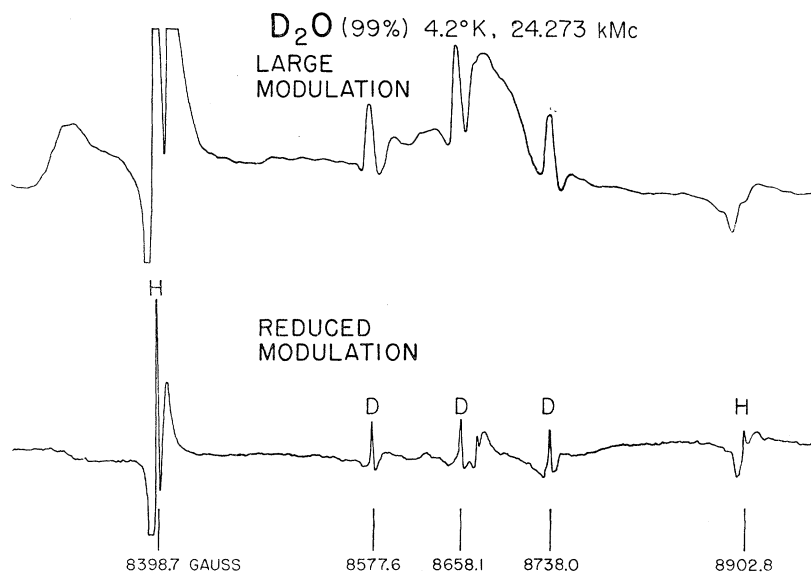


FIG. 2. Electron spin resonances of gamma-irradiated D_2O (with an H_2O or HOD impurity) at $4.2^\circ K$. The components marked with D arise from deuterium atoms; those marked with H, from H atoms. The signals are approximately second derivatives of the actual resonance curves.

in our experiments. This dependence of the anomaly upon frequency will be evident from the discussion to follow.

The mechanism which we propose for decreasing T_1 is a resonant spin-spin interaction similar to that treated by Abragam and Proctor⁷ for nuclear resonances and by Feher and Gere⁸ for electronic resonance interaction of Fe and P centers in silicon semiconductor doped with Fe and P. To account for the anomaly by this mechanism we postulate that a second free radical produced by irradiation of the H_2O at $4.2^\circ K$ has a g factor sufficiently greater than that of the essentially free spin value of the H atom that its resonance overlaps the lower field component ($M_I = +\frac{1}{2}$) at the field value (9 kilogauss) required for resonance at 25 kMc/sec, but not at the fields required for an observation at 9.3 kMc/sec. Furthermore, we must assume that the second free radical is formed sufficiently near the H atoms that the electronic spin-spin interaction with the hydrogen is able to execute the transfer of the energy and that the secondary free radical has a significantly shorter T_1 (a more rapid spin lattice relaxation) than that of the H atom.

After detecting this anomaly we made observations with large modulation amplitudes, which favor detection of broad lines, and thereby were able to detect a broad absorption in the vicinity of the $M_I = +\frac{1}{2}$ hydrogen line. The peak of this broad resonance is at a slightly lower field than is the $M_I = +\frac{1}{2}$ of hydrogen, although the broad resonance evidently overlaps the hydrogen resonance. See Fig. 2. If the displacement of this broad resonance from the center of the hydrogen doublet arises from its having a g factor greater than that of the free electron spin, at 9.5 kMc/sec its peak would occur between the H lines only about $\frac{1}{3}$ as far

from their center as at 25 kMc/sec. Such a broad resonance is evident at this position in the curve observed at 9.3 kMc/sec for irradiated H_2O at $4.2^\circ K$ by Piette, Rempel and Weaver.⁴

