

Electronic Kinetic Energy in Gases at High Pressures

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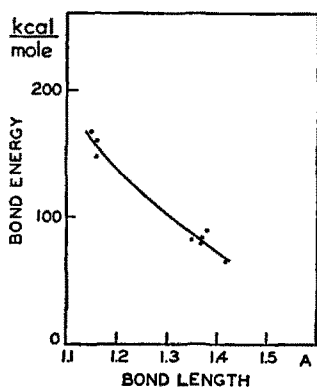


FIG. 3. C-N bond.

atoms, obtainable with the molecular orbital treatment.² There exist many uncertainties for a relation of this type since we know but little about the true charges in π -electrons near the linked atoms and about the C-C distance in many conjugated systems. We know, e.g., that the 2 and 3 atoms of butadiene have low charge and that their distance is high (1.46Å), and that the meso-phenanthrene-type atoms have high charge and short bond (1.35Å in pyrene, 1.38Å in dibenzanthracene and coronene, following Robertson).³

On the other hand the calculations give (1.00+1.00) π -electrons both for the ethylene carbon atoms and for two carbon atoms linked together in benzene, the interatomic distances being 1.35 and 1.39Å, respectively. This may be due to our too rough calculations of charge densities. The limiting cases should be acetylene with 4 π -electrons upon its two carbon atoms (1.20Å) and ethane with zero π -electrons upon his two carbon atoms and with C-C distance 1.54Å.

* In such curves the heat of vaporization of carbon has been assumed, for an easier comparison with the well-known data of Pauling (L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939)), as 125 kcal/mole, following the old data of Bichowski and Rossini (F. R. Bichowski and D. R. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936)). In any way the data may be transformed, assuming a new heat of vaporization (see reference 1, and also K. S. Pitzer, J. Am. Chem. Soc. 20, 2140 (1948)), by a simple shifting of the curves. All the heats of dissociation have been recalculated from the heats of combustion, corrected to the gaseous state of the molecules, referred to by Wheland (G. W. Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc., New York, 1944)). From the same author have been obtained the interatomic distances.

¹ J. L. Kavanau, J. Chem. Phys. 17, 738 (1949).
² C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A191, 39 (1947).
³ J. M. Robertson, Acta Crystall. 1, 101 (1948).

Electronic Kinetic Energy in Gases at High Pressures

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 May 31, 1950

APPLICATION of the virial theorem to a substance of volume V and pressure p gives

$$\Delta\bar{T} = 3\Delta(pV) - \Delta U, \quad (1)$$

where \bar{T} is the average kinetic energy of electrons and nuclei and U is the total energy.¹ Michels *et al.*² have used this result to calculate changes in average kinetic energy brought about by compression of gases; $\Delta(pV)$ was directly measured and ΔU was calculated from the observed P - V - T relationships. $\Delta\bar{T}$ was found to increase with pressure, and it was pointed out that this must be due to an increase in electronic kinetic energy. It was shown that a change of the correct order of magnitude in electronic kinetic energy could be demonstrated by solving the wave equation for the hydrogen atom with the boundary condition that $\Psi=0$ at $r=r_0$.³ It is of interest to try to interpret these results

on a molecular basis, particularly because such an interpretation may enable one to discuss the effects of pressures greater than those used by Michels (3×10^3 atmos.).

Slater⁴ has pointed out that, for a diatomic molecule,

$$\bar{T} = -E - R(dE/dR), \quad (2)$$

where E is the electronic energy, as a function of the internuclear distance R . This shows that as the nuclei are moved closer together than the equilibrium distance, there is a sharp rise in kinetic energy, and a relatively flat rise in total energy. Thus, if the compression of a gas composed of diatomic molecules could be regarded as pushing the nuclei a little closer together, the qualitative explanation of the effect is clear. The large effect of compression on the kinetic energy is very striking, but it is notable that a compression which increases the kinetic energy by an amount as great as the dissociation energy of the molecule leads to only a small increase in total energy. Using the $E(R)$ function and constants given by Linnett,⁵ we may use (2) to calculate how E and \bar{T} vary with R for nitrogen:

$R(\text{\AA})$	$E(\text{kcal./mole})$	$\Delta\bar{T}(\text{kcal./mole})$
1.094	0.00	0.00
1.092	0.01	6.9
1.050	3.45	172.

