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Electron-Electron Double Resonance Investigations of Irradiated Organic Crystals: The Influence of Deuterium Substitution*

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Abstract

Electron-electron double resonance (ELDOR) investigations of irradiated organic crystals have shown promising uses of deuterium substitution in the ELDOR identification of magnetically different radicals associated with a poorly resolved ESR spectrum. Replacement of the water of crystallization in potassium acetate crystals with deuterium oxide has removed the proton spin-flip lines in the ELDOR spectrum of the methyl radical and has permitted fewer ELDOR combination lines from magnetically different radicals to be observed at 77°K. A study of the hydrogen-deuterium exchange reactions in irradiated glycine-d_3 and ℓ-alanine crystals has shown the absence of ELDOR lines at the deuteron hyperfine frequency a_D and the absence of hydrogen-deuterium combination lines, but the presence of an intense line at the proton hyperfine splitting frequency. In addition a significant decrease in the intermolecular cross exchange near room temperature permitted a separation of the proton ELDOR spectra for each hydrogen-deuterium exchange reaction making it possible to identify the different simultaneously occurring reactions.

Introduction

During the past several years a number of radiation damage studies have been carried out on irradiated single organic crystals using ESR techniques.(1) These studies have shown that several radical species (i.e., negatively and positively charged primaries) are formed in the radiation damage process at temperatures at or below 77°K.(1) As the temperature is raised, a variety of additional radicals are formed by the decay of these primaries. Thus, several radicals are usually present at a given temperature. Although the ESR technique has proven valuable in identifying the radicals belonging to a radiation decay process, these studies have been hampered by poor resolution, resulting from the simultaneous overlap of ESR spectra from several radicals. Several methods have been used to increase the spectral resolution. These include; *annealing* which is useful only when the radical under investigation is stable at the annealing temperature; isotopic *substitution*, useful when either the synthetic preparation is practical or when the starting isotopic compound is not too prohibitively expensive; *microwave saturation*, useful when one radical saturates with more difficulty than the others.

In addition two double resonance techniques (ENDOR[2] and ELDOR)[3] have also been used and appear to be generally applicable to resolution enhancement problems. ENDOR investigations have been particularly valuable in resolving the small hyperfine splittings which appear as a single unresolved broad ESR line in single crystal studies.[4] These studies have led to the identification of the radicals involved. On the other hand, the ELDOR technique has been used[3] to separate the ESR lines of one crystal site of $\cdot CH_2COOH$ from that of another in irradiated malonic acid and provided the evidence for the presence of a stereo-selective radiation damage process.

Even though these double resonance approaches have been successful, rather specific relaxation conditions must exist in order to observe a double resonance spectrum. In fact, certain ENDOR investigations of irradiated crystals have failed to result in any ENDOR spectra.(5) ELDOR investigations can only be used to separate overlapping ESR spectra when the intra-molecular relaxation conditions are predominant at the investigated temperature.[3] Recent investigations[3] have shown that this condition can be present near room temperature in irradiated crystals. Furthermore, ELDOR investigations near room temperatures also show[6-10] that the substituents attached to the radicals influence the relaxation conditions to such a degree that characteristic ELDOR spectra are observed for each class of radicals. In fact, so characteristic are these ELDOR spectra that the ESR line assignments can be deduced from the type of ELDOR spectrum obtained.

However, at temperatures lower than 50°K, it has been shown[11] that intermolecular cross relaxation rates (spectral diffusion rates) are in general greater than spin-lattice relaxation rates and thus it is impossible to saturate one line of a spectrum without partially saturating the others. Thus ELDOR spectra obtained under these conditions would contain lines from all radicals, and an assignment of the individual ESR lines to the correct radical species using ELDOR data is not usually possible.

Nevertheless, we wish to report the results of some ELDOR experiments which suggest that the intermolecular relaxation conditions at 77°K can be altered by deuterium substitution sufficiently to facilitate the assignment of ESR lines in certain irradiated crystals. The effect of deuterium substitution on relaxation conditions will be examined in the case where matrix protons (which give rise to spin-flip lines)[12] have been replaced by deuterium nuclei in the case where protons which give rise to small unresolvable ESR hyperfine splittings (< 5 gauss) have been replaced with deuterium, and in the case where the alpha hydrogen has been replaced by deuterium.