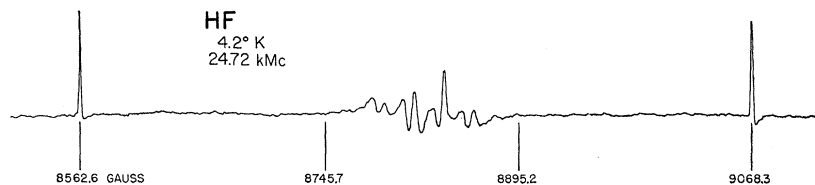
It is interesting to speculate on the nature of the secondary free radical whose resonance overlaps the $M_I = +\frac{1}{2}$ line of hydrogen at 25 kMc/sec. A similar one must be formed from D_2O since the same anomaly is observed for an H_2O impurity in D_2O . Furthermore, it must require for its formation a cluster of water molecules. Recent experiments in this laboratory (R. G. Patten and W. Gordy, to be published) show that for dilute solutions of H_2O in DNA or RNA the H lines produced from the H_2O have equal intensity. In a study of an irradiated single crystal of ice at $77^\circ K$, McMillan, Matheson, and Smaller³ reported the OH radical and a second unidentified free radical having a rather large anisotropy in g with $g_{\parallel} = 2.00$ and $g_{\perp} = 2.04$, which they suggest might be $(H_2O)^+$. The g value necessary for such a resonance to coincide with the lower H line is 2.06, and the broad peak which we observed at fields lower than the $M_I = +\frac{1}{2}$ hydrogen line at 25 kMc/sec corresponds to $g = 2.07$ approximately. It is interesting, however, that this radical causes no anomaly in the relative intensities of the D lines in D_2O , since its g factor would probably spread over the region from 2.00 to 2.07. Probably it and the OD resonance are broad enough to overlap all three D components and thus provide an equally rapid relaxation process for them. The OH resonance for which McMillan, Matheson, and Smaller report the values $g = 2.0127$, $g = 2.0077$, and $A = 41.3$ gauss, would not overlap the H lines at either 25 kMc/sec or at 9.3 kMc/sec. Also the quadrupole moment of the D nucleus provides another indirect relaxation process for the electronic spin of trapped D atoms.

Strangely, in the experiments on D_2O rated to have

⁷ A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1957).

⁸ G. Feher and E. A. Gere, Phys. Rev. **114**, 1245 (1959).

FIG. 3. Electron spin resonance (approximately second derivative) for gamma-irradiated HF at 4.2°K. The outer components arise from H atoms; the central absorption, possibly from F_2^- or F_3^- .



better than 99% deuterium concentration, we observed the lower H line to be stronger than the D lines, and the higher H line to be comparable in strength to the D lines. When placing the D_2O sample in the cavity we took reasonable care to prevent H and D exchange. Two different commercial samples of D_2O were used. Both gave similar results. These preliminary results on D_2O suggest that H is more readily formed by irradiation of the mixed isotropic sample than is D. The implication is that excitons produced by irradiation move about in the sample so that the particular bonds broken depend more on their ease of rupture than on their concentration in the sample. However, no such anomaly was reported by Seigel, Flournoy, and Baum⁵ for a mixed sample containing 20% H_2O . Additional experiments which we plan to make are needed before one can be sure of the suggested interpretation given here.

The hydrogen lines in the D_2O matrix are about three times sharper than those in the H_2O matrix. Since the nuclear dipole moment of H is 3.2 times that of D, this result indicates that the predominant broadening process of the H lines in the H_2O is the interaction of neighboring nuclear dipoles with the electron spin. However, the sharp H lines, also the sharp D lines, in the D_2O matrix are superimposed upon broader ones. This indicates that the atoms giving rise to the resonances in the D_2O matrix do not all have the same environment. Some are perhaps trapped near other free radicals which cause abnormal broadening of the lines. The line-broadening process in these systems is complicated and arises from diverse sources. In this work, we shall not attempt a quantitative treatment.

In the D_2O curve there is a small, sharp peak at a g factor essentially that for the free electron spin. We do not know the origin of this peak; perhaps it arises from an unknown impurity.

H_2S

No signals from H atoms were detected for H_2S irradiated with the same dosage at 4.2°K and observed under the same conditions as those for the H_2O and D_2O . Only a broad, unresolved, asymmetric signal with a g factor extending over the region from 2.00 to 2.06 was detected. We suspect that this arises from a free radical in which the electron spin density is concentrated on an S atom such as SH or H_2S^- . The contrast of H_2O with H_2S in the formation of H atoms will be discussed later.

