less discharge. A greatly reduced image of a 15 cm discharge tube was focussed for λ2540 on the slit of a Hilger E31 quartz spectrograph, and the spectrum photographed while
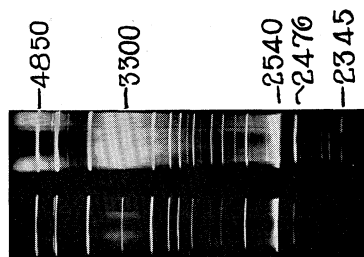

Fig. 1.

the center of the discharge tube was heated by a blow torch. The spectrum for two exposure times is shown in Fig. 1. The difference between the center and edges represents the effect produced by heat. The pressure may be considered to be the same for all portions of the tube.

Heating is observed to destroy the 4850 band and to greatly reduce the intensities of the bands at 2345, 2476, 2540, and the continuous spectrum between 2536 and 3300. Moderate heating enhances 3300 but strong heating destroys it. The majority of the mercury arc lines are unaffected by heat but 5460, 4358, 4047, and 4077 are noticeably weakened.

The fact that most of the mercury arc lines are not affected by heat indicates that the discharge conditions are nearly the same in the heated and unheated portions of the tube. The weakening of the bands must be due to the destruction of mercury molecules by heat. The weakening of the lines probably results from collisions of the first kind which carry excited atoms to higher energy states.

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January 25, 1932.

The Resultant Electric Moment of Complex Molecules

The purpose here is to express the average resultant dipole moment in a form which may be readily evaluated provided that the potential energy associated with distortion of the molecule is known. The individual moments are assumed constant. A molecule may be idealized as a framework of lines along the valence bonds connecting the atoms. About certain of these bonds there is rotation. The experimental electric moment may be regarded as the vector sum of a series of electric moments lying along each of these lines. The moment along some lines may be zero. Let us begin with some end line and number them consecutively 1, 2, 3, etc., along the longest chain until another end line is reached. At points where there is branching the numbering along the different lines is to be distinguished by primes. Now consider a set of unit vectors lying along these lines with their directions pointing toward increasing numbers. Let θ_j be the angle which two consecutive vectors $j-1$ and j make with each other, being zero when they point in the same direction. Let us choose sets of right-handed rectangular coordinate systems in the following way. Each unit vector j coincides in position and direction with the x_j axis of a coordinate system. y_j lies in the plane determined by x_j and x_{j-1} in such a way that the angle between the positive direction of y_j and the negative direction of x_{j-1} is acute. A right-hand screw progressing along positive x_{j-1} turns through an angle, θ_j, in passing from positive z_{j-1} to positive z_j. The transformation A_j, which when applied to the components of a vector referred to the j coordinates transforms it to the $j-1$ coordinate system, is:

$$A_j = \begin{vmatrix} \cos\theta_j & -\sin\theta_j & 0 \\ \sin\theta_j\cos\theta_j & \cos\theta_j\cos\phi_j & -\sin\phi_j \\ \sin\theta_j\sin\phi_j & \cos\theta_j\sin\phi_j & \cos\phi_j \end{vmatrix}. \quad (1)$$

By repeated transformation each electric moment $c_{xj}e_{xj}$ referred to the j coordinates can be referred to a particular set of coordinates, say the set of index 1. e_{xj} is the unit vector in the x_j direction and c_{xj} gives the magnitude and sign of the electric moment in the x_j direction. The above method of specifying coordinates does not fix ϕ_2, which is taken to be equal to zero, which then determines A_2. The resultant vector sum of the n electric moments referred to coordinate system 1 is then

$$C_{x1}e_{x1} + C_{y1}e_{y1} + C_{z1}e_{z1} = \sum_{j=1}^{n} \prod_{k=2}^{j} A_k c_{xj}e_{xj} \quad (2)$$

k and j include primed suffixes where there are side chains. The term $j=1$ in the summation (2) is to mean $c_{x1}e_{x1}$.