The force required to bring about a given change in R and hence in \bar{T} can thus be obtained from spectroscopic data; moreover, the corresponding pressure required can be obtained from Michels' experimental work. From this force and pressure the "effective area" of the molecule can be calculated. This "effective area" should be about the same as that of the van der Waals sphere, but close agreement is not to be expected: Michels' results on the hydrogen atom suggest that the area might be greater. The results for nitrogen are of the correct order, and their approximate constancy with increasing pressure suggests that this viewpoint is justifiable. They are as follows:

$\Delta\bar{T}(\text{kcal.})$ Area (\AA^2)	1	2	3	4	5	6
	143	151	152	149	145	142.

The "effective area" seems to be decreasing at high pressures; thus $\Delta\bar{T}$ calculated from it for still higher pressures is likely to be an upper limit. In nitrogen at 10^6 atmospheres, for example, 180 kcal. is an upper limit to the change in kinetic energy, and 4 kcal. to the change in energy. Dissociation should take place at about 10^6 atmospheres.

¹ Schottky, Physik. Zeits. 21, 232 (1920).

² Michels *et al.*, Physica 4, 981 (1937).

³ Michels and de Groot, *ibid.* 16, 183 (1950).

⁴ Slater, J. Chem. Phys. 1, 687 (1933).

⁵ Linnett, Trans. Faraday Soc. 36, 1123 (1940).

Configuration of the Tartaric Ion

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June 14, 1950

IN A Letter to the Editor, E. E. Turner and K. Lonsdale¹ have recently called attention to the two possible configurations for *d*-tartaric acid in the crystalline state, H-atoms and OH-groups being arranged approximately in a plane and the carboxyl groups staying either both in front of behind the plane of the paper, or one in front and the other behind. We think the second configuration is the only correct one.

Some years ago, we recorded and studied² the infra-red absorption spectra, between the wave-lengths of approximately 6-15 μ , for a series of metallic tartrates (11 dextro, 7 laevo, 8 meso and 5 racemic) in the powder state. *d*- (and *l*-) tartrates have a spectrum formed of numerous bands, whose number is greatly reduced in the case of mesotartrates and racemates; the individual positions of bands differ in the three cases of *d* (or *l*), meso, and racemic.

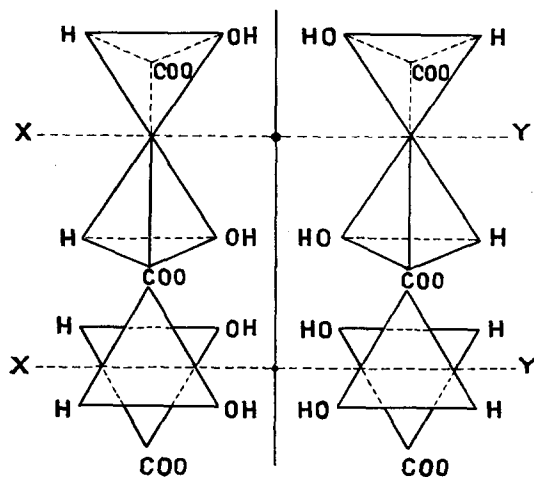


Fig. 1

Fig. 2

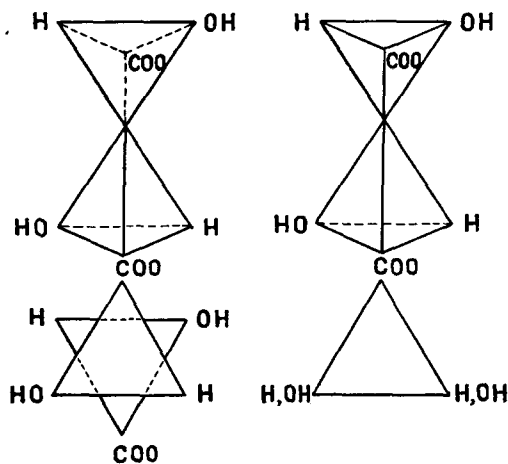


Fig. 3

Fig. 4

With our hypothesis, the *d*-tartaric ion is shown in Fig. 1 and *l*-tartaric ion in Fig. 2 or inversely, but without any possible choice. We call again attention to the fact that this configuration is in accordance with the crystal structure as determined by x-rays.³ On the other hand, the mesotartaric ion is represented by Fig. 3. In all cases, the horizontal projection is a hexagon.

