On the Charge Distribution in Linear $XY_2$ Molecules from Infrared Intensity Data. A Correction Note

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Methods for the determination of the charge distribution on atoms in molecules are currently of great interest. Some years ago the present author presented some calculations on the systems $UO_2^{2+}$ and $HgCl_4$ based on measurements of the infrared absorption intensity of the $v_3$ vibration. However, in the transformation of the $|\partial \mu / \partial Q_4|$ values to $|\partial \mu / \partial r_1|$ a mistake was made.

The calculation involved (cf. eqn (14) of Ref. 1) the concept of $\partial \mu / \partial r_1$ referring to the partial derivative of the dipole moment of the linear $XY_2$ molecule with the $Y-X$ distance, $r_1$, the other distance, $r_2$, being kept constant. When applying the calculated value of $\partial \mu / \partial r_1$ to the estimation of charges on a fixed charge model like

$$
\begin{align*}
  -q + 2q & \quad Y-X-Y \\
  & \quad Y-X-Y
\end{align*}
$$

it was regrettably not realised fully by the present author that $\partial \mu / \partial r_1$ should be interpreted as $\left( \partial \mu / \partial r_1 \right)_r$, i.e. both $r_1$ and $r_2$ were then considered as variable. Hence, the equation $\left| \partial \mu / \partial r \right| = 2q$ was incorrectly applied, identifying $\left| \partial \mu / \partial r_1 \right|$ with $\left| \partial \mu / \partial r \right|_r$.

However, recent papers, especially those of Orville-Thomas and coworkers, make it most clear that the quantity obtainable — and obtained in the model work of the previous paper on $UO_2^{2+}$ — is the bond moment derivative, i.e. $(\partial \mu / \partial r_1)_r$.

Hence, it follows immediately since

$$
\mu = q r_1 - q r_2
$$

that

$$
(\partial \mu / \partial r_1) = q
$$

Having once realised this, it is obvious that the charges calculated from this type of fixed charge model must be multiplied by a factor of 2. This yields (cf. p. 992 of Ref. 1) an almost completely ionic $-1.95.8-1.9$ bonding of the $UO_2^{2+}$ unit $(O-U-O)$ as well as of the $HgCl_4$ unit $(-1, +2, -1; \text{cf. p. 73 of Ref. 2})$. This indicates that the fixed charge model is not a very good guide to the charge distribution of these molecules.

However, it is important to remember that if the bond moment is $\mu_1 = q r_1$, the bond moment derivative $\partial \mu_1 / \partial r_1$ can be expressed as

$$
\frac{\partial \mu_1}{\partial r_1} = q + r_1 \frac{\partial q}{\partial r_1}
$$

This relation has been applied, e.g., on the results of measurements on the $V_{O}^{2+}$ ion in aqueous solution. It seems that if independent information on the value of $q$ were available, eqn. (3) could give increased characterisation of the electronic structure of the molecule by the derivative $\partial q / \partial r_1$.

Thus, adopting an estimate on the low side of $q_{Hg}$ in $UO_2$, e.g. $q_{U} = 2.5$, we obtain (with $r_{UO} = 1.7 \text{ Å}$)

$$
\frac{\partial q}{\partial r_1} = \frac{1.9 - 0.25}{1.7} \approx 1.0 \text{ a.u./Å}
$$

For the $HgCl_4$ case one obtains similarly (as $q_{Hg}$ has been estimated to be $-0.5$ from NQR measurements and $r_{HgCl} = 2.29 \text{ Å}$)

$$
\frac{\partial q}{\partial r_1} = \frac{1.0 - 0.5}{2.3} = 0.22 \text{ a.u./Å}
$$

Indeed, if the set of intensity values found$^2$ for $r_{HgCl}$ in nonhydrogen bonding solvents is used, the estimated value of $\partial \mu_1 / \partial r_1$ reduces to about 0.78 and hence $\partial q / \partial r_1$ has a still lower value (0.12 a.u./Å). It may be that such calculations can be of some use in indicating the degree of mobility of charges over the bonds in question.

The error of calculation described above was pointed out to me by Dr. Graham A. Bowmaker, University of Auckland. I wish to express my sincere gratitude to him for his interest in my work and for continued discussions. I also wish to thank Dr. Feil A. Miller, University of Pittsburgh, for his comments on the subject and his kind interest.

Experimental. PPO, (M_r = 40,000), a commercial product from General Electric Co., was dissolved in α-pinene¹ and PPOO, (M_r = 70,000), synthesized as described in Ref. 2, in cyclohexanone. After dissolution of the PPO sample, the solution was held at 353 K for 5 days. The solution of the PPOO sample was stored at room temperature for the same period of time. After the crystals of PPO had been separated from α-pinene, they were washed several times with ether and dried under vacuum. Cyclohexanone was removed from the crystalline PPOO in a Hoesi HT 125 vacuum desiccator. The samples (about 5 mg) were coated with a layer of gold about 200 Å thick and scanned with a Jeolco JSM-U3 scanning electron microscope. The tilting angle of the specimen was 45°. Calorimetric studies were carried out with a Perkin-Elmer 1B differential scanning calorimeter. The weight of the PPOO sample was 15 mg and the scan speed 16°/min.

Studies of Crystals of 2,6-Disubstituted Polyphenylene Ethers with a Scanning Electron Microscope

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Barrales-Rienda crystallized poly(2,6-dimethyl-1,4-phenylene ether) (PPO)* from α-pinene and obtained a melting point of 507 K for the polymer crystals.¹ He also investigated the crystals with an optical microscope, but as far as we know, no high-resolution studies of the crystals have been conducted with a scanning electron microscope (SEM). In order to elucidate the crystalline structure of PPO and also that of the analogous poly(2,6-dimethoxy-1,4-phenylene ether) (PPOO), we have studied crystals of the mentioned polymers by the SEM technique and compared details of the micrographs with the results of DSC measurements.

* PPO is a trademark of the General Electric Co., U.S.A.