If the length of the resultant vector is C, then, taking the scalar product, one obtains:

$$C^2 = C^2{}_{x1} + C^2{}_{y1} + C^2{}_{z1}$$
$$= \left(\left(\sum_{j=1}^{n}\prod_{k=2}^{j}A_k c_{xj}e_{xj}\right),\left(\sum_{j=1}^{n}\prod_{k=2}^{j}A_k c_{xj}e_{xj}\right)\right)$$
$$= \left(\left(\sum_{j=1}^{n} c_{xj}e_{xj}\right),\right.$$
$$\left.\left(\sum_{j=1}^{n}\prod_{k=s}^{2}A'_k\sum_{j=1}^{n}\prod_{k=2}^{j}A_k c_{xj}e_{xj}\right)\right) \quad (3)$$
$$= \sum_{j=1}^{n} c^2{}_{xs}$$
$$+ 2\sum_{j=1}^{n}\sum_{s<j}[(c_{xj}e_{xj}),\ (A'_j \cdots A'_s c_{xs}e_{xs})]$$

A_j is the reverse transformation to A_j and is obtained from A_j by transposing rows into columns. To avoid a more complicated notation the result given in (3) is for a straight chain. The general result independent of the number of branching chains, may be stated. The square of the resultant electric moment is the sum of the squares of the individual moments plus twice all the possible scalar products of all the individual moments after one of these moments has been transformed by consecutive transformations along the reference frame to the coordinate system of the other. Having obtained a resultant for a set of vectors in a given configuration we now proceed to evaluate the average of this resultant weighted with the frequency with which the various configurations occur. The average of C^2 will be called $C^2{}_a$. The averaging is accomplished by evaluating the quantity:

$$C^2_a = \frac{\int c^2 e^{-E/kT}\sin\theta_2 d\theta_2\cdots\sin\theta_m d\theta_m d\phi_e\cdots d\phi_m}{\int e^{-E/kT}\sin\theta_2 d\theta_2\cdots\sin\theta_m d\theta_m d\phi_2\cdots d\phi_m}\cdot(4)$$

In certain cases (4) must be replaced by a summation over discrete energy levels. E is the energy expressed as a function of all the angles. The angles have indices running between 2 and m. Each θ is integrated between the limits 0 and π and each ϕ between the limits 0 and 2π.

Certain special cases are of interest. If E can be broken up into a sum of potential functions each of which only involves a θ_k

and ϕ_k with the same index k, then the averaging can be carried out on the elements of each matrix before multiplying the matrices. A particularly simple case is that for which there is a very sharp minimum in E for a particular value of each angle θ and where E is independent of every angle ϕ. Then A'_k becomes, after averaging over all the angles

$$A'_k = \begin{vmatrix} \cos\theta_k & 0 & 0 \\ \sin\theta_k & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (5)$$

where θ_k is now the angle corresponding to the minimum in the potential energy. Eq. (3) then becomes

$$C^2_a = \sum_{j=1}^{n}c^2{}_{xj} + 2\sum_{j=1}^{n}\sum_{s<j}\prod_{k=j}^{s+1}\cos\theta_k c_{xj}c_{xs} \quad (6)$$

Eq. (6) may be stated in words. For free rotation about connecting lines the mean square sum of n vectors is equal to the sum of the squares of the lengths of the separate vectors, plus twice all the possible products of the lengths of two vectors multiplied by the product of the cosines of the angles θ_k made by the directed lines connecting the pair. θ_k is zero when the directed lines are continuations of each other. The product, $c_j c_s$, of the lengths of the vectors is positive if they point in the same direction in passing along a chain.

In organic molecules where stiff structures such as rings or double bonds occur, a frame may be chosen consisting simply of the straight lines about which there is free rotation. A group of moments inside the stiff structure is represented by a resultant vector passing through the nearest point of rotation and is essentially a side chain of one link. If free rotation is assumed (6) is then immediately applicable to this simplified framework. Every molecule is a special case of either (3) or (6).

