

Table 1. CONSTANTS FOR AUBe

State	T_{00}	$\Delta G_{\frac{1}{2}}$	$x_e\omega_e$
$B \frac{1}{2} (^2\Pi_{\frac{1}{2}})$	18,956.66	622.28	
$A \frac{1}{2} (^2\Sigma^+)$	17,194.86	647.56	
$X \ ^2\Sigma^+$	0	600.61	3.53

State	B_0	$10^3\alpha$	p_0^*	$r_0, \text{Å}$
B	0.47736	4.01	+ 0.0183	2.024
A	0.49044	4.60	- 0.1056	1.997
X	0.45882	3.97	$\gamma = 0$	2.064 _e

* In Tables 1 and 2, p_0 is the Ω -type doubling parameter, given by $F_0 - F_2 = p_0(J + \frac{1}{2})$, where c refers to the + level, d to the - level, of $J = \frac{1}{2}$.

Table 2. CONSTANTS FOR AuMg

State	T_{00}	$\Delta G_{\frac{1}{2}}$
$B \frac{1}{2} (^2\Pi_{\frac{1}{2}})$	19,507.51	
$A \frac{1}{2} (^2\Sigma^+)$	18,409.03	334.88
$X \ ^2\Sigma^+$	0	306.11

State	B_0	$10^3\alpha$	p_0	$r_0, \text{Å}$
B	0.14036		+ 0.0036	2.370
A	0.14195	1.37	- 0.0282	2.357
X	0.18170	0.73	$\gamma = 0$	2.446 _e

Table 3. CONSTANTS FOR AuGa, AuSi, AuGe

AuGa ¹⁰	State	T_{00}	ω_e	$x_e\omega_e$	$y_e\omega_e$
	$A (0^+)$	13,058.0	218.82	1.185	- 0.0064
	$X (0^+)$	0	225.62	0.567	- 0.0014

D_0 , by extrapolation, 46 kcal mole⁻¹

State	AuSi*	AuGe†
A	T_{00} 13,632	T_{00} 13,740
	$\Delta G_{\frac{1}{2}}$ 386.0	$\Delta G_{\frac{1}{2}}$ 244
$X_0 (^2\Pi_{3/2})$	1,071	1,552
$X_1 (^2\Pi_{\frac{1}{2}})$	0	0
	$\Delta G_{\frac{1}{2}}$ 391.2	$\Delta G_{\frac{1}{2}}$ 251.7

* Multiple-headed bands degraded in both directions.
† Multiple-headed bands degraded to the red.

Table 4. VALUES OF K_e'' (10^{-5} DYNE-CM)

AuBe	1.87	AuAl	1.55	AuSi	2.23
AuMg	1.20	AuGa	1.53	AuGe	2.03
AuCa	0.96				

AuGa and to AuGe is confirmed by the vibrational isotope effect. Preliminary values of the constants are given in Table 3. AuIn shows red degraded bands in the region 5600–6400 Å; but these have not yet been analysed.

Some values of the force-constants for the ground-states are given in Table 4. These show that, judged by this criterion, the bond-strengths increase monotonously in the series AuMg, AuAl, AuSi and AuCa, AuGa, AuGe.

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¹ Barrow, R. F., and Travis, D. N., *Proc. Roy. Soc., A*, 273, 133 (1963).
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Nuclear Magnetic Resonance of Adsorbed Molecules

In connexion with earlier investigations on the spectroscopic behaviour of substances in the adsorbed state¹ we have tried to discover whether it is possible to observe nuclear magnetic resonance signals of molecules adsorbed on solid surfaces. Observations have already been reported on the magnetic resonance line of water on hygroscopic substances and water included in starch, albumin², zeolites³ and hydrated Portland cements⁴. In the present communication it is shown with a sample of mesitylene that it is possible to observe relatively sharp proton resonance lines of adsorbed molecules. This was not to be expected as the widths of the nuclear magnetic resonance lines in the solid-state are so strongly broadened, due to the spin-spin relaxation, that the signals, covering a wide range of frequencies, became often not observable. On the other

hand, for many compounds evidence has been obtained concerning motion of the molecules in the crystal by observation of the nuclear magnetic resonance lines⁵.

