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

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Methods for the determination or estimation of charges 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 $HgCl_2$ based on measurements of the infrared absorption intensity of the ν_3 vibration.[1-2] However, in the transformation of the $|\partial\mu/\partial Q_3|$ values to $|\partial\mu/\partial r|$ 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 YXY 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

$$\overset{-q}{Y} - \overset{+2q}{X} - \overset{-q}{Y}$$

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

However, recent papers, especially those of Orville-Thomas and coworkers,[3-5] make it most clear that the quantity obtainable – and obtained in the model work[6] of the previous paper[1] on UO_2^{2+} – is the bond moment derivative, *i.e.* $(\partial\mu/\partial r_1)_{r_2}$.

Hence, it follows immediately since

$$\mu = qr_1 - qr_2 \tag{1}$$

that

$$(\partial\mu/\partial r_1)' = q \tag{2}$$

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 bonding of the UO_2^{2+} unit $(\overset{-1.9}{O} - \overset{5.8}{U} - \overset{-1.9}{O})$ as well as of the $HgCl_2$ unit (–1, +2, –1; *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 $\mu_1 = qr_1$ the bond moment derivative $\partial\mu_1/\partial r_1$ can be expressed as

$$\frac{\partial\mu_1}{\partial r_1} = q + r_1\frac{\partial q}{\partial r_1} \tag{3}$$

This relation has been applied, *e.g.*, on the results of measurements on the VO^{2+} ion in aqueous solution.[7] 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_U in UO_2, *e.g.* $q_U = 2.5$, we obtain (with $r_{UO} = 1.7$ Å[8])

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

For the $HgCl_2$ case one obtains similarly (as q_{Cl} has been estimated to be –0.5 from NQR measurements[9] and $r_{HgCl} = 2.29$ Å[10])

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

Indeed, if the set of intensity values found[2] for $\nu_{3\ HgCl_2}$ 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[11] 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. Foil A. Miller, University of Pittsburgh, for his comments on the subject and his kind interest.

1. Larsson, R. *Acta Chem. Scand.* **22** (1968) 983.
2. Larsson, R. *Acta Chem. Scand.* **23** (1969) 70.
3. Rowland Davies, P. and Orville-Thomas, W. J. *J. Mol. Struct.* **4** (1969) 163.
4. Thomas, G. A., Ladd, J. A. and Orville-Thomas, W. J. *J. Mol. Struct.* **4** (1969) 179.

5. Thomas, G. A., Jalsovszky, G., Ladd, J. A. and Orville-Thomas, W. J. *J. Mol. Struct.* 8 (1971) 1.
6. Robinson, D. Z. *J. Chem. Phys.* **19** (1951) 881.
7. Larsson, R. and Nunziata, G. *Acta Chem. Scand.* **24** (1970) 1.
8. Zachariasen, W. H. and Plettinger, H. A. *Acta Cryst.* **12** (1959) 526.
9. Negita, H., Tanaka, T., Okuda, T. and Shimada, H. *Inorg. Chem.* **5** (1966) 2126.
10. Akishin, P. A., Spiridonov, V. P. and Khodchenkov, A. N. *Zh. Fiz. Khim.* **33** (1959) 20.
11. Person, W. B. and Hall, L. C. *Spectrochim. Acta* **20** (1964) 771.

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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.

Experimental. PPO, ($\bar{M}_v = 40\,000$), a commercial product from General Electric Co., was dissolved in α-pinene[1] and PPOO, ($\bar{M}_v = 70\,000$), 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 Hösli 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.

Fig. 1a. Crystals of PPO (6000×).

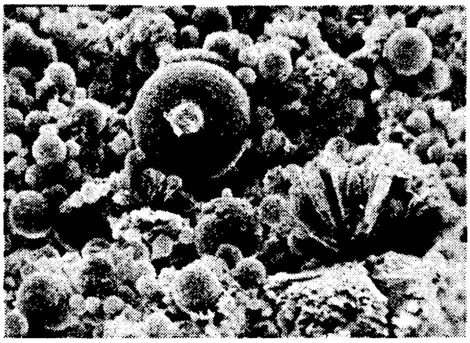

Fig. 1b. Crystals of PPOO (4500×).

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