

## Electron Spin Resonance of an Irradiated Single Crystal of N-Carbamyl Glycine

D. V. G. L. Narasimha Rao and Mikio Katayama

Citation: *The Journal of Chemical Physics* **37**, 382 (1962); doi: 10.1063/1.1701330

View online: <http://dx.doi.org/10.1063/1.1701330>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/37/2?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[Electron Spin Resonance of Irradiated Single Crystals of Succinamide](#)

*J. Chem. Phys.* **44**, 2823 (1966); 10.1063/1.1727134

[Electron Spin Resonance of a  \$\gamma\$ -Irradiated Single Crystal of N-Acetyl Methionine](#)

*J. Chem. Phys.* **37**, 13 (1962); 10.1063/1.1732935

[Electron Spin Resonance of an Irradiated Single Crystal of N-Acetylglycine](#)

*J. Chem. Phys.* **33**, 1599 (1960); 10.1063/1.1731468

[Single Crystal Electron Spin Resonance Spectra for x-Irradiated Glycine](#)

*J. Chem. Phys.* **31**, 859 (1959); 10.1063/1.1730491

[Electron Spin Resonance in an Irradiated Single Crystal of Dimethylglyoxime](#)

*J. Chem. Phys.* **30**, 1590 (1959); 10.1063/1.1730244

---



**NEW Special Topic Sections**

**NOW ONLINE**  
Lithium Niobate Properties and Applications:  
Reviews of Emerging Trends

**AIP** | Applied Physics  
Reviews

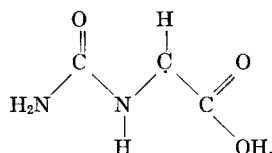
# Electron Spin Resonance of an Irradiated Single Crystal of *N*-Carbamyl Glycine\*

D. V. G. L. NARASIMHA RAO† AND MIKIO KATAYAMA‡

Department of Physics, Duke University, Durham, North Carolina

(Received March 15, 1962)

The electron spin resonance spectra of  $\gamma$ -irradiated single crystals of *N*-carbamyl glycine have been measured at 9 and 23 kMc/sec for various orientations of crystals in the external magnetic field. From the analysis of the hyperfine-interaction constants the free radical produced by  $\gamma$  irradiation is found to be



The spin density at the carbon atom is 75% and the free radical is similar to that produced from acetyl-glycine and glycylglycine.

A DETAILED study of the electron spin resonance (ESR) spectra of irradiated single crystals of acetylalanine<sup>1</sup> and glycylglycine<sup>2</sup> has been made in this laboratory. The free radical was shown to be of the form  $\text{XCHCOOH}$  with the unpaired electron mostly localized on the carbon atom. An additional free radical of this type has now been found from analysis of the

source for about 24 h. The ESR spectra of the irradiated crystals were measured at 9 and 23 kMc/sec for different orientations in the external magnetic field  $H$  at room temperature. Details of the experimental procedure have been given in a previous communication.<sup>4</sup>

As the planes  $\{001\}$  and  $\{110\}$  are easily identified, the two reference axes  $b$  and  $c$  are necessarily deter-

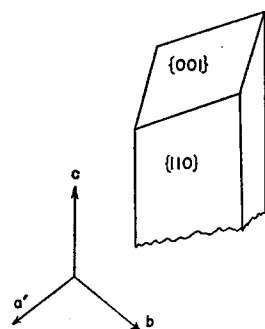


FIG. 1. Crystal form and coordinate-axes system employed.

ESR spectra of  $\gamma$ -irradiated single crystals of the peptide *N*-carbamyl glycine (hydantoic acid) and its deuterated derivative.

Single crystals of *N*-carbamyl glycine



were grown by slow evaporation of an aqueous solution. According to Groth<sup>3</sup> the crystal possesses monoclinic symmetry with  $a:b:c=0.662:1:1.535$  and with  $\beta=99^\circ$ .

