

InfraRed Absorption Spectra at Low Temperatures

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TABLE II. Burning velocity ratios of butadiene-1,3 with normal air and helium air mixtures.

Total pressure	ratio: $r = (V)_H / (V)_A$			ratio: $(V)p = 1 / (V)p = 0.5$			
	Obs. ^a	Calc. ^a	Calc.	Mixture	Obs. ^a	Calc. ^a	Calc.
1 atmos.	3.3	3.2	3.1	air	0.81	0.88	0.86
0.5	3.4	3.1	3.1	He air	0.80	0.90	0.87

^a See reference 1.TABLE III. Burning velocity ratios of flames in CO-O₂-He and CO-O₂-A mixture with H₂O (mole fraction: 0.0269).

Mole fraction of inert gas	{CO}/[O ₂] = 0.503		Ratio: $r = (V)_H / (V)_A$							
	Obs. ^a	Calc. ^b	= 1.083		= 1.234		= 2.698			
0.10	1.05	1.07	1.09	1.07	1.05	1.07	1.03	1.07		
0.15	1.09	1.12	1.12	1.10	1.09	1.10	1.06	1.10		
0.20	1.13	1.15	1.19	1.14	1.13	1.14	1.08	1.14		
0.25	—	—	1.25	1.18	1.16	1.18	—	—		

^a See reference 4.^b Formula (2).

study of the ratios of burning velocities in mixtures of CO-O₂-H₂O with helium or argon as investigated by Fiok and Roeder⁶ by means of the soap bubble method. It is then found that (Table III)

$$r = \frac{V \text{ in mixture with He}}{V \text{ in mixture with A}} = \left[\frac{\rho_u \text{ of the mixture with A}}{\rho_u \text{ of the mixture with He}} \right]^{\frac{1}{2}}. \quad (2)$$

These remarks as well as others show that at present the theory of shock and combustion waves supplemented by the hypothesis of the projection of the hydrogen atoms (which explains the pressure drop in the combustion zone) yields a rather complete interpretation of the influence of various factors on the burning velocities in gas mixtures.

¹ Badin, Stuart, and Pease, *J. Chem. Phys.* **17**, 324 (1949).² E. Jouguet, *La Mécanique des Explosifs* (Ed. Doin, Paris, 1947).³ N. Manson, *Comptes Rendus* **226**, 230 (1948); *Revue de l'Institut Français du Pétrole* **4**, No. 7, 9 (1949).⁴ In the comparison of values of V calculated by means of Eq. (1) and measured by the burner method, one must not forget that the latter method yields (as B. Lewis and G. von Elbe, *J. Chem. Phys.* **11**, 75 (1943) and others have shown) a certain average velocity along the flame cone and not the velocity actually defined in theory.⁶ E. F. Fiok and Ch. Roeder, N.A.C.A. Report No. 553.

Infra-Red Absorption Spectra at Low Temperatures

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July 18, 1949

THE temperature dependence of infra-red absorption bands has been studied by Avery and Ellis,¹ who state that for several aliphatic hydrocarbons there is a distinct sharpening of the bands in going from room temperature to -195°C. They interpret their results on the basis of Bjerrum's formula, according to which the separation of the maxima of the P and R branches of an absorption band is proportional to T_{ab} .² This formula obviously only applies to gases, and would not be expected to hold for liquids and solids, whose spectra do not normally exhibit rotational structure. All the compounds studied by Avery and Ellis were either liquid or solid at -195°C, and it is surprising to find that Bjerrum's formula is even approximately true. For low boiling gases, such as ethane, appreciable narrowing of the bands will occur before the gas liquefies, and thus we might expect the low temperature spectrum of the liquid to have narrower bands than the gas at room temperature, quite apart from any changes accom-

panying liquefaction. In the case of 2,2-dimethylbutane, which boils at 50°C, it is difficult on this basis to see why the bands of the liquid spectrum at -195°C should be much narrower than those in the vapor at room temperature. It is even more surprising that the narrowing actually observed by Avery and Ellis is in good agreement with the Bjerrum formula. In our opinion this agreement is entirely fortuitous, since comparison with spectrogram No. 245 issued by the American Petroleum Institute shows that the absorption bands in the spectrum of liquid 2,2-dimethylbutane at room temperature have the same width as those in the low temperature spectrum given by Avery and Ellis. The band-narrowing attributed by these authors to the temperature effect is thus seen to be entirely due to the change of state.