Experimental

Single crystals of potassium acetate were grown by slow evaporation in two different solvents: D_2O and concentrated acetic acid. The crystals were irradiated at 77°K with 40kv X-rays and were investigated without warming to higher temperature. Single crystals of glycine were grown from D_2O and irradiated at 77°K. ELDOR investigations were carried out at several temperatures. The ELDOR spectra were run on a standard Varian E-800 ELDOR accessory coupled to a Varian E-12 ESR spectrometer. All spectra were taken with the power of the observing klystron set to less than one-half the power required for maximum ESR signal. Full microwave power of the pumping klystron equal to 336 mw at the input flange to the cavity and 100KHz field modulation were used throughout the study. The liquid nitrogen dewar used restricted the maximum ELDOR frequency to 170MHz.

Results

Deuterium Substitution: Replacement of Water of Crystallization with D_2O

The ESR spectrum of irradiated potassium acetate at 77°K which was grown in concentrated acetic acid is given in figure 1. The predominant lines of 1:3:3:1 intensity have been shown to be due to the methyl radical. The additional lines of somewhat reduced intensity are due to $\dot{C}H_2COOH$ and other radical fragments. The ELDOR spectrum observed with the magnetic field positioned at the center of the high field ESR absorption line (i.e., at cross-over position of the first derivative high field ($m_I = -3/2$) line) is given in figure 1. Notable is the intense first derivative line at 64MHz, the hyperfine splitting of the methyl radical. Flanking this line are two satellite lines at 50 and 78 MHz usually referred to as spin-flip lines[12]. These lines arise when a neighboring proton nuclear spin attached to a diamagnetic molecule flips simultaneously with the electron spin. The spin-flip lines are observed to saturate with more difficulty than the main ESR line[12], however posses saturation properties related to that of the main ESR line. For instance, if the main ESR line saturates with ease, then less microwave power will be required to saturate the spin-flip lines than when the main line saturates with difficulty. In fact, in those cases where other radical ESR spectra do not overlap the spin-flip lines, an ELDOR experiment can be carried out with the observing field positioned at a spin-flip line. The ELDOR spectrum to a large degree will appear similar to that obtained with the observing magnetic field positioned at the main ESR line. This suggests that a cross relaxation mechanism[16] plays a predominant role in the transfer of saturation from the main ESR line to the spin-flip line or alternatively from the spin-flip line to the ESR line. It is also noted in figure 1 that the distorted line shape of the spin-flip line at 50MHz is a result of the spin-flip line overlapping with the radical line at A.

Another ELDOR line was found to appear at 128MHz corresponding to a line at twice the hyperfine splitting of the methyl radical. Satellite lines were also observed at 142 and 114 MHz. No other lines were observed.

On the other hand, ELDOR investigations of the methyl radical in irradiated potassium acetate grown from D_2O (KAC. $2D_2O$) gave somewhat different results. The ESR spectrum of irradiated KAC• $2D_2O$ given in figure 2 shows the lines of several radicals in addition to those of the methyl radical. The relative concentration of methyl radicals to that of $\dot{C}H_2\acute{C}OOH$ or other radicals has been shown to be dependent on the cation and the waters of crystallization present(13). Nevertheless, ELDOR investigations carried out for the high field ($m_I = -3/2$) ESR line of the methyl radical show predominant lines at υ_H, $a_H^{me} = 64$MHz, 2 $a_H^{me} = 128$MHz and a smaller forbidden line at 25MHz. No lines from the chemically different radicals are observed. It was noted that the relative ELDOR signal intensity has decreased by a factor of 2 over that of the undeuterated lattice. More important is the lack of proton spin-flip lines. This increase in resolution permits a more precise measurement of the hyperfine splitting constant due to the lack of interfering lines from overlapped spectra. When the observing field was set at the $m_I = -1/2$ (second high field line) ESR line, a similar ESR spectrum appeared with the added ELDOR lines from radical B. ELDOR lines from radical B were also observed in the case of irradiated potassium acetate trihydrate suggesting that a significant cross-relaxation exists between radical B and the methyl radical.

Deuterium as a Substituent: Unresolved Proton Hyperfine Splittings

To further determine the role that deuterium substitution may play in the ELDOR investigations of radiation processes, the $NH_3^+CH_2\dot{C}OO^-$ radical in irradiated glycine was selected for study because the ESR spectrum showed the presence of unresolved proton splittings due to a rotating NH_3^+ group. In addition these same hydrogens could be exchanged with deuterium.

The ESR spectrum of the $NH_3^+CH_2\dot{C}OO^-$ radical in irradiated glycine appears as a broad doublet at 77°K(14) due to the overlap of an approximately equal nitrogen and amine proton splittings with that of a 25 gauss methylene proton doublet split by a 3 gauss doublet from the second methylene proton. It has been also suggested(14) that this doublet overlaps the spectrum of the $NH_3^+\dot{C}H_2$ radical at 77°K.

