

| | | | | | |
|-----------|----------|-------------------|-----------|----------|-------------------|
| 5428.3 Å. | 18,416.9 | cm. ⁻¹ | 5140.3 Å. | 19,448.7 | cm. ⁻¹ |
| 14.5 | 463.8 | } 46.9 | 28.1 | 495.0 | } 46.3 |
| 02.5 | 504.8 | | 16.2 | 540.3 | |

The mean separation between adjacent heads is thus about 45 cm.⁻¹ and the origin of the lower state may be estimated to lie at 48,520.5 - 45 = 48,475.5 cm.⁻¹ above $X^1\Sigma^+$. This estimate is in excellent agreement with the value of ν_{00} for $a^3\Pi - X^1\Sigma^+$ obtained from the rotational analysis⁶ of the Cameron bands, namely, 48,473.9, cm.⁻¹.

It seems, therefore, quite certain that the Herman bands form the $\nu' - 0$ progression in the transition $e^3\Sigma^- - a^3\Pi$. No doubt other bands of this system remain to be found at longer wave-lengths.

R. F. BARROW

Physical Chemistry Laboratory,
University of Oxford.

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Identification of the Radical $\cdot\text{CH}_2(\text{CO}_2\text{H})$

In recent years a number of free radicals trapped in irradiated solids have been identified from their electron-spin resonance spectra. In particular, radicals of the form $\text{XH}\ddot{\text{C}}\text{CO}_2\text{H}$ or $\text{XH}\ddot{\text{C}}\text{CO}_2^-$ are known with $X = \text{CH}_3$ (ref. 1), NH_3^+ (ref. 2), OH (ref. 3), CO_2H (ref. 4), Cl (Pooley, D., and Whiffen, D. H., unpublished work), $\text{CH}_2\text{CO}_2\text{H}$ (ref. 5), and $\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ (unpublished work by A. H., J. R. M. and D. H. W.). Hitherto, however, the parent radical $\cdot\text{CH}_2(\text{CO}_2\text{H})$ has remained unidentified. This radical has now been identified in γ -irradiated malonic acid, $\text{CH}_2(\text{CO}_2\text{H})_2$. McConnell *et al.*⁴ have fully investigated the radical $\dot{\text{C}}\text{H}(\text{CO}_2\text{H})_2$ which is also formed when malonic acid is γ -irradiated; they reported that lines not due to $\cdot\text{CH}(\text{CO}_2\text{H})_2$ appeared in the spectra of freshly irradiated crystals, and could be removed by heating the crystals to 50° C. for 24 hr.

A detailed study of the spectrum of irradiated malonic acid was undertaken using an electron resonance spectrometer operating at 9,000 Mc./s. A single crystal of malonic acid was γ -irradiated at liquid-nitrogen temperature. Its room-temperature spectrum indicated that at least three radicals were present. For a general orientation of the crystal with respect to the magnetic field, all three radicals have different g values, and each has a spectrum symmetrical about its own centre. If the hyperfine structure of the spectrum of each radical can be analysed, it is possible to identify the radical. For some crystal orientations, however, exact analysis is difficult because of overlapping of the spectra of different radicals. The spectrum of a freshly irradiated single crystal of malonic acid consisted of two exceedingly strong and narrow lines due⁴ to the radical $\cdot\text{CH}(\text{CO}_2\text{H})_2$. In addition, we observed four sharp lines of equal intensity approximately one-fifth as strong as the spectrum of $\cdot\text{CH}(\text{CO}_2\text{H})_2$. A third radical was also present, but its spectrum was still weaker and the radical has not yet been positively identified.

The spectrum of intermediate intensity indicates the presence of a radical in which there is hyperfine interaction with two hydrogen nuclei. This spectrum could be analysed for a sufficient number of orientations to obtain a complete coupling tensor for each hydrogen atom. However, the precision is less than that which would be attainable if this were the only radical present. The principal values of the coupling tensor of one hydrogen atom were -91, -56 and -30 Mc./s., and for the other -92, -59 and -37 Mc./s. These values are essentially those to be expected for a hydrogen atom attached directly to the free radical centre^{2,4,6}. They have therefore been given a negative sign, although this is not obtained directly from the spectra. The coupling tensors identify the radical as $\cdot\text{CH}_2(\text{CO}_2\text{H})$, since no other radical with two hydrogens on the free-radical carbon atom is anticipated from the irradiation of malonic acid. The slight differences between the two tensors are less than the probable experimental error (± 4 Mc./s.), although the two hydrogen atoms are not in crystallographically equivalent positions in the trapping site, and their coupling tensors need not, therefore, be absolutely identical. It appears that the methylene group ($-\dot{\text{C}}\text{H}_2$) in the radical is not rotating about the C—C bond, since free rotation would lead to a spectrum having three hyperfine lines with intensity ratios 1 : 2 : 1 for all crystal orientations.

It is expected^{2,6} that the least negative, intermediate, and most negative principal values of the coupling tensor will occur for directions parallel to the C—H bond, perpendicular to the plane of the radical, and in the plane of the radical but perpendicular to the C—H bond, respectively. The intermediate axes for both tensors therefore should be parallel to each other. This was found to be the case, the experimental value for the angle between the intermediate axes of the two tensors being 4° with an error of approximately 5°. The major and minor axes of each tensor should intersect at an angle equal to the HCH angle. This angle was calculated from the tensors to be $116 \pm 5^\circ$. In a planar radical, this angle would be 120° for strict sp^2 hybridization, although van der Waals repulsion between the hydrogen atoms and the carboxylic acid group might give rise to a slight reduction in this value.

The electron-resonance spectra of irradiated malonic acid thus support a planar structure for the substituted methyl radical, in agreement with previous work⁷ on the methyl radical itself.

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A. HORSFIELD
J. R. MORTON
D. H. WHIFFEN

Basic Physics Division,
National Physical Laboratory,
Teddington, Middlesex.

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