Fig. 1 shows that the two resonance lines of mesitylene at 2.25 and 6.78 p.p.m. appear relatively sharp at a coverage of two molecular layers on the surface of silica (specific surface 175 m²/g) (A), the line-widths being double as great as in the liquid state (E). With increasing number of molecular layers the line-widths increase asymptotically to a value of $\Delta\nu = 60$ c/s for the widths at half maximum. A probable interpretation of these facts is possible by the assumption that at low surface coverage the degree of freedom of the adsorbed molecules is great enough to create conditions which smooth the local magnetic field of the environment and lead to relatively sharp lines. With an increasing number of layers a lattice-like order is established within the first layers due to orientation of the polarized molecules by the solid surface. This order is causing, by the local field of the spin-spin interaction, a broadening of the resonance lines.

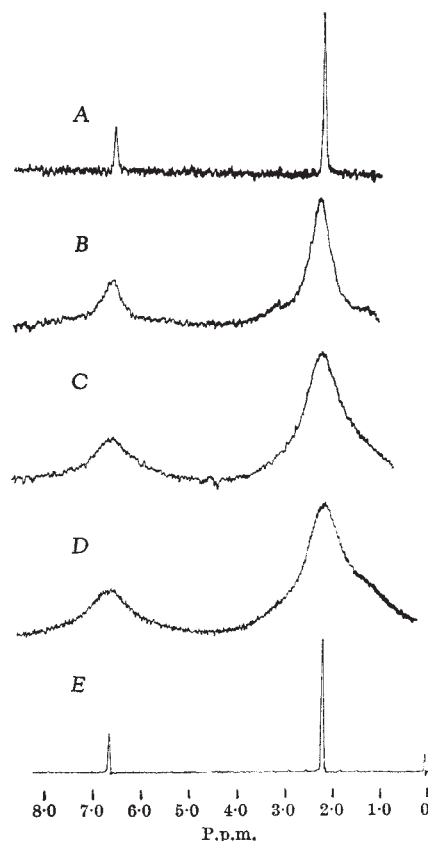


Fig. 1. Nuclear magnetic resonance lines of mesitylene adsorbed on silica. Number of molecular layers: (A) 2, (B) 6, (C) 13, (D) 30. (E) is the pure liquid

One would expect that the resonance frequencies would be shifted by the adsorption to higher as well as to lower magnetic fields, because the electric charges are locally altered within the adsorbed molecules by the polarization on the solid surface. This has not been observed, at least in the case of mesitylene. The relative position of the two lines are not altered by the adsorption. On the other hand, a change of the relative integral intensity of the proton signals in the CH_3 - and CH -groups is observed. The ratio of the integral intensities of the two lines is in the liquid state 3 : 1, while in the adsorbed state this ratio tends with increasing number of layers to the value 4.5. This indicates that the magnetic dipole transitions of the protons in the CH_3 -groups are becoming more frequent than those of the CH -group or that the last ones are becom-

ing less frequent. A decision between these alternatives by measuring the absolute integral intensities is complicated by a contraction of the samples with increasing adsorption, which changes their apparent density by a factor nearly 5. In the case of adsorbed pyridine at a bimolecular coverage two nuclear magnetic resonance lines could be observed at nearly the same regions as the lines of liquid pyridine. The lines of the adsorbed pyridine, however, do not show any fine structure indicating a change in the spin-spin interaction by the adsorption.

A practical application of these observations would proceed on the following lines: (1) an extension of the nuclear magnetic resonance measurements to insoluble substances would be possible using the adsorbed state; (2) special information could be expected about the adsorbed sites of the molecules and the changes in the population of the energy levels by the adsorption.

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³ Ducros-Parc, *Bull. de groupe Ampère, C.R. 9me Coll.*, Sept. 12-16, 1960.

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Effect of Column Pressure on Column Efficiency

In a recent communication given by Amos and Hurrell¹, the authors stated that it was difficult to obtain high efficiencies or adequate resolving power, when packed 0.25-in. external diameter (4 mm internal diameter) analytical chromatographic columns were used in association with thermal conductivity detectors. It was suggested

that by using narrower bore columns and capillary restrictions at the end of the column the efficiency could be improved, an effect that had been demonstrated by Scott² some time earlier.

Higher efficiencies can be obtained by: (1) reducing the diffusivity in the gas phase, and (2) minimizing the gas velocity gradient along the column. These two conditions can be obtained by decreasing the inlet/outlet pressure ratio and by increasing the column pressure.