We have recently obtained the infra-red spectra of several solids at room temperature and at -180°C, and find no systematic change of band-width with temperature. In general there is little or no narrowing of the bands with decreasing temperature, though minor changes in the spectrum do sometimes occur, due perhaps to changes in crystal structure or to λ -point transitions. In the case of a mixture of higher paraffins (Nujol), there is practically no change in going from the liquid at room temperature to the solid at -180°C.

In a later paper² Avery and Morrison imply that the Bjerrum formula holds quite generally, irrespective of the state of the sample, and suggest that further narrowing of absorption bands may be obtained by using liquid hydrogen or helium as cooling agents. In view of our results we consider this to be unlikely, since most compounds are solid at -195°C, and we do not consider that any further decrease in temperature will result in appreciable narrowing of the absorption bands.

A full report of our investigations will be published subsequently.

¹ W. H. Avery and C. F. Ellis, *J. Chem. Phys.* **10**, 10 (1942).² W. H. Avery and J. R. Morrison, *J. App. Phys.* **18**, 960 (1947).

Infra-Red and Raman Spectra of Hexachloroethane

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July 7, 1949

AS a part of a series of researches on intra-molecular rotation we studied the Raman spectrum of hexachloroethane.¹ This was also studied by Hamilton and Cleveland in various solutions.² Recently, one of us has calculated the normal vibrations of ethane-like molecules in the staggered form D_{3d} by use of the Urey-Bradley field.³ However, it is evident from the symmetry of the molecule that the normal frequencies of this form are coincident with those of the eclipsed form D_{3h} , so far as the interaction between the chlorine atoms attached to different movable parts of the molecule is neglected. Therefore, for the discrimination between these two molecular forms we have to refer to the selection rule: in other words, we must observe not only the Raman effect but also the infra-red absorption.

TABLE I. Infra-red and Raman spectra of hexachloroethane.

Infra-red spectrum*		Raman spectrum	
Wave number (cm ⁻¹)	Intensity	Wave number (cm ⁻¹)	Intensity
675	Medium	140	1 broad
		169	2 broad
		224	6
769	Strong	341	5
		432	10
1008	Weak	853	2
		974	1

* The spectrum observed in CCl₄ solution was essentially the same as that in the solid state.

TABLE II. The comparison of the observed and the calculated fundamental frequencies of hexachloroethane.

Type	Calculated* (cm ⁻¹)	Raman observed	Type	Calculated* (cm ⁻¹)	Infra-red observed
A _{1g}	198	169	A _{2u}	382	—
	432	432		729	675
	1008	974			
E _g	218	224	E _u	134	—
	322	341		278	—
	889	853		744	769

*For the form of the potential function and the values of the force constants see reference 3.

The absorption spectra (8–16 μ) were observed in the solid state and in carbon tetrachloride solution. The experimental technique and the apparatus used were essentially the same as described in our previous paper.⁴ The result is shown in Table I. The band observed at 1008 cm⁻¹ is very weak and might be assigned to one of the combination tones.

The Raman spectra were remeasured in the solid state. In Table I the result is shown, which is in good agreement with that obtained by Hamilton and Cleveland.² The existence of a line at 169 cm⁻¹ reported by them was confirmed. It seems that there was found a line at 140 cm⁻¹ by Hg- ϵ excitation, but we are not sure if this is really a Raman line, because there is a weak mercury line practically at the same position. We can assign the line at 169 cm⁻¹ to a deformation vibration of the molecule and that at 140 cm⁻¹ to the lattice vibration, because the latter was not observed by Hamilton and Cleveland in the spectra of solutions.

The two infra-red active vibrations expected for the staggered form were detected by the present experiment (see Table II). The other three frequencies also active in the infra-red lie out of the observable region of our apparatus. If the molecular form were the eclipsed one, the frequency 769 cm⁻¹ of E_u observed in the infra-red spectra should also appear in the Raman effect. However, no Raman line was detected in this frequency region. We can, therefore, conclude in conformity with our previous result that the stable configuration of hexachloroethane is the staggered form D_{3d}. This conclusion had been established by our electron diffraction investigation.⁵

The calculated frequencies of the Raman active vibrations are in good agreement with the observed values (see Table II). This agreement shows that the Urey-Bradley field is an adequate potential function for the treatment of the normal vibration of such a molecule.