The crystals were irradiated in a cobalt-60  $\gamma$ -ray

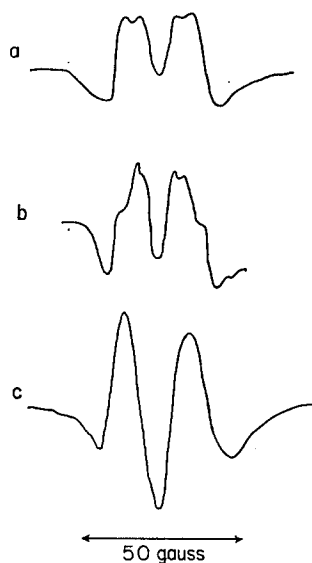


FIG. 2. ESR spectra (second derivatives of actual resonance absorption) of an irradiated single crystal of *N*-carbamyl glycine at 9 kMc/sec. (a)  $H$  parallel to  $c$  axis. (b)  $H$  perpendicular to  $b$  axis and making  $45^\circ$  with  $c$  axis. (c)  $H$  parallel to  $a'$  axis.

\* This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research, Air Research and Development Command.

† Present address: Physics Department, Andhra University, Waltair, India.

‡ On leave from the University of Electro-Communication, Tokyo, Japan.

<sup>1</sup> I. Miyagawa, Y. Kurita, and W. Gordy, J. Chem. Phys. **33**, 1599 (1960).

<sup>2</sup> M. Katayama and W. Gordy, J. Chem. Phys. **35**, 117 (1961).

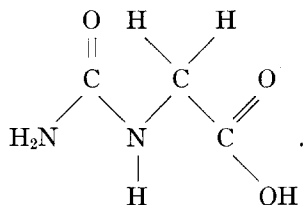
<sup>3</sup> P. Groth, Chem. Kryst., **3**, 552 (1900).

mined. The  $a'$  axis is chosen perpendicular to both the  $b$  and  $c$  axes. The reference coordinates are shown in Fig. 1. Figure 2 shows the ESR patterns for different orientations of the crystal about the  $b$  axis with the  $b$  axis perpendicular to the external magnetic field. When the magnetic field is parallel to the  $c$  axis the pattern consists of a doublet of 20-G spacing which has an apparent doublet substructure of 5 G. Upon the

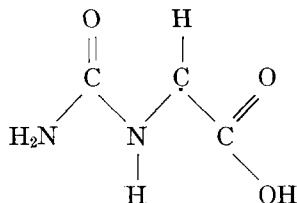
<sup>4</sup> D. V. G. L. Narasimha Rao and W. Gordy, J. Chem. Phys. **35**, 362 (1961).

slight rotation of the crystal from  $c$  about the  $b$  axis, a triplet substructure becomes apparent [see Fig. 2(b)]. The splittings between the component lines of the triplet is small but is noticeably anisotropic. The apparent doublet substructure for some orientations must arise from an incompletely resolved triplet substructure distorted by the modulation method used in detection. Katayama and Gordy<sup>2</sup> have shown in the ESR analysis of irradiated glycylglycine that an incompletely resolved  $N^{14}$  substructure can appear as a doublet when second-derivative phase-sensitive detection is used. Figure 2(c) shows the spectrum when  $H$  is parallel to the  $a'$  axis. For this orientation the triplet substructure, which we assume to arise from  $N^{14}$ , is completely unresolved, and we observe only a doublet of about 24-G splitting, which we believe to arise from a single proton. The ESR patterns were essentially the same at 9 and at 23 kMc/sec, and the splittings are equal at the two frequencies.

The chemical formula of the undamaged molecule is



From consideration of the similarity of this molecule to glycylglycine and the similarity of ESR patterns of the two molecules when irradiated, a free radical of the form



is produced by the loss of an H atom from the carbon indicated by the dot. Additional confirmation of the suggested model has been obtained from measurements on a deuterated crystal. The spectra were found to be essentially the same as those for the normal sample for corresponding orientations in the external magnetic field. This comparison shows that the proton of the

TABLE I. Principal elements for nuclear hyperfine constants for proton and direction cosine.

Principal values	Observed direction cosine				
	Observed	Semi-empirical	$a'$	$b$	$c$
$A_x^H$	26.0 G	-29 G	$\pm 0.91$	$\mp 0.05$	$\mp 0.37$
$A_y^H$	22	-20	$\mp 0.06$	$\pm 0.97$	$\mp 0.10$
$A_z^H$	10	-7	$\pm 0.40$	$\pm 0.15$	$\pm 0.90$

TABLE II. Principal elements of nuclear coupling for  $N^{14}$  and their direction cosines.