HF AND HCl

Strong signals of hydrogen atoms were observed for HF irradiated at 4.2°K with gamma ray dosages of 10^6 r. We were unable to detect signals of H atoms from HCl irradiated with the same dosages and observed under the same conditions. Figure 3 shows the resonance for HF. In addition to the signals of the H atoms, there is a complex pattern near the center, probably arising from free radicals of the form $(FF)^-$ or $(F_3)^-$. A comparable resonance is observed for HCl, but with no signals from H atoms.

Table I provides a comparison of the doublet spacing of H atoms in the different substances we studied. The spacing of the H doublet in HF is 506 gauss. Although the line width cannot be measured accurately with our method of detection, it is apparent that the lines of the H atom in irradiated HF are sharp, of the order of 2 gauss half-width. The g factors of Table I were calculated from the observed line positions with the Breit-Rabi formula.

H_2 AND CH_4

The electron spin resonance of hydrogen atoms and CH_3 radicals produced by gamma-irradiation of CH_4 at low temperatures has been detected previously.⁹ Electron bombardment has been used to produce detectable atomic H resonance signals in solid H_2 at 4.2°K. Our results on these two substances agree with those of the earlier workers. From the relative intensities of their components, the H and the CH_3 radicals appear to be produced in equal amounts from CH_4 , as they should be. See Fig. 4. Interestingly, the atomic hydrogen lines, and also the CH_3 lines of irradiated methane at 4.2°K are broad, about 16 gauss, whereas the H lines of irradiated H_2 are sharp, of the order of a gauss in width. Since dipolar broadening by inter-

TABLE I. Hydrogen lines at 4.2°K.

Matrix substance	g factor	Doublet spacing (gauss)	Line breadths ^a (gauss)
CH_4	2.002	504	16
H_2O	2.0025	504	12
D_2O	2.0030	504	4
HF	2.0018	506	2.5
H_2	2.0020	504	~1

^a Approximate widths between half-power points.

⁹ L. A. Wall, D. W. Brown, and Roland E. Florin, Faraday Soc. Informal Discussion on Free Radical Stabilization (Sheffield, England) 18 (1958) (unpublished).

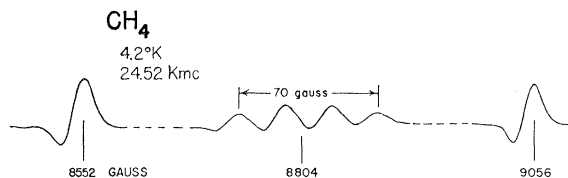


FIG. 4. Electron spin resonance (approximately second derivative) of gamma-irradiated CH_4 . Outer components arise from H atoms; central quartet, from CH_3 radicals. *Note added in proof.* The number 24.52 kmc should read 24.685 kmc.

action of the H atoms with nearby H nuclei should in a completely rigid medium be even greater in H_2 than in CH_4 , it seems reasonable to postulate that these interactions are largely averaged out by rapid tunneling or other motions in the H_2 matrix, which do not occur in the CH_4 matrix. The lines in γ -irradiated CH_4 may have significant broadening caused by mutual interactions of the free radicals which are probably trapped near each other when they are produced by direct irradiation of solid CH_4 at 4.2°K . It is interesting that H and CH_3 radicals produced in gases and trapped in a CH_4 matrix at 4.2°K are reported by Jen *et al.*¹⁰ to have line breadths of only 4.7 and 4.5 gauss, respectively.

NaH AND LiH

No signals of hydrogen atoms could be detected for either LiH or NaH after irradiation with 10^6 r at 4.2°K . For both, a fairly broad resonance with apparently unresolvable structure was observed in the region of $g=2.0$. For NaH there was an additional strong, sharp resonance with $g=2.005$ and with half-widths of the order of a gauss or less. A similarly sharp resonance was obtained for both LiH and NaH with irradiation and observation of the samples at room temperature. In addition, for NaH we observed a wide spectrum with many broad but resolved components, similar to that recently reported by Doyle and Williams.¹¹ They also observed the sharp resonance, which they attributed to colloidal particles of metallic sodium. The wide spectrum is an F -center resonance¹¹ with a 19-line, Na hyperfine structure, as expected for the deBoer model.