The ELDOR spectrum of this doublet given in Fig. 3 is composed of an intense line at the proton Zeeman frequency (presumably due in part to the spin-flip transitions) and two forbidden transitions at 30 and 47 MHz which appear to be due to the doublet ESR splitting from $NH_3^+CH_2\dot{C}OO^-$. The ELDOR lines at 30 and 47 MHz could also be the forbidden lines of $NH_3^+\dot{C}H_2$.

Upon deuteration the broad doublet ESR spectrum narrows as a result of the amine protons being replaced by deuterium. Surprisingly no ELDOR lines are observed at 14, 30 or 47 MHz although the doublet splittings from the methylene protons are still observed in the ESR spectrum. A rather large build-up of ELDOR intensity is observed below 14MHz possibly due to the deuterium splittings. The absence of ELDOR spectral lines may be due to the lack of proton spin-flip lines coupled with the change in the rotational correlation time of the NH_3^+ group.

Deuterium as a Substituent: Resolved Proton Hyperfine Splittings

The ESR spectrum of glycine single crystals irradiated at 77°K and warmed to room temperature is a superposition of an intense ESR spectrum of the $NH_3^+\dot{C}HCOO^-$ radical and a weaker set of lines due to the $\dot{C}H_2COO^-$ radical. Along the c axis, the hyperfine splitting of the three equivalent amine protons equals 50MHz while the alpha proton splitting equals 80MHz.

From these observations, it might be presumed that the $ND_3^+\dot{C}HCOO^-$ and $\dot{C}H_2COO^-$ radicals would be observed in irradiated crystals of glycine grown from deuterium oxide where the amine protons have been exchanged with deuterium. However, Gautney and Miyagawa(15) have found considerable evidence that several complex hydrogen-deuterium exchange reactions take place. The ESR spectrum of irradiated glycine-d_3 crystals mounted with the magnetic field near the c axis is given in figure 4. The ELDOR spectrum taken with the magnetic field positioned at any one of the ESR lines indicated by the arrows resulted in a narrow ELDOR line at the proton nuclear Zeeman frequency and another broaden line corresponding to the amine proton splitting. The absence of an ELDOR line at 80MHz (the hyperfine splitting of the alpha proton in this direction) and analysis of the ESR spectrum, indicates that the spectrum is that of $ND_2H^+\dot{C}DCOO^-$ resulting from a hydrogen-deuterium exchange reaction with $ND_3{}^+\dot{C}HCOO^-$. Notable is the lack of any resolvable deuterium combination lines at 48MHz. The broad (9MHz width) ELDOR line at 48MHz may be a result of small combination lines with the ^{14}N nuclues. This suggestion is supported by ELDOR studies of irradiated ^{15}N-substituted glycine-d_3 which showed a narrowing (line width 6MHz) of this line.

Upon raising the temperature to 100°C for several hours, the ELDOR line at 48MHz decreased with time and eventually disappeared. The resulting ESR pattern appeared to be that of the $ND_3{}^+\dot{C}DCOO^-$ radical. A search for ELDOR lines at the deuterium hyperfine frequency failed and thus they are presumed to be weak.

The lack of deuterium ELDOR lines in the presence of proton splittings appears to be quite general. Attempts at observing the deuterium-proton ELDOR combination lines or deuterium ELDOR lines at a_D for radicals formed in the deuterium-hydrogen exchange reaction ($CDH_2\dot{C}HCOOD$) previously reported(17) for irradiated L-alanine crystals have also failed. The deuterium hyperfine splittings ($\sim$12MHz) for the $CH_2D\dot{C}HCOOD$ is similar to those found in the $NHD_2^+\dot{C}DCOO^-$ radical. Since several instrument problems have prevented the best signal to noise ratio from being obtained, we can only conclude that ELDOR lines at a_D = 12MHz are weak (<5% of the ESR signal height) under the very best of instrumental conditions.

The ELDOR spectrum at the proton hyperfine splitting frequency for the $CH_3\dot{C}HCOOD$ radical at 30°C taken along the c crystal axis was shown to be a combination of 2 lines; an enhanced ELDOR line due to the methyl group protons and a reduced line due to the alpha proton. Since the hyperfine splittings of the two types of protons are nearly equal, a complex ELDOR line is observed as a function of the observing magnetic field. However, an ELDOR spectrum taken with the magnetic field positioned at the bottom of the first derivative ESR line for the partially hydrogen-deuterium exchange radical, still shows an enhanced line as well as a reduced line. This highly suggests that the partially deuterated radical is not purely $CH_3\dot{C}DCOOD$ where only an enhanced line should have been observed, but more likely $CH_2D\dot{C}HCOOD$ or a mixture of $CH_2D\dot{C}HCOOD$ and $CH_3CD\dot{C}OOD$. This substaniates the earlier findings of Miyagawa and his co-workers(17). It is interesting to note the ability of deuterium to first substitute for a proton in the methyl group.