Principal elements		Direction cosine		
	Observed	$a'$	$b$	$c$
$A_x^N$	3 G	$\pm 0.7$	$\mp 0.3$	$\mp 0.6$
$A_y^H$	4	$\mp 0.3$	$\mp 0.94$	$\pm 0.2$
$A_z^H$	2	$\pm 0.7$	0.0	$\pm 0.7$

OH group does not have observable coupling with the electron spin.

The spin Hamiltonian for the free radical can be expressed with sufficient accuracy for our purpose as

$$\begin{aligned} \mathcal{H} = & \beta H_Z (g_{ZZ} S_Z + g_{ZX} S_X + g_{ZY} S_Y) \\ & + (A_{ZZ}^H I_Z^H + A_{ZX}^H I_X^H + A_{ZY}^H I_Y^H) S_Z \\ & + (A_{ZZ}^N I_Z^N + A_{ZX}^N I_X^N + A_{ZY}^N I_Y^N) S_Z, \end{aligned}$$

where  $X$ ,  $Y$ , and  $Z$  represent the space-fixed axes with the applied field  $H$  chosen along  $Z$ . The  $g$ 's are the significant elements of the spectroscopic splitting factor. They are almost isotropic in our free radical. The values are  $2.0033 \pm 0.0004$ . The  $A^H$ 's and  $I^H$ 's represent the elements of the nuclear-coupling tensor and the components of the nuclear-spin vector of the CH hydrogen nucleus. The  $A^N$ 's and  $I^N$ 's represent the corresponding quantities for the N of the NH group. The nuclear paramagnetic term  $g_I \beta_I I_Z H_Z$  is neglected because the forbidden transitions<sup>5</sup> were not of observable intensity. These transitions were probably obscured by the incompletely resolved  $N^{14}$  splitting. The equation and the methods used for obtaining the principal elements of the  $A$  tensor have been outlined by Katayama and Gordy.<sup>2</sup> For brevity they will not be given here.

The principal elements of the CH proton coupling and their direction cosines with respect to the  $a'bc$  coordinates are shown in Table I. Since all the principal elements have the same sign, the isotropic term  $A_f = (A_x + A_y + A_z)/3$  is 19 G in magnitude. From it the spin density on the CH carbon atom is estimated as 0.75 from the equation<sup>6</sup>  $\rho_c = A_f/Q$ , where  $Q = 25$  G. Both  $Q$  and  $A_f$  are known to be negative in sign. From a proportional reduction of the principal values calculated by McConnell and Strathdee<sup>7</sup> for the pure dipole-dipole coupling of a CH proton with an unpaired electron entirely in a  $p$  orbital of the C atom, we obtained the dipole-dipole couplings for  $\rho_c = 0.75$  as 11.7 G for the laboratory field along the CH bond, -1.3 G with  $H$  along the  $p_z$  orbital, and -10.4 G with the field perpendicular to both the  $p_z$  orbital and the CH

<sup>5</sup> I. Miyagawa and W. Gordy, J. Chem. Phys. **32**, 255 (1960); H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, J. Am. Chem. Soc. **82**, 766 (1960).

<sup>6</sup> H. M. McConnell, J. Chem. Phys. **24**, 764 (1956); S. I. Weissman, *ibid.* **25**, 890 (1956).

<sup>7</sup> H. M. McConnell and O. Strathdee, Mol. Phys. **2**, 129 (1959).

bond. Adding these values to the Fermi term  $A_f = -19$  G, we obtain the semitheoretical values  $-7.3$ ,  $-20.3$ , and  $-29.4$  G, respectively, for the principal elements listed in Table I. In magnitude, these values agree reasonably well with the observed principal values.

