

Note on the Absorption Spectrum of some
Organic Vapours.

DURING some measurements of absorption spectra in the Schumann region we have photographed also the absorption spectra of acetyl chloride, acetyl bromide, and trichloroacetyl chloride down till 1510 A.U. Preliminary results have been used already in an earlier publication of this laboratory¹, but since those figures have been not very accurate, we should like to state the definite results here. The following table shows the

absorption maxima of the three substances at shorter wave-length together with those in the near ultraviolet recorded previously.¹

The first maximum, identical with the point of predissociation known in formaldehyde and related molecules, appears in all these substances. The two chlorides show two more maxima each at shorter wave-length, but in acetyl bromide we have not been able to trace corresponding maxima.

The difference between the two first maxima agrees well with similar differences found by Scheibe and his co-workers² in the

TABLE I.

	I Maximum		II Maximum		III Maximum		Δ II-I	Δ III-II
	AU (air)	cm ⁻¹ (vac)	AU	cm ⁻¹	AU	cm ⁻¹		
CH ₃ ·CO·Cl	2750	36353	2305	43371	2017	49563	7018	6192
CH ₃ ·CO·Br .. .	2500	39988
CCl ₃ ·CO·Cl	2575	38823	2140	46714	1675	59701	7891	12937

case of ethers and alcohols and might be due to the excitation of the radicals CH₃ and CCl₃ respectively. The energy represented by the second maximum appears not to be sufficient to account for the rupture of the double bond of the carbonyl radical. The large difference between acetylchloride and trichloroacetyl chloride seems to exclude a photo-dissociation in which the bonds of the radical and the chloride atom are fissured simultaneously. Therefore this energy difference represents probably an other excitation of one of the radicals; the experimental data are, however, not yet sufficient to decide these questions.

C. M. BHASKER RAO.
R. SAMUEL.

Muslim University,
Aligarh,
Department of Physics,
May 8, 1935.

¹ *Ind. Jour. Phys.*, 1934, 8, 537.

² *Z. phys. Chem. (B)*, 1933, 20, 283; 1934, 25, 52.

On the Linkage of HCl.

WITH respect to the discussion¹ in *Current Science* on the continuous absorption spectrum and the nature of the linkage in molecules like HCl, HI, etc., I should like to draw attention to the fact, that also other

properties of these molecules have to be considered, since the continuous absorption spectrum is by no means a rigorously valid criterion of ionic linkage. It will be sufficient to mention only two such properties here:—

(i) HCl and HI are not conductors of electricity in the liquid state in the complete absence of water. We can easily conceive that a molecule (AgCl is an example) possesses covalent linkage in the vapour state and electro-valent linkage in solution or the molten state. The converse behaviour, however, would be very difficult to understand.

(ii) According to the wave-mechanical theory of the Raman effect, worked out by Placzek² on the basis of the polarisability of the molecule, a molecule with a single electrovalent bond is not able to show the Raman effect. The molecules HCl, HBr and HI show the Raman effect not only in the liquid state and even in solution in some solvents without dipolemoment, but also in the vapour state. Hence they are covalently linked in the gaseous state, and this agrees with Franck's original conclusion derived from their absorption spectrum.

As to Franck's criterion of the ionic linkage, *i.e.*, the dissociation of the excited term into normal atoms, it has been pointed out by him several times³ that it cannot be

rigorously valid since we know that intersections of the U/r curves of the electronic terms of a covalent molecule among themselves are quite possible. If two such terms, *i.e.*, an attractive and a repulsive one, originate from the same level of the separated atoms, this is equivalent to an intersection for the purpose of the application of Franck's criterion, since it represents an intersection at very large internuclear distance.

To my mind particularly the existence of the Raman effect appears to be decisive and I have therefore treated these molecules as covalently bound in the vapour state in my "Report on Absorption Spectra and Chemical Linkage" contributed to the "Symposium on Molecular Spectra" of the Indian Academy in August 1934, which has just been published and where a discussion of the experimental detail of absorption spectra can be found. There seems to be little doubt that the shift of the red wave limit is due to a different distribution of the molecules among the vibrational levels of the ground term, which is indeed a very common phenomenon. Similar remarks apply to the molecule $N \equiv N = O$ of which we know not only the Raman effect, but also the dipole moment, Kerr constant, etc.

Department of Physics, R. SAMUEL.
Muslim University,
Aligarh,
May 8, 1935.

¹ S. Dutta and B. Chakrobarty, *Curr. Sci.*, 1934, 3, 349, 478; A. K. Dutta, *Ibid.*, 1934, 3, 477.

² *Z. f. Phys.*, 1931, 70, 84; *Handb. d. Radl.*, VI.

³ J. Franck, *Nature*, 1931, 127, 19; Franck and Kuhn, *Bull. Ac. Sci.* (Allahabad), 1932, 2, 223.

On the Ratio of the Temperature Coefficients of Surface Tension and Thermal Expansion.

IN a letter to the Editor of *Current Science* (published in the March 1935 issue, p. 418), Sibaiya shows that the observed constancy of the above ratio can be deduced from Laplace's theory of Capillarity. It is interesting to note that on the experimental side, the constancy follows at once from the observed validity of the parachor law. For we have,

$$\gamma = \frac{P^{\frac{1}{3}}}{V^{\frac{1}{3}}} \quad \dots \quad (1)$$

$$\text{whence} \quad \frac{\frac{1}{\gamma} \frac{d\gamma}{dT}}{\frac{1}{V} \frac{dV}{dT}} = 4 \quad \dots \quad (2)$$

Both (1) and (2) follow from a modification of Edser's theory of liquids which has recently been discussed by the author in a number of papers.¹ For on this theory we have

$$\gamma = \frac{\pi \mu}{4(m-5)\sigma^{m+1}} \quad \dots \quad (3)$$

where μ is the coefficient of the attractive force between the molecules, m is the force index, and σ is the average diameter of the spherical space kept clear around a molecule by its thermal movements at T .

The close-packing equation

$$N \sigma^3 = V \sqrt{2} \quad \dots \quad (4)$$

when combined with (3) gives

$$\gamma = \frac{K}{V^{\frac{m+1}{3}}} \quad \dots \quad (5)$$

where K is a constant.

Hence

$$\frac{\frac{1}{\gamma} \frac{d\gamma}{dT}}{\frac{1}{V} \frac{dV}{dT}} = \frac{m+1}{3} \quad \dots \quad (6)$$

(5) and (6) reduce to (1) and (2) if m is put equal to 11.

As shown in Table IV² the observed value of the left hand side of (2) for normal liquids is 3.4-4.2 rather than 2-3 as stated by Willows and Hatschek.³ The wide validity of the parachor law confirms the approximate value 4.

T. S. WHEELER.

Department of Chemistry,
Royal Institute of Science,
Bombay.

April 2, 1935.

¹ *Ind. Jour. Phys.*, 1934, 8, 530.

² *Ind. Jour. Phys.*, *loc. cit.*, 535.

³ *Surface Tension and Surface Energy*, 1915, p. 7.

THE ratio of the temperature coefficients of surface tension and density as derived from the parachor law is 4. Wheeler has shown¹ that the experimentally observed ratio for some organic liquids lies between 3.44 and 4.16, giving for the force index m a value either 9, 10 or 11. Laplace's theory gives for the ratio a value equal to 2; and under special assumptions the ratio becomes $2(1+\epsilon)$. If the parachor value is to be accepted we have to assume that $\epsilon = 1$. Most organic liquids and liquefied gases give a value for the ratio ranging between