Discussion:

Intermolecular cross-relaxation processes have been shown to be a dominant mode of relaxation at low temperature(11) (77°K or lower) and are therefore assumed to be the dominant relaxation mechanism in this study. In addition, intramolecular motion exhibited by substituents of radicals has been shown(11) to increase the transfer of spins via intermolecular cross-relaxation routes (spin diffusion). Because of this, the methyl radical which is known to undergo rotation (even possibly precession) about its 3-fold axis gives rise to an intense ELDOR spectrum at 77°K. ELDOR lines from magnetically different radicals were also observed in the irradiated hydrated acetate crystals. The observation of an ELDOR line for radical B and not for line A_2 of radical $A(CH_2COO^-)$ when the observing magnetic field was positioned at $m_I = -1/2$, suggests that not only the magnitude of the cross relaxation process but also the relaxation properties of the individual radicals play a role in the observation of ELDOR lines. The g value of radical B (2.012) differs considerably from that of radical A (2.003_4) in this crystal direction. It has been shown(11) that the ratio of the relaxation times of the two radicals will depend upon the ratio of the squares of the g anisotropy of the two radicals. Assuming that radical B has a larger g anisotropy that A (based only on the magnitude of the g values in this direction) would explain the apparent difference. On the other hand, the g anisotropy for the $\dot{C}H_2COO^-$ and $\dot{C}H_3$ radicals is quite similar and therefore the difference in relaxation times depends on the motion undergone by the methyl radical and not by $\dot{C}H_2COO^-$.

The only ELDOR lines attributed to radical A, appeared as a distorted spin-flip line (See figure 1). However, this same line was absent in the deuterated crystal lattice. In addition, a number of lines from other radicals was observed in the ESR spectrum, yet only an ELDOR line from radical B was observed. The absence of these additional spectral lines, (except for radical B) as well as the decrease in the methyl radical ELDOR signal height could in part be due to the lack of proton spin-flip lines. A reason for this is as follows: It has been observed experimentally that saturation is efficiently transferred from the main ESR line to the proton spin-flip line(6). Since these spin-flip lines are located ± 14 MHz from the main observing ESR line, overlap of the spin-flip line (line width ~7MHz) with an adjacent radical ESR line can be substantial, providing a direct path for transfer of saturation between radicals. A similar transfer of saturation was shown to occur for the overlap of the ^{7}Li double frequency NMR line and the ^{19}F line at low magnetic fields(18). On the other hand, deuterium spin-flip lines are located only ± 2 MHz from the main line, resulting in a large decrease in the spectral overlap and a like-wise decrease in cross relaxation between magnetically different radicals. Thus if this cross-relaxation mechanism was dominant then the above spectral absence would be expected. The decrease in the ELDOR signal height must then also reflect a decrease in the spin diffusion between radicals which are magneticaly alike.

The absence of the forbidden ELDOR spectral lines of $ND_3^+CH_2\dot{C}OO^-$ could be due to a reduction in the intermolecular cross relaxation upon deuteration. However more likely, the replacement of the amine hydrogens for deuteriums are the subsequent narrowing of the ESR lines preventing an efficient modulation of the spectral diffusion by the reorientation of the NH_3^+ group.

The reduction of intermolecular cross-relaxation upon deuteration as a significant relaxation mechanism apparently is observed near room temperature. For it was observed to be absent in the ELDOR study of the H-D exchange reactions of $CH_3\dot{C}HCOOD$ to $CH_2D\dot{C}HCOOD$ above 240°K in irradiated l-alanine(17) crystals grown from D_2O. This is to be contrasted to irradiated malonic acid crystals grown from water where measureable cross relaxation was observed(3) above 300°K between two crystals sites of $\dot{C}H_2COOH$.

Replacement of the alpha proton for a deuterium may not only affect the cross relaxation mechanism but may also affect the intramolecular relaxation mechanism.