We would like to point out that the *d*- (or *l*-) tartaric ion possesses but *one* binary axis *XY* located in the plane of the paper. Thence, a few molecular vibrations are forbidden in infra-red absorption; this fact explains the very complicated spectra we recorded. Moreover, a good agreement was found between infra-red bands and Raman lines. The mesotartaric ion possesses only *one* center of symmetry; thus, one-half of the fundamental vibrations is inactive in absorption; accordingly, the infra-red spectrum has been simplified and we may notice an alternance between absorption and diffusion spectra; the racemic ion is then formed as a *compound* (not a mixture) of a dextro and laevo-ion. The whole assembly possesses but *one* center of symmetry, and in accordance with the selection rules, the racemic differs from the mesotartaric ion only by the fact that an assembly of two ions is concerned. If racemates were formed by simple juxtaposition of a *d*- and *l*-ion, we would find exactly the same number of infra-red band in the active and racemic forms, but experiments show that it is not the case.

If Fischer's convention be kept (with the carboxylic groups either ahead or behind the plane determined by hydrogen and OH-groups), the meso-tartaric ion should be shown as in Fig. 4; but this picture is false since there is no element of symmetry to explain a decrease of the recorded infra-red bands with regard to those of the active tartrates.

¹ E. E. Turner and K. Lonsdale, J. Chem. Phys. 18, 156 (1950).

² C. Duval and J. Lecomte, Comptes Rendus 219, 483 (1944); Communication à la Société Chimique de France, January 26, 1945; Bull. Soc. Chim. 19, 477 (1946); Communication à la Société de Minéralogie, April 12, 1945; Bull. Soc. franç. Min. 69, 56 (1946).

³ Bevers and Stern, Nature 162, 864 (1948).

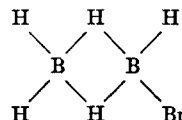
Microwave Spectra of Bromodiborane and Vinyl Bromide*

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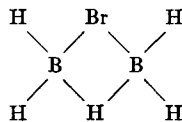
June 1, 1950

SIXTY-EIGHT lines have been observed in the microwave spectrum of bromodiborane (B_2H_5Br). By assuming a configuration



with the ring plane normal to the plane of symmetry, it is possible to assign forty-five lines as various bromine nuclear quadrupole multiplets of $J=2 \rightarrow 3$ and $J=3 \rightarrow 4$ transitions. Twenty-nine lines (belonging to the most abundant isotopic species, with both boron atoms having weight eleven) are fitted with six independent parameters. Lines were found for each of the four isotopic species with mixed boron weights expected for a structure in which the boron atoms are not symmetrically located (see Table I). The aplanarity, which is clearly observable ($I_A + I_B - I_C = 4.1 \pm 0.8$ in atomic units) corresponds to a separation of the bridge hydrogen atoms of 2.0 ± 0.2 Å. This and the parameters of Tables I and II reproduce the observed frequencies with an average error of 0.2 megacycle. A structural determination is now in progress. No fine structure attributable to boron quadrupolar effects was resolved.

In order to consider the possibility of a structure with the bromine atom in the bridge,



the frequencies to be expected for this configuration were calculated. They could not be made to conform to the observed spectrum for any reasonable $\angle B-Br-B$ or $B-Br$ distance. Now was the observed boron isotopic pattern compatible with a structure of

TABLE I. Rotational parameters of B_2H_5Br .*

Isotopic species	$b-c$	$b+c$	I_B	I_C
11-11-79	228.17 \pm 0.06	6511.13 \pm 0.10	149.989 \pm 0.004	160.883 \pm 0.004
11-11-81	225.80 \pm 0.06	6475.70 \pm 0.10	150.835 \pm 0.004	161.734 \pm 0.004
10-11-79	245.30 \pm 0.06	6802.13 \pm 0.10	143.431 \pm 0.004	154.163 \pm 0.004
10-11-81		6766.4 \pm 0.2		
11-10-79	222.57 \pm 0.06	6574.67 \pm 0.2	148.710 \pm 0.008	159.131 \pm 0.008
11-10-81	220.1 \pm 0.2	6539.8 \pm 0.2	149.53 \pm 0.01	159.95 \pm 0.01

* Isotopic weights are for the atoms B-B-Br reading from left to right in the structural formula given. b and c are the two smaller reciprocal moments of inertia in megacycles, I_B and I_C the corresponding moments in atomic units. Probable errors are given.