Confirmation of this idea has been forthcoming in the analysis of the electronic spectra of several partly deuterated benzenes. In 1:3:5- $C_6H_3D_3$, the excited state frequencies, 3138 cm^{-1} and 2337 cm^{-1} , can be assigned to $A_1'(H)$ and $A_1'(D)$ vibrations respectively. The corresponding values for the ground-state are 3053 cm^{-1} and 2282 cm^{-1} . Perhaps the strongest argument is that, in the absorption spectrum of 1:4- $C_6H_4D_2$, the progression corresponding to the C_6H_5 progression 0-0 + 3085 + 923 ν_1' is doubled, while that corresponding to the C_6D_5 progression 0-0 + 2320 + 879 ν_1' remains single; whereas, in the spectrum of 1:2:4:5- $C_6H_3D_3$, the former progression is single and the latter double. In C_6H_6 and C_6D_6 , Spomer assigned the

frequencies 3085 and 2320 cm^{-1} to a combination of an $E_g(C)$ and an $A_{1g}(H)$ vibration, whereas we have assigned them to a fundamental $E_g^+(H)$ vibration. For $C_6H_4D_2$ and $C_6H_3D_3$ the distinction follows that, whereas Spomer's view would permit only the two A_g hydrogen-stretching vibrations to start progressions, our analysis additionally allows the related B_{1g} vibration to give the extra progression which in each case is observed. A summary of the ground- and excited-state

frequencies (in cm^{-1}) of the A_{1g} , B_{1g} and E_g^+ -like hydrogen-stretching vibrations of some isotopic benzenes is given below.

State	D_6H_6			$D_3H_3D_3$			V_h	
	Sym.	C_6H_6	C_6D_6	Sym.	$C_6H_3D_3$		$C_6H_4D_2$	$C_6H_3D_3$
Ground	B_{1g}	3060	2290	A_1'	2282	A_g		
Excited		3138	2337		2337			
Ground	A_{1g}	3062	2293		3053		2280	3045
Excited		3130	2361		3138		2353	3132
Ground	E_g^+	3047	2264		3055		3055	2285
Excited		3085	2320		3085		3085	2356
Ground	E_g^+	3047	2264		3042	B_{1g}	3042	2272
Excited		3085	2320		3077		3077	2334

In 1:3:5- $C_6H_3D_3$, two main progressions are observed. One, in 893 cm^{-1} , corresponds to the $A_{1g}(C)$ progression, 923 cm^{-1} in C_6H_6 , and 879 cm^{-1} in C_6D_6 . The other, in 987 cm^{-1} , corresponds to the $B_{1g}(C)$ vibration, which in C_6H_6 and C_6D_6 cannot produce progressions; but, as modified in $C_6H_3D_3$, can do so. The frequencies 893 and 987 cm^{-1} belong to the A_1' class of $C_6H_3D_3$ vibrations, and, from these and other known frequencies, we can, using the product theorem, calculate, for the inactive $B_{1g}(C)$ frequencies of excited C_6H_3 and C_6D_3 , the values 1001 and 948 cm^{-1} respectively.

Sklar, Spomer, Nordheim and Teller have determined the frequencies of the two $E_g(C)$ vibrations of excited C_6H_6 and C_6D_6 ,^{2,3} and we have dealt above with the E_g^+ (H-stretching) vibration. The frequencies

of the E_g^+ (H-bending) vibration are identified through the observed progressions 0-0 + 1045 + 923 ν_1' of C_6H_6 and 0-0 + 775 + 879 ν_1' of C_6D_6 . The frequencies 1045 and 775 cm^{-1} must belong to vibrations having E_g^+ symmetry, and we have assigned them to the E_g^+ (H-bending) vibration. The resulting product ratio,

$$\Pi E_g^+(C_6H_6) / \Pi E_g^+(C_6D_6) = 1.965,$$

compares well with the ground-state value 1.967. Further confirmation arises from assignments in the A_g class of 1:4- $C_6H_4D_2$ and 1:2:4:5- $C_6H_3D_3$ vibrations.

Wilson's potential function for benzene contains four in-plane force constants, which may be considered as denoting C-stretching (F), H-stretching (f), C-bending (D), and H-bending (d).^{4,5} The C_6H_6 and C_6D_6 frequencies which are now available for the calculation of these constants for the excited state of benzene are listed below, together with the corresponding ground-state frequencies and the percentage changes which accompany electronic excitation.