If an END mechanism(19) is dominant for the proton under study, then upon deuteration the intensity of the deuterium ELDOR lines should decrease by the ratio $\gamma^2_D/\gamma^2_H = 1/42$. This appears to be the explanation for at least two cases, those being the lack of deuterium lines at a_D for $ND_2H^+\dot{C}DCOO^-$ in irradiated glycine-d_3 and for $CH_2\dot{D}CHCOOD$ in irradiated l-alanine grown in D_2O.

The appearance of a sharp ELDOR line at a_H for $ND_2H^+\dot{C}DCOO^-$ (there being no observed combination lines with deuterium) probably reflects the difference in the T_1's for proton and deuterium. A smaller T_1 would be expected for the deuterium nuclei, resulting in only ELDOR lines at a_H, no proton-deuterium combination lines being possible. A similar difference in T_1's occurred for the protons and nitrogens in DPPH $^{(20)}$.

Summary:

In many instances, proton spin-flip lines will be observed as satellite lines of the allowed-allowed ELDOR lines for radicals found in irradiated organic crystals. These satellite lines can overlap with other ELDOR lines and thus decrease the ELDOR resolution. However a significant increase in ELDOR resolution can be obtained for those radicals where the matrix protons responsible for the spin-flip lines can be exchanged with deuterons.

ELDOR spectra obtained from radicals in which a deuteron has been substituted for either an alpha or beta proton, consists of a line at the proton hyperfine frequency, and the absence of a line at the deuteron hyperfine frequency or lines at various combination of deuteron-proton hyperfine frequencies. By observing the change in the intensity of the proton ELDOR lines along with the change in the ESR spectrum as a function of time permits the identity of the radicals produced in proton-deuteron exchange reactions.

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Caption

Figure 1.

The ESR spectrum observed (upper spectrum) for an irradiated crystal of potassium acetate grown in a concentrated acetic acid solution. The ESR spectrum consists of a four line pattern of 1:3:3:1 intensity ratio due to the methyl radical, a set of lines A_1, A_2, A_3 belonging to the $\dot{C}H_2COO^-$ radical and a broad line B denoting an unidentified radical. The ELDOR spectrum (lower spectrum) taken with the observing field positioned at the field given by the arrow consists of a line at a_H = 64MHz, two spin-flip lines at 50 and 78MHz. ELDOR lines at $2a_H$ and $2a_H \pm 14$MHz were also observed but are not shown.

Figure 2.

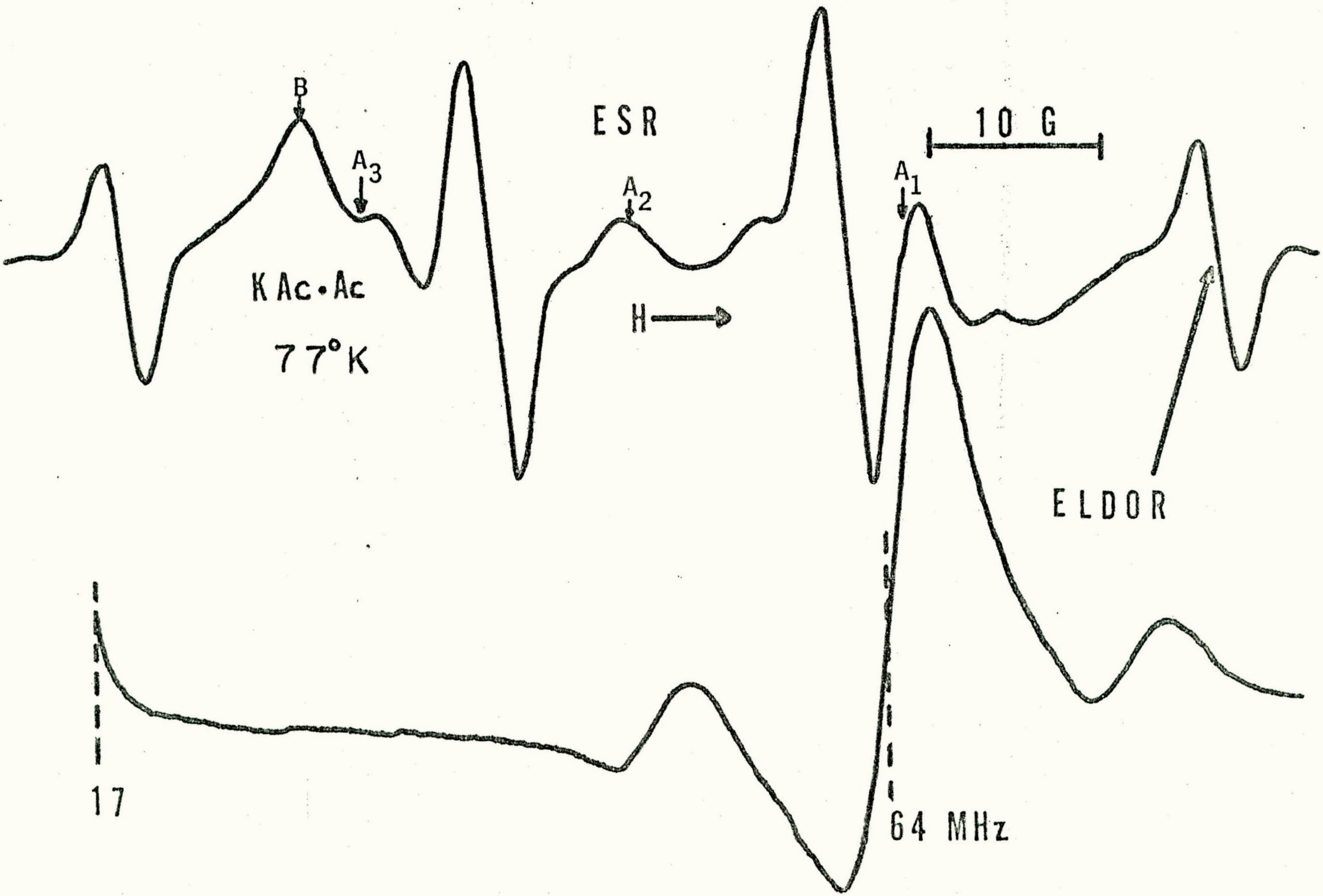
The ESR spectrum (upper portion) observed for irradiated crystals of potassium acetate grown in deuterium oxide. The spectrum of the methyl radical (denoted by dashed lines) is overlapped with the ESR spectrum of the unidentified radical B, the spectrum of $\dot{C}H_2COO^-$ and an intense central line. The ELDOR spectrum (lower portion) with the observed field set at the position of the arrow consists of a single methyl radical line at $a_H = 64$MHz and at $2a_H = 128$MHz and the absence of any spin-flip lines.