¹ S. Mizushima and Y. Morino, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 29, 188 (1936).

² D. T. Hamilton and F. F. Cleveland, *J. Chem. Phys.* 12, 249 (1944).

³ T. Simanouti, *J. Chem. Phys.* 17, 734 (1949).

⁴ Simanouti, Turuta, and Mizushima, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 42, 51 (1946).

⁵ Y. Morino and M. Iwasaki, *J. Chem. Phys.* 17, 216 (1949).

Viscoelastic and Photoelastic Properties of Polystyrene above Its Softening Temperature

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IN a study of creep, recovery after creep, stress relaxation, and optical anisotropy of polystyrene films above their softening temperature, we have obtained certain results which appear to be of significance in obtaining a better understanding of the mecha-

TABLE I. Creep of polystyrene at 110°C.

Time (sec.)	Elongation %	Birefringence A/mil	Stress lb./in. ²	Birefringence stress
0	0	0	24.4	—
40	22.1	-217	29.8	-7.28
75	33.3	-289	32.5	-8.90
130	46.5	-324	35.7	-9.08
190	57.2	-359	38.3	-9.38
275	69.3	-373	41.3	-9.02
375	83.9	-413	44.9	-9.22
480	99.5	-448	48.7	-9.22
590	116.4	-485	52.8	-9.18
700	132	-513	56.6	-9.08
820	154	-556	62.0	-8.97
940	173	-605	66.6	-9.08
1060	193	-634	71.5	-8.88

nism of viscoelastic deformations and of the molecular structure, not only of polystyrene, but also of so-called linear and amorphous linear high polymers in general.

Table I gives the strain and birefringence (A/mil) as a function of time at 110°C, when a constant weight is applied to a film* made from unfractionated polystyrene ($\eta=1.13$). As the cross section changes during the run, the stress per unit area varies also, and column 4 of Table I gives the actual values of stress calculated from the elongation using a Poisson's ratio of 0.5. Column 5 shows the ratio of the birefringence to stress which is constant except for the initial part of the run. It can also be seen that the ratio of birefringence to strain changes continuously. Similar experiments at other temperatures and with films made from fractionated polystyrene ($\eta=1.56$ ($\eta=0.59$)) and a film consisting of a mixture of fractionated polystyrene and a low molecular weight compound showed that this ratio is not only independent of stress, strain, and time but also does not depend on molecular weight within the investigated range and depends only very slightly on temperature.

Table II shows the stress and birefringence relaxation of a polystyrene film. Again the ratio of birefringence to stress is essentially independent of time and is the same as obtained from the "creep" experiment given in Table I. The significant feature of this experiment is the fact that this stretched film recovered almost completely when the external force was removed at any time during the relaxation process of stress and birefringence.

Finally, it was found that repeated stress and birefringence relaxation runs (cycling) on the same film had an effect on the shape and magnitude of the stress and birefringence relaxation curves; cycling always decreases the magnitude of the stress and leads to a more rapid initial stress decay. Similarly, it was found that repeated creep runs (in shear) did not yield identical curves but frequently gave higher initial compliances on consecutive runs.

In an attempt to find at least a qualitative interpretation of these results, we have come to the conclusion that the usual assumptions made to explain the viscoelastic behavior of linear high polymers¹—retarded elastic deformation and viscous flow—are not sufficient but that it becomes necessary to assume the existence of a semipermanent network structure.^{2,3} This structure

TABLE II. Stress and birefringence relaxation in polystyrene at 110°C (elongation = 95 percent).

Time (sec.)	Birefringence A/mil	Stress lb./in. ²	Birefringence stress
0	—	—	—
45	-738	>75	—
90	-573	62.5	-9.17
135	-516	56.0	-9.22
170	-476	50.8	-9.36
245	-426	46.8	-9.10
300	-410	44.3	-9.25
400	-369	40.2	-9.17
475	-361	39.1	-9.24
600	-343	36.5	-9.40
730	-311	33.9	-9.18
900	-295	33.9	-8.72
950	-287	32.6	-8.80