

Dipole Moments of Polyatomic Molecules

In calculating the dipole moments of polyatomic molecules, it is assumed that the observed moment is vectorially composed of the moments of the various links or bonds. The bond moments so deduced have no simple relationship to the values calculated from the internuclear distances and the electronic charge. The valency angles calculated from them vary and do not agree with theoretical values or even those found by other methods; interactions of the bond moments have been postulated in order to produce agreement between the calculated and the observed values. There is no vector between the bonds connected by single links due to free rotation or uncoupling.

These and other difficulties in the interpretation of dipole moments of polyatomic compounds are simplified by the conception that the dipole action is due to the rotation of the needle-shaped dipole¹, and each bond affects the polarization with the components of the other bonds calculated along the connecting links. The moments of the bonds are uncoupled when connected by single links. In the case of rigid molecules, the bond moments are affected inductively by the components along the connecting links and then add up vectorially.

Thus, according to vectorial addition, the observed moment in a triatomic molecule ABA is (I) $R = m^2 + m^2 + 2mm \cos \theta$, where m is the AB bond moment and θ is the ABA angle and the molecule is polarized along BR , where the angle ABR is $\theta/2$. According to the new law, (II) $R = m + m \cos \theta$, and the direction is along each BA .

When the dipoles are separated by a single connecting link with the same angle, the observed moment according to the new law is (III) $R = m + m \cos \theta^2$. If one more additional link making the same angle is introduced, the resultant is $m + m \cos \theta^3$. If the link bonds have their own moments, the respective

components have to be added, paying regard to the sign. When the two end bonds are dissimilar, the resultant is represented by the arithmetic mean of the values calculated in the direction of each bond, or by the rule of squares.

In water the bond moment OH is $\frac{1}{2}$ ionic or dipolar ($2.5D$), which, using 105° as HOH angle, gives 1.88 as the dipole moment of the H_2O molecule (obs. $1.87D$). The calculated value for hydrogen peroxide assuming the tetrahedral angle for $H-O-O$ is $2.22D$ (obs. 2.14). The $C-O$ bond is $\frac{1}{2}$ ionic ($3.5D$) in alcohols and acids and $\frac{1}{4}$ ionic ($1.75D$) in ethers, which leads to $1.68D$ for the dipole moment of all alcohols and 1.13 for all ethers. The dipole moments of substituted anisoles are also in full agreement with the calculated values. The $C=O$ bond is $\frac{1}{2}$ ionic and the calculated bond moment 2.98 is observed in all ketones. The calculated dipole moment of acetic acid is $1.76D$ (obs. $1.71D$). The uncoupling of $C=O$ and OH bonds takes place owing to free rotation along the link $C-O$. The dipole moment of ethylene dichloride is $1.69 \times (1 - \cos \theta^2) = 1.50D$ (obs. $1.5D$ at 200°); of quinol dimethyl ether using COC angle 105° , found in dimethylether, is $1.75 (1 - \cos 75^\circ)^2 = 1.64D$ (obs. $1.67D$).

The law of component moments accounts quantitatively for the anomaly of flexible molecules, the ortho, meta, para moments in aromatic compounds, the substituted anisoles, the dihenols and nonthe molecules and theoretical values of angles and bond moments. Details will be published elsewhere.

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Dec. 26.

¹ NATURE, 153, 222 (1944).