Figure 3:

The ELDOR spectra observed for the broadened ESR doublet of the $NH_3^+CH_2\dot{C}OO^-$ radical (lower spectrum H) and the narrowed ESR doublet of $ND_3^+CH_2\dot{C}OO^-$ (upper spectrum D). The first derivative ELDOR line at 14MHz in spectrum H is attributed to the proton NMR Zeeman frequency while the lines at 30 and 47 MHz are attributed to the forbidden ELDOR lines of the ESR doublet.

Figure 4:

The ESR and ELDOR spectra taken at 40°C along c//H for an irradiated single crystal of glycine-d_3 ($ND_3^+CH_2COO^-$), the arrows point to observing ESR positions at which the ELDOR spectrum was obtained. Notably a well resolved ELDOR spectrum is obtained with lines at 14.3MHz and 47.5MHz attributed to a proton spin-flip transition and the proton line from $ND_2H^+\dot{C}DCOO^-$. No combination lines with deuterium are observed.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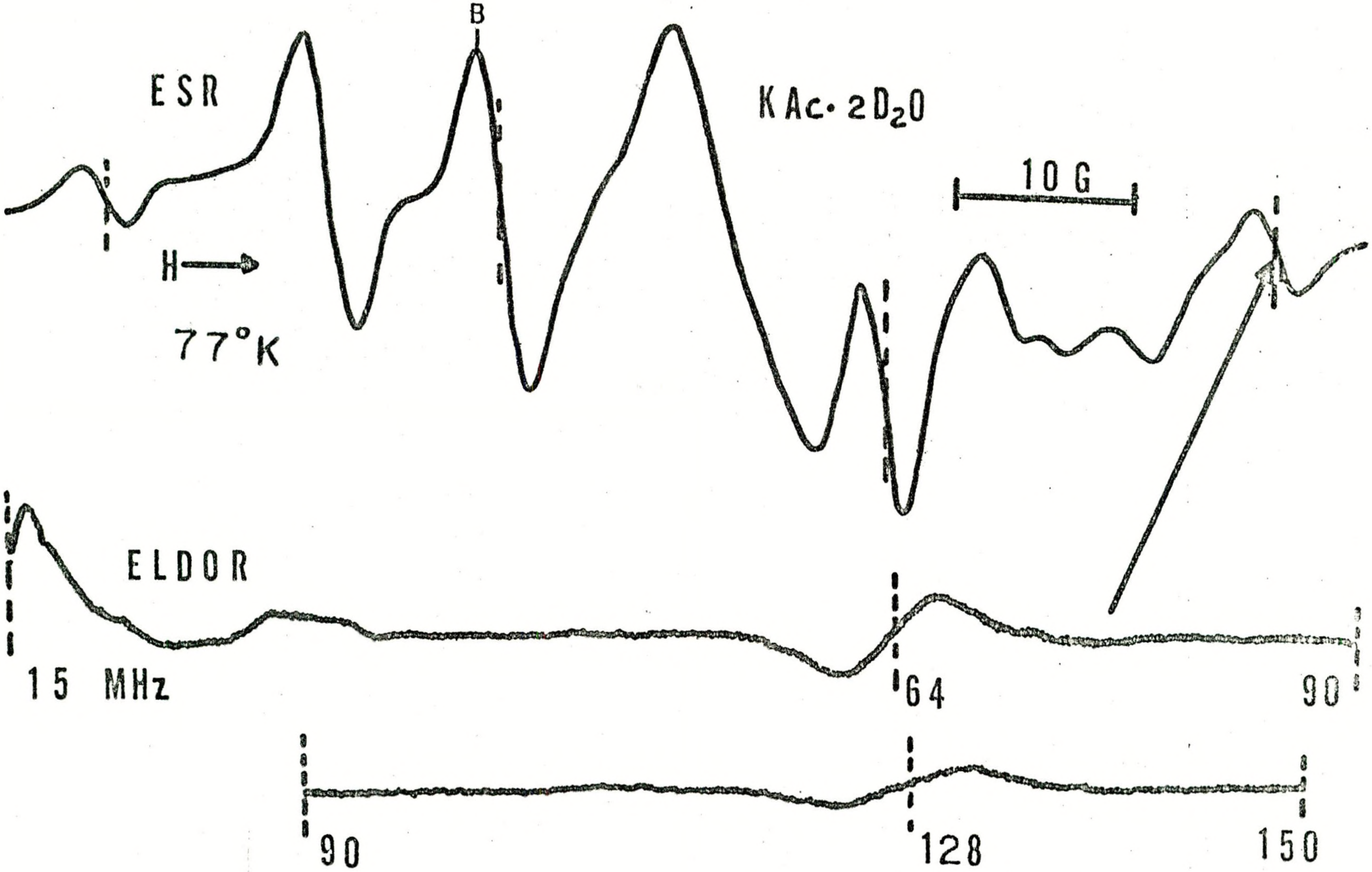
