

## Second-order Effects Observed in the Electron Spin Resonance Spectra of Methyl Radicals Stabilised on Silica at 77 K

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**Summary** A marked dependence of e.s.r. spectral line width on surface coverage has been observed in methyl radicals stabilised on silica surfaces; at low surface coverage partial resolution of the second-order splitting is obtained, although the intensity of the lines appears not to agree with the theoretical 1:2 ratio; a computer simulation of this effect shows that the observed results are consistent with theory provided that both the line width and separation are considered.

ELECTRON SPIN RESONANCE linewidth studies of methyl radicals stabilised on silica surfaces have been reported.<sup>1-4</sup> We have found a marked dependence of the spectral linewidths on surface coverage (Table). This dependence has

TABLE. Linewidth<sup>a</sup> dependence on surface coverage observed at 77 K from silica gel samples pretreated at 1073 K

% Coverage	Linewidths/mT ( $\pm 0.02$ )				2nd order splitting/mT ( $\pm 0.02$ )
	Line 1	Line 3	Line 3'	Line 1'	
0.24	0.65	0.32	0.20	0.41	0.23
2.1	0.63	0.32	0.22	0.39	0.23
8.6	1.1	0.70	0.40	0.57	ca. 0.16
30	1.8	1.25	0.52	0.70	—

<sup>a</sup> Linewidths in this paper refer to the peak-to-peak width of the 1st derivative curve.

not been previously reported and was not anticipated at low coverages; however, the data suggest that dipolar broadening is significant at coverages greater than ca. 2%. Since the linewidth data reported to date will include a contribution from this effect, the conclusions of earlier studies are thus in need of review. In addition it has been found that by using low surface coverages ( $\leq 2\%$ ) of methyl iodide on silica surfaces it was possible to observe a partial resolution of the second-order splitting;<sup>5</sup> although this splitting has been observed previously,<sup>2</sup> it does not appear that the resulting distortion, caused by partial resolution, has been

allowed for in linewidth calculations. In view of the wide utility of such linewidth data it was desirable to undertake a careful study of the second-order spectrum of methyl radicals.

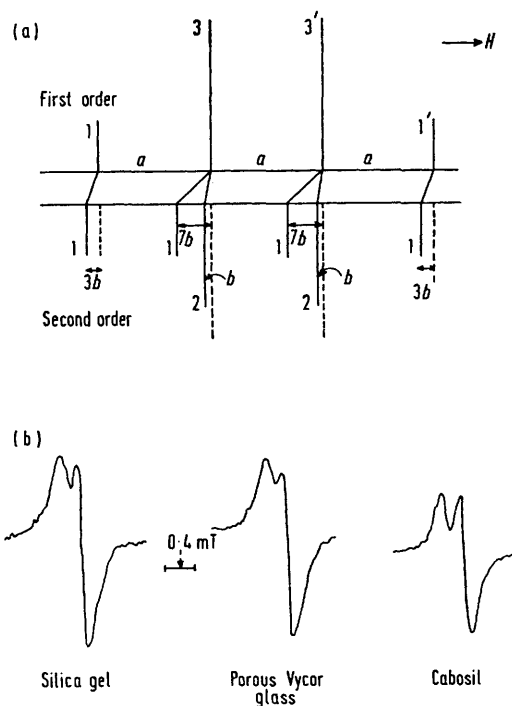


FIGURE 1. (a) Representation of the first- and second-order spectra of the methyl radical:  $b = a^2/4\nu_0$ , where  $\nu_0$  is the frequency at the centre of the first-order spectrum. (b) Second-order splittings observed for line 3' for various silica samples pretreated at 1073 K.

According to second-order theory<sup>5</sup> the central pair of lines will be split into two components with a separation of *ca.* 0.24 mT and an intensity ratio of 1:2 on increasing field (Figure 1a). From the spectra shown in Figure 1b it at first appears that although a splitting has occurred, the observed intensity is not 1:2. However, it may be shown that this anomaly is due to partial overlap of two lines.

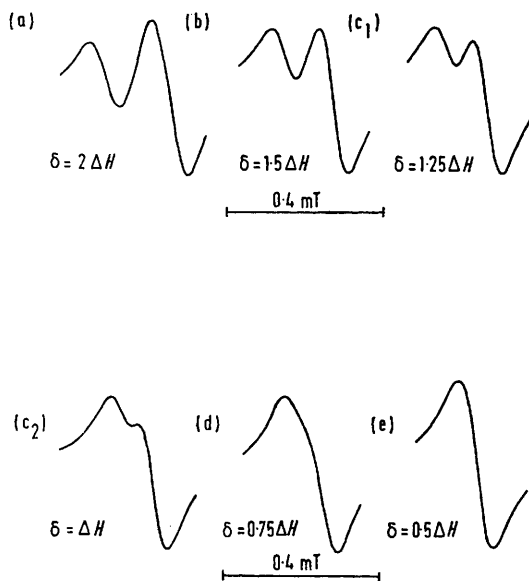


FIGURE 2. Simulated spectra of the second-order splitting;  $\delta$  is the separation between two composite lines with intensities in the ratio 1:2.