Fig. 1 shows the flow diagram of the apparatus used in the series of experiments. A 6-ft. copper column was packed with 15 per cent squalane on 60-80 B.S. mesh brickdust and installed in a Pye Argon Chromatograph analyser unit. Pressure gauges (0-60 p.s.i.g.) were fitted at the column inlet and outlet and an Edwards high-vacuum needle valve placed between the column exit pressure gauge and the Gow-Mac katharometer. 'Calor' gas samples were injected into the high-pressure line to the column using a pneumatic gas sampling valve. Argon was used as carrier gas, a separate detector reference flow was utilized and the detector and column maintained at 75° C. Propane, a component of the 'Calor' gas sample, has been taken as an example to illustrate the effect of column pressure on column efficiency.

Chromatograms were obtained for pressure differences of 2.5, 5, 10 and 15 p.s.i. across the column at inlet pressures of 20, 30, 40, 50 and 60 p.s.i.g. Curves were plotted of column flow rate against efficiency for both variation of inlet pressure and pressure drop across the column (Fig. 2). It can be seen that the increase in column efficiency with increased column inlet pressure steadily reduces with increase in pressure drop across the column. This indicates that the best improvement of column efficiency can be obtained by utilizing high column inlet pressures and small pressure differences across the column.

From the practical point of view, the usefulness of this effect is apparent. Separation of ethane, propane, iso- and *n*-butane and iso- and *n*-pentane was achieved in 13 min using a 6-ft. copper column packed with 15 per cent squalane on 60-80 B.S. mesh brickdust, with an inlet pressure of 60 p.s.i.g. and a pressure difference of

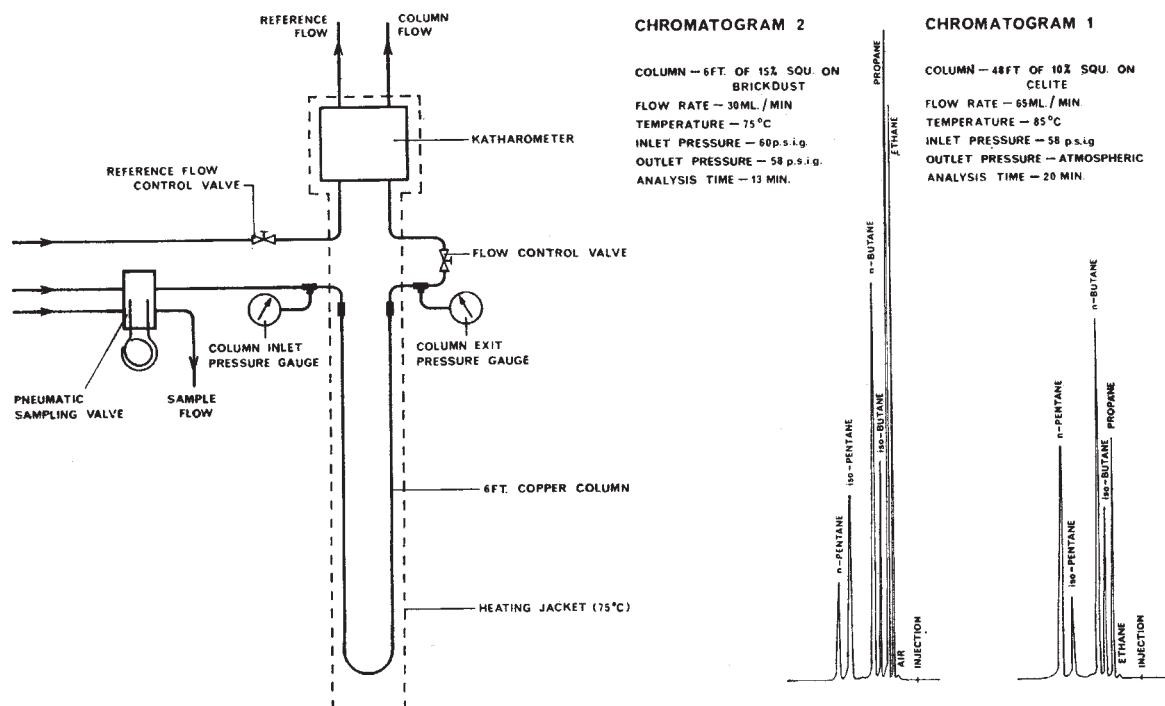


Fig. 1. Schematic flow diagram of apparatus, and chromatograms