The sharp resonance which we observed for gamma-irradiated LiH at room temperature was observed earlier by Doyle, Ingram, and Smith¹² for uv-irradiated LiH. They attributed the resonance to colloidal particles of lithium produced by the irradiation. Interestingly, our results do not show the sharp resonance when the sample is gamma-irradiated at 4.2°K . A reasonable explanation is that the colloidal particles are not formed by irradiation at 4.2°K because of the inability of the H atoms to escape and of the Li atoms to move together

at this low temperature. Probably the colloidal particles which give the sharp resonance in NaH irradiated at 4.2°K are already present in the commercial samples, as suggested by Doyle and Williams.¹¹

OTHER SUBSTANCES

We have irradiated and observed polyethylene at 4.2°K under conditions similar to those employed for CH_4 and H_2 . No H lines were detected, only a broad, central resonance with $g=2.00$. Other polymers such as polyglycine and the nucleic acids DNA and RNA, which have been investigated with similar procedures by Raymond A. Patten in this laboratory, showed no atomic hydrogen lines after gamma-ray dosages comparable to those employed here. Likewise, no atomic hydrogen lines were found by Walter Boulden in similarly treated NH_3 .

MECHANISM FOR H PRODUCTION IN SOLIDS AT LOW TEMPERATURES

Comparisons of the results here suggest possible mechanisms for the production of H atoms by irradiation of substances at low temperatures. To us, it seems particularly significant that we get H atoms from H_2O but not from H_2S , from HF but not from HCl. Because of their large dipole moments and the possibility of hydrogen bonding, we can safely assume that a rigid matrix is formed by each of these substances at 4.2°K . There is no significant displacement of the atoms by the 1.3-Mev γ rays. Thus it seems that we must seek an explanation which does not require displacement of the H atom completely away from its parent molecule nor from its original site in the lattice.

A striking correlation here is that the atoms from which the H atom is released, F and O, are first-row elements, whereas those from which it is not released are second-row elements. The properties of the corresponding first- and second-row elements differ principally in size, electronegativity, and type of orbitals. The greater size of the second-row elements, it seems to us, should rather contribute to the ease of breaking off the H. The differences in H production must therefore arise primarily from the other two properties, i.e., from the significantly greater electronegativity of the first-row elements and from the available d orbitals in the valence shell of the second row elements, as we shall explain.

We propose a mechanism for production of H atoms from HF and H_2O which does not require the displacement of H atoms, but only of electrons. The ionic character-electronegativity rule,¹³

$$\text{i.c.} = (x_1 - x_2)/2,$$

where x_1 and x_2 are the electronegativities of the bonded atoms, $x_{\text{F}}=3.9$ and $x_{\text{H}}=2.1$, indicates that HF is very nearly ionic. For simplicity, we assume the rigid solid

¹⁰ C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, *Phys. Rev.* **112**, 1169 (1958).

¹¹ W. T. Doyle and W. L. Williams, *Phys. Rev. Letters* **6**, 537 (1961).

¹² W. T. Doyle, D. J. E. Ingram, and M. J. A. Smith, *Phys. Rev. Letters* **2**, 497 (1959).

¹³ W. Gordy, *J. Chem. Phys.* **19**, 792 (1951).

to be completely ionic. In this ionic molecule any electron removed by the irradiation must be from the F^- . If impurities are neglected, it seems reasonable that the electrons would be captured by the H^+ ions rather than by the F^- ions provided that they are removed by Compton recoil too far to be recaptured by the original F. Thus the H atoms are formed by addition of an electron to an H^+ ion which is already surrounded by and trapped by closed-shell F^- ions. The F atom formed in the process would be expected to interact with the adjacent F^- ion to form a complex^{13,14} $(F-F)^-$, found for LiF, or perhaps higher complexes such as $(F_3)^{--}$. Because of their difference in electronegativity there would be no comparable exchange interaction between H and F.