Figure 2 shows the result of a computer simulation of this effect. Values of the linewidth ( $\Delta H$ ) for the two individual lines were assumed, and their separation ( $\delta$ ) was varied. Lorentzian line shapes were used in these calculations. A comparison of the input data and the simulated spectra indicates that some distortion occurs and that cases (b) to (e) are sensitive to the value of  $\delta$  relative to  $\Delta H$ . Cases (b) and (c) are in good agreement with the observed effect on Cabosil† and silica gel surfaces respectively. Although it is possible that the two lines could result from incomplete averaging of either the *g* or hyperfine anisotropies, this is unlikely since they can still be observed at 300 K. At this temperature the radical would be expected to have a greater degree of freedom and thus the spectrum would exhibit smaller contributions from any anisotropic terms. The observed value of the splitting,  $0.23 \pm 0.02$  mT, is in good agreement with theory. It may be seen from this simulation that in order to observe the second order splitting the separation  $\delta$  of the two components must be  $\geq \Delta H$ . If  $\delta < \Delta H$  resolution is not observed and the lines are grossly distorted; the observed intensities and the poor

resolution on line 3, which is broader than line 3', are completely accounted for if both  $\delta$  and  $\Delta H$  are considered.

It is seen that the interpretation of methyl radical spectra obtained on u.v. irradiation of low surface coverages of methyl iodide may be in error unless a detailed analysis of any additional splitting or line broadening due to second-order effects is made. For example, Gardner and Casey<sup>1</sup> used calculations involving linewidths to obtain a value of tumbling frequency for the methyl radical produced on photolysis of less than a monolayer of MeI on silica gel. They point out that their value of  $2.0 \times 10^7$  s<sup>-1</sup> is of the order of  $10^8$  slower than normal free rotation and suggest considerable hindrance to free rotation.

In the present study those calculations were repeated for low surface coverages, when it was found that for  $< 2\%$  coverage, provided the contribution due to second-order splitting is considered, the tumbling frequency was  $2.2 \times 10^{11}$  s<sup>-1</sup>, indicating free rotation. Kazanskii<sup>6</sup> suggested that a modification of relaxation theories developed by McConnell and others<sup>7</sup> to consider only *g* tensor anisotropies would explain the commonly observed asymmetry of the lines with respect to the base line. This would, however, give rise to a broadening which depends on  $M_I^2$ . From Figure 3 it can be seen that symmetry about the centre is

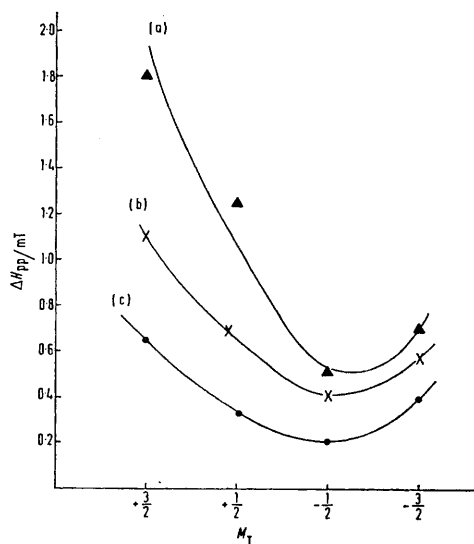


FIGURE 3.  $\Delta H$  vs.  $M_I$  for different surface coverages: (a) 30% coverage; (b) 8%; (c)  $\leq 2\%$ .

approached but only for low surface coverages where contributions to the linewidth from second-order effects can be allowed for. The marked asymmetry of a similar plot by Gardner and Casey probably arises from the high surface coverages used.

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† Cabosil is manufactured by high temperature oxidation or flame hydrolysis of silicon tetrachloride, and was obtained from Cabot Carbon Ltd.

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<sup>4</sup> S. Kubota, M. Iwaizumi, and T. Isobe, *Bull. Chem. Soc. Japan*, 1970, **14**, 2684.

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<sup>6</sup> G. B. Parhskii, G. M. Zhidomirov, and V. B. Kazanskii, *Zhur. Strukt. khim.*, 1963, **4**, 364.

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