These equations apply equally well if the vectors are the distances between atoms instead of the electric moments. For example assuming free rotation the root mean square distance, C_a, between the first and $(n+1)$st carbon atoms of a paraffin chain is

$$C_a = c_1(n + 2(n-1)\cos\theta$$
$$+ 2(n-2)\cos^2\theta\cdots + 2\cos^{n-1}\theta)^{1/2}$$

where c_1 is the distance between neighboring carbon atoms and where the angles between the successive bonds are zero for a straight chain.

These relationships are being used in connection with approximate calculations of potential energies in the interpretation of the observed lengths and electric moments of organic molecules.

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January 29, 1932.

Another New X-ray Non-Diagram Line

In a recent letter to the Editor (Phys. Rev. Feb. 1, 1932) the writer gave values for the wave-lengths of a non-diagram line found in the K spectrum of molybdenum, rhodium, palladium, and silver. The line was provisionally christened β_4 and its possible origin indicated.

The search for faint lines has been continued. Close to β_1 on the short wave-length side another and somewhat fainter line has been found and will be referred to as β_5. The wave-length was determined on a double-crystal spectrometer working in the second order. The International Critical Table values of λ for $\gamma(\beta_2)$ and β_1 were accepted and the wave-length of β_5 found by interpolation. For convenience in determining the probable origin of the new line, its frequency was computed as on page 35, Vol. VI, International Critical Tables. The frequency of the new line was then compared with differences of limiting frequencies of x-ray levels as given in the tables.

The line may be explained as the result of either of two equivalent double transitions, i.e., $(M_{21}{\rightarrow}K)+(M_{22}{\rightarrow}M_{11})$ or $(M_{22}{\rightarrow}K)+(M_{21}{\rightarrow}M_{11})$. Both demand a double ionization resulting from the simultaneous removal

of a K and an M_{11} electron and both demand an improbable transition from one M level to another, but a line less than one one thousandth as intense as β_1 must have something very improbable in its origin.

	$\lambda\beta_5$(X.U.)	$\nu\beta_5$	$(\nu K \lim - \nu M_{21})$ $+ (\nu M_{11} - \nu M_{22})$
Mo	629.46	1448.4	1448.5
Rh	542.87	1679.4	1679.6
Pd	517.84	1760.6	1760.1
Ag	494.27	1844.7	1844.3

Two groups of even fainter lines have been detected. One group lies at the foot of γ on the long wave-length side. The other group lies at the foot of β_2 on the long wave-length side. Each group seems to consist of about five overlapping lines. The present rather uncertain determinations of their wave-lengths indicate that they cannot be explained by any combination of transitions between known x-ray energy levels.

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Note on the New Effect Produced by Action of X-rays on Matter

G. I. Pokrowski[1] reported in this journal the results of a series of experiments to determine what effect x-ray irradiation of metals may have. These experiments seem to show that when elements of high atomic number are irradiated with x-rays, they acquire feeble radioactive properties. Two methods were used to demonstrate this feeble radioactivity; first, the ionization produced by the irradiated samples, and second, the scintillations produced on a screen of zinc blende placed near the irradiated samples. For the first method, the irradiated element was placed in an ionization chamber, and the current was measured with an electroscope. Measurements showed that the ionization produced decreased with the time after the

end of x-ray irradiation, but in the case of lead, was measurable 90 minutes after irradiation. A table showing this variation was also given.

An attempt was made by the writer to measure the ionization current produced by metals irradiated with x-rays. The samples were irradiated with 45 kv and with 160 kv x-rays at a distance of about 20 cm from the x-ray tube targets, and for various times. They were then placed in a copper ionization chamber, and the ionization current was measured with a Lindemann electrometer, with a voltage sensitivity of 400 divisions per volt.

[1] G. I. Pokrowski, Phys. Rev. **38,** 925 (1931).