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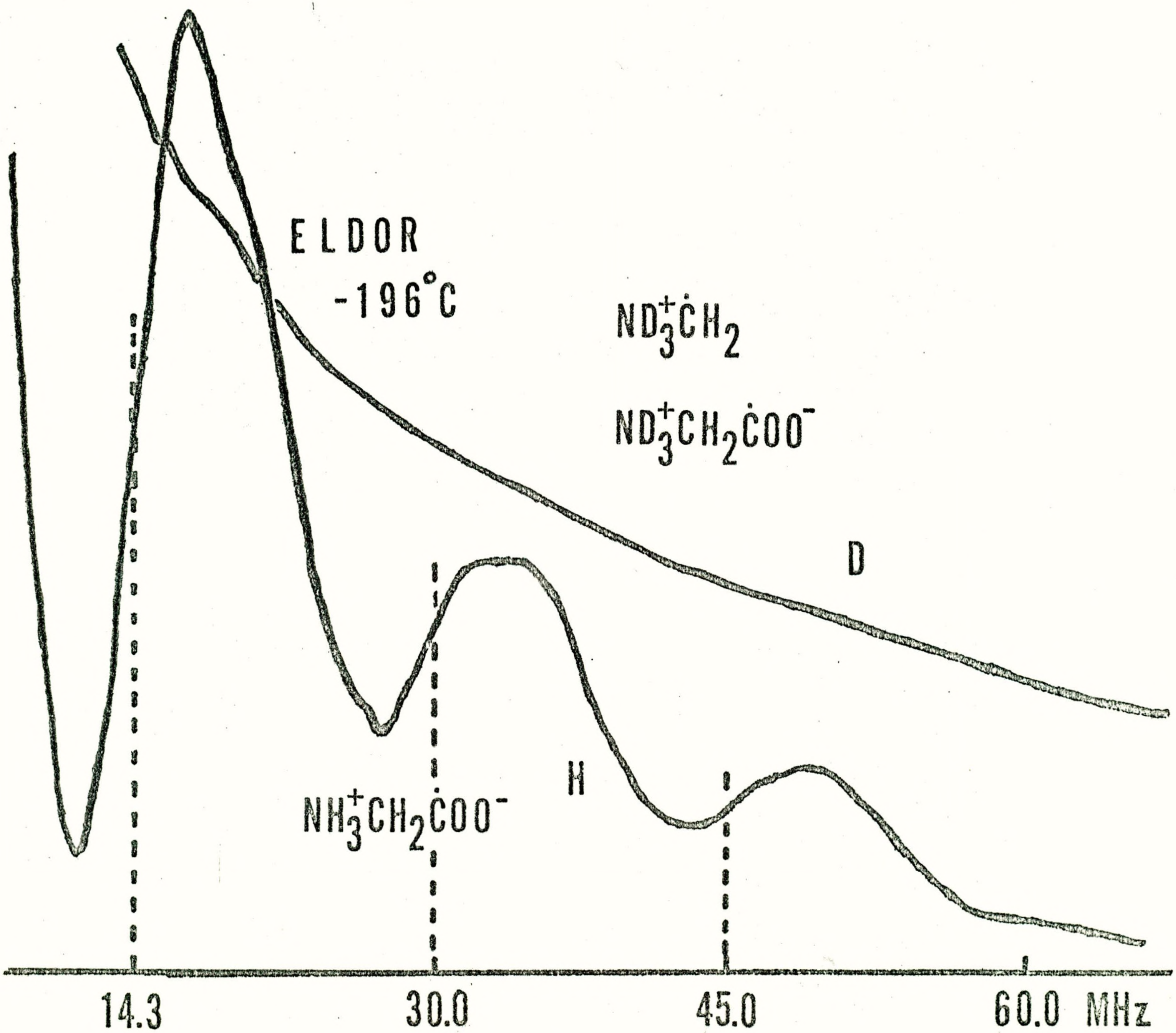
ELDOR
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$ND_3^+CH_2\dot{C}OO^-$
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H
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30.0
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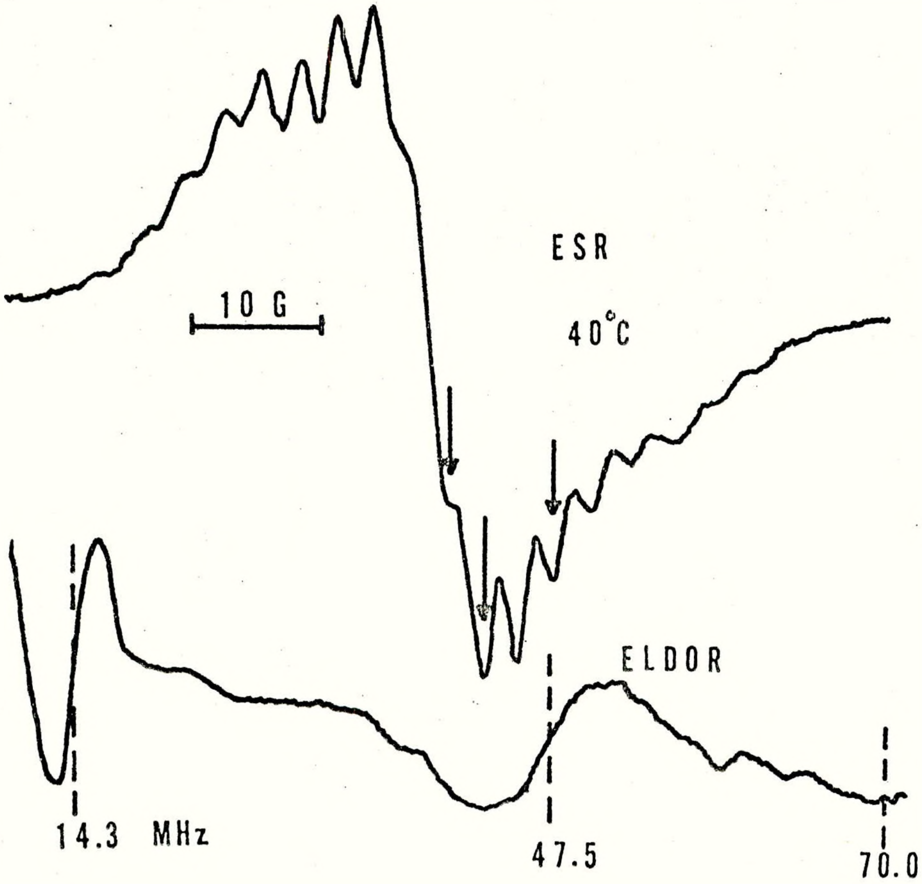
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ELDOR
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70.0