The principal elements and their direction cosines for the  $N^{14}$  couplings are listed in Table II. Because of the incomplete resolution of the  $N^{14}$  hyperfine structure, these elements are measured only approximately. The small  $N^{14}$  splitting might arise from three mechanisms which give rise to couplings of comparable magnitude. These are (1) direct dipole-dipole coupling between the  $N^{14}$  nuclear magnetic moment and the electron spin density on the CH carbon; (2) coupling caused by the negative spin density induced on  $N^{14}$  through the large spin density on the CH carbon to which the nitro-

gen is bonded (this negative spin density arises from a spin polarization of the NC bond through configuration interaction on the carbon); and (3) coupling of positive electron spin density on the  $N^{14}$  resulting from  $\pi$  bonding by the odd electron. Attempts were made by Katayama and Gordy to estimate the  $N^{14}$  coupling expected from these three mechanisms in the similar free radical produced by irradiation of glycylglycine. The small inaccurate coupling elements obtained for  $N^{14}$  do not warrant the analysis here. They show, however, that the spin density on the  $N^{14}$  cannot be large and is probably less than 5%.

The authors are grateful to the U. S. Educational Foundation in India and Japan for awarding them Fulbright travel grants. We are deeply indebted to Professor Walter Gordy and Dr. Robert Lontz for valuable suggestions and discussions.

## Modification of the Rydberg-Klein-Rees Method for Obtaining Potential Curves for Doublet States Intermediate Between Hund's Cases (a) and (b)\*

JOSEPH T. VANDERSLICE

*Institute for Molecular Physics, University of Maryland, College Park, Maryland*

(Received March 16, 1962)

The Rydberg-Klein-Rees method for obtaining potential-energy curves from band-spectroscopic data has been modified in order to handle doublet electronic states intermediate between Hund's cases (a) and (b). In the derivation, the spin-orbit coupling constant has been taken to be independent of distance. The modified equations have been used to recalculate the curves for the  $X^2\Pi$  state of NO.

### INTRODUCTION

THE Rydberg-Klein-Rees (RKR) procedure is a semiclassical method which appears to yield reliable potential energy curves of diatomic systems from the measured vibrational and rotational energy levels of the molecule.<sup>1</sup> This method has been developed for cases where the effective potential energy can be written in the form  $V(r) + K/r^2$ , where  $V(r)$  is the potential energy for the nonrotating molecule and where  $K$  is not a function of  $r$ . Hence, the electronic states of molecules which are classified as either Hund's case (a) or (b),<sup>2</sup> i.e., where the centrifugal energy is written as

$$(h^2/8\pi\mu r^2) J(J+1)$$

or

$$(h^2/8\pi\mu r^2) N(N+1),$$

can be treated by this method. However, in cases where the spin-orbit coupling and the rotational energy are of the same order of magnitude, the case is intermediate between (a) and (b), and the effective potential energy is of more complicated form than that given above.<sup>3</sup> It is the purpose of this paper to suggest a modification of the RKR method which enables one to obtain reliable curves for the intermediate cases.

The standard RKR method has previously been applied to the  $^2\Pi$  ground state of NO<sup>4</sup> which is intermediate between cases (a) and (b). Although the  $^2\Pi_1$  and  $^2\Pi_2$  curves so calculated were sufficiently accurate for kinetic-theory application, they exhibited a crossing that was disturbing and which indicated that the method was not completely reliable. For many purposes, particularly for studying rotational predissociation due to curve crossing, much more accurate curves are required.<sup>5</sup> The modification of the RKR method suggested here has been used to recalculate the curves for these two states of NO with the result that the curves no longer cross.

<sup>3</sup> E. Hill and J. H. Van Vleck, *Phys. Rev.* **32**, 250 (1928).

<sup>4</sup> J. T. Vanderslice, E. A. Mason, and W. G. Maisch, *J. Chem. Phys.* **31**, 738 (1959); **33**, 614 (1960).

<sup>5</sup> R. S. Mulliken, *J. Chem. Phys.* **33**, 247 (1960).

\* This research has been supported in part by the Office of Naval Research.

<sup>1</sup> R. Rydberg, *Z. Physik* **73**, 376 (1931); **80**, 514 (1933); O. Klein, *ibid.* **76**, 226 (1932); A. L. G. Rees, *Proc. Phys. Soc. (London)* **59**, 998 (1947); J. T. Vanderslice, E. A. Mason, E. R. Lippincott, and W. G. Maisch, *J. Mol. Spectroscopy* **3**, 17 (1959); **5**, 83 (1960).

<sup>2</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), Chap. V.