A similar mechanism to that proposed for HF would also apply to H_2O , although the difference in electronegativity of H and O is somewhat less, 1.4, and the number of hydrogens per molecule is twice as great. We assume that the oxygens are already approximately negative and hence have a closed shell and that the H^+ and OH radicals are produced at the original site of the ionization, or alternately perhaps H_2O^+ or $(H_2OOH_2)^+$. The recoiling electron is captured by the *almost* positively charged hydrogen of the water molecule rather than by the *almost* negatively charged oxygen. Thus H atoms and free O-H groups are formed at the site of capture of the electron. The negative charge of the O-H would be shared by the H of the group and by the other hydrogens and oxygens of the surrounding water molecules to which it would form a hydrogen-bonded complex. There would be no significant electron exchange between the hydrogen atom and the O-H because of the large difference in electronegativity of the H and O. Evidently the bonded H atoms of the H_2O molecules are sufficiently shielded by the oxygen from the free H atoms that there is no strong interaction with them. This mechanism would account for the formation of H atoms and OH free radicals but not for the third radical which seems required for explanation of the anomalous intensities of the H doublets. This third radical must be formed at the site of the original ionization and could be an H_2O^+ or an $(H_2OOH_2)^+$ radical.

When HCl is ionized by irradiation, an H^+ ion and a Cl atom should be formed just as an H^+ ion and an F atom are formed from HF. The Cl would then form $(Cl-Cl)^-$ complexes analogous to $(F-F)^-$ complexes such as are found in irradiated alkali chlorides.^{14,15} The

recoiling electron, however, is not captured by H^+ ions to form H atoms, as in HF, but is captured in the d orbital of the Cl, probably forming $(H-Cl)^-$ or an hydrogen-bonded complex involving this species.

The removal of an electron from H_2S might leave simply $(H_2S)^+$, or possibly H^+ and SH free radicals. However, the capture of a recoiling electron by H_2S in the rigid lattice would not likely produce H atoms, as is thought to occur for HF and H_2O , but would rather produce H_2S^- with the odd electron residing mainly on the d orbital of the S.

This mechanism which we have proposed for HF and H_2O (the capture of recoiling electrons by H^+ ions) obviously cannot apply to the formation of H atoms in H_2 and CH_4 , in which the bonding is mainly covalent. The formation of H atoms from them would require the breaking of a covalent bond. It seems reasonable to postulate that the complete breaking of such covalent bonds to form free H atoms depends upon the ability of the H atoms to move away from their particular site in the lattice. Otherwise the spin density of the H atoms may be shared with the atoms originally bonded covalently to the H. Between these small, nonpolar molecules, however, the intermolecular interactions are weak, and atomic motions through barrier tunneling probably occur even at 4.2°K. This would not be true of polymers like polyethylene and polyglycine which give no hydrogen lines when irradiated at 4.2°K, although there is strong indirect evidence for the formation of H atoms through the breaking of C-H bonds when they are irradiated at room temperature.

From the evidence accumulated we conclude that in substances having H^+ ions or essentially ionically bonded hydrogens, the H atoms are formed without the necessity of atomic displacement simply by capture of recoiling electrons by H^+ ions. In substances having only essentially covalently bonded hydrogens, the production of H atoms requires atomic displacement in addition to ionizing radiation. Thus in substances with only covalently bonded hydrogens the formation of H atoms seems probable only if the structure is sufficiently loose at the temperature of the irradiation for escape of the H atoms from their original sites in the lattice. This requirement is satisfied for H_2 and CH_4 at 4.2°K, but not likely for polyethylene or polyglycine. Atoms having an electronegativity of about 3 (N and Cl) when bonded to hydrogen (electronegativity 2.1) have roughly 55% covalent character and 45% ionic character. Such bonds are probably near the border line but in HCl or NH_3 do not appear to have sufficient ionic character to lead to the formation of H atoms by the first process.

¹⁴ W. Kanzig, Phys. Rev. **99**, 1890 (1955).

¹⁵ T. E. Castner and W. Kanzig, J. Phys. Chem. Solids **3**, 178 (1957).