Vibration	C_6H_6			C_6D_6		
	Ground	Excited	% change	Ground	Excited	% change
$A_{1g}(C)$	992	923	-7	943	879	-7
$A_{1g}(H)$	3062	3130	+2	2293	2361	+3
$B_{1g}(C)$	1010	1001	-1	963	948	-2
$B_{1g}(H)$	3060	3138	+2	2290	2337	+2
$E_g^+(C1)$	606	520	-14	577	499	-14
$E_g^+(C2)$	1596	1476	-8	1551	1408	-9
$E_g^+(H1)$	3047	3085	+1	2265	2320	+2
$E_g^+(H2)$	1178	1045	-11	867	775	-11

Some force constants (in 10^6 dynes/cm.), calculated from these frequencies using Kohlrausch's form of Wilson's equations, are listed

below, together with the ground-state values calculated from the same equations. The constants F and f were calculated from the A_{1g} frequencies, while D and d were obtained from the B_{1g} and E_g^+ frequencies.

		F	f	D	d
C_6H_6	ground	7.6	5.0	0.77	0.60
	excited	6.5	5.3	0.56	0.45
C_6D_6	ground	7.6	5.1	0.82	0.57
	excited	6.5	5.3	0.57	0.46

These constants cannot be regarded as more than provisional, and are given to indicate the approximate amounts by which force constants change as a result of electronic excitation. It is interesting to note the smaller changes in these in-plane force constants, as compared with reductions of the out-of-plane constants by 50 per cent or more.¹

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June 22.

- ¹ *Nature*, **157**, 46 (1946).
- ² *J. Chem. Phys.*, **7**, 207 (1939).
- ³ *J. Chem. Phys.*, **8**, 705 (1940).
- ⁴ *J. Chem. Soc.*, 256 (1946).
- ⁵ *Phys. Rev.*, **45**, 712 (1934).
- ⁶ *Z. Phys. Chem.*, **30**, 307 (1935).

Topography of Crystal Faces

IN *Nature* of May 4, Tolansky and Wilcock¹ report various features of the topography of the face of a diamond crystal, and conclude that the triangular pits often seen on the faces are due to growth, not to solution: a layer, spreading across the crystal face, does not at first cover a particular region but grows all round it, afterwards closing in on it from three directions to form a triangular pit. We wish to report that, in observing certain crystals growing from solution, we have often seen this sort of thing actually happening—not of course on diamond, but on crystals of water-soluble substances, notably potassium dihydrogen phosphate. The layers we have seen, since they are easily visible under the microscope, are much thicker than those seen by Tolansky and Wilcock on diamond. Two further points are worth mentioning. One is that these pits are often irregular in shape; this is natural enough when the advancing edges of the layers are irregular, as is the case more often than not when growth is rapid. Irregular pits found on finished crystals may therefore be due to growth, no less than regular ones. The second point is that the pits often become completely filled in, there being afterwards no visible trace of their existence.

With regard to the stepped pyramids seen by Tolansky and Wilcock on diamond, we have seen similar features on a number of crystals, again on a much larger scale. Two photographs showing examples of these are shown in a recently published book by one of us.² Layers of octagonal shape have been seen on crystals of sodium chloride; hexagonal layers are sometimes seen on cadmium iodide, but the shape is more often nearly circular. On octahedral faces of lead nitrate crystals, the layers are roughly triangular, but tend to have rounded or irregular edges. The thickness of the layers varies greatly with the conditions of growth, and is profoundly affected by the presence of certain impurities. Usually layers spread from a single point, roughly in the centre of a crystal face; but we have occasionally seen more than one system of layers on the same face, each spreading from a different point. On most of the crystals we have observed, the layers are much thinner near the centre than towards the edge of a face: thin layers, spreading more rapidly than thicker ones, can sometimes be seen overtaking lower layers, thus adding to their thickness. It seems likely that a process of this kind—the building of thick layers from thinner ones—goes on, right down to the ionic scale. A system of submicroscopic layers would constitute a low pyramid of vicinal faces, and the curvature of vicinal faces mentioned by Tolansky and Wilcock may well be connected with a gradual change of layer thickness from the centre of a face towards the edges.

A more detailed account of this work will be published elsewhere.

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¹ Tolansky, S., and Wilcock, W. L., *Nature*, **157**, 583 (1946).

² Bunn, C. W., "Chemical Crystallography" (Clarendon Press, 1945).

A Convenient and Efficient Fractionating Column and its Use in the Separation of the Heavy Isotopes of Hydrogen and Oxygen

THE performance of a fractionating column recently constructed and used in this Department prompts us to place on record its chief characteristics. The column is packed with miniature (1/16 in.) Θ -shaped 'rings' of phosphor-bronze gauze (100 mesh) and is enclosed in a vacuum jacket containing multiple, concentric aluminium reflectors. The length of the packed section is 12 ft. and its internal diameter is