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INTERPRETATION OF INFRARED INTENSITIES BASED ON THE ATOMIC POLAR TENSOR PARTITION. THE ROH MOLECULES (R = H, CH₃, NH₂, OH, F)

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SUMMARY

The Atomic Polar Tensors (APT) of the H atom for ROH molecules where R = H, CH₃, NH₂, HO and F, are calculated by the *ab initio* method using the 4-31 G basis set. The results are interpreted in terms of the charge, charge-flux, atomic dipole flux and homopolar dipole flux contributions.

INTRODUCTION

It is well known that the experimental infrared intensities are directly related to the electronic charge distribution in the molecule. The purpose of this work is to look for a better insight of the electronic charge fluctuations induced by the vibrational motion, by using *ab initio* quantum mechanical calculations. The APT formalism (ref. 1) is one of the methods used for interpreting and predicting infrared intensities. In the Polar Tensor formalism, for any given atom α in the molecule, there exists an APT, represented by a 3×3 matrix $\tilde{p}_X^{(\alpha)}$, whose elements are the quantities $\partial p_\tau / \partial \xi_\alpha = P_{\tau\xi}$, where p_τ are the components of the dipole moment vector for $\tau = x, y, z$ and ξ are the nuclear coordinates X, Y, Z of atom α . So, if p is taken as the column dipole moment vector, we can write

$$\tilde{p}_X^{(\alpha)} = \nabla_\alpha p.$$

For a closed shell molecule described by a single determinant wavefunction in the LCAO approximation, the expectation value for the p_τ operator in the atomic system of units is given by

$$\langle \tilde{p}_\tau \rangle = - \sum_{\mu\nu} P_{\mu\nu} \langle \phi_\mu | \tau | \phi_\nu \rangle + \sum_A Z_A \xi_A \quad (1)$$

where $P_{\mu\nu}$ is the density matrix element and μ, ν are the atomic orbitals. By using the Mulliken populational analysis (ref. 2), the nuclear charge Z_A can be rewritten and after some algebra, the following expression for the dipole moment is obtained (ref. 3)

$$\langle \tilde{p}_\tau \rangle = \sum_A q_A \xi_A - \sum_A \sum_{\mu < \nu} 2P_{\mu\nu} \tau_{\mu\nu}^A - \sum_{A < B} \sum_\mu \sum_\nu 2P_{\mu\nu} \tau_{\mu\nu}^{AB} \quad \text{where} \quad (2)$$

$$\bar{\tau}_{\mu\nu}^A = \langle \phi_\mu | \tau - \epsilon_A | \phi_\nu \rangle \text{ and } \bar{\epsilon}_{\mu\nu}^{AB} = \langle \phi_\mu | \tau - \frac{\epsilon_A + \epsilon_B}{2} | \phi_\nu \rangle.$$

In the above equation, q_A is the Mulliken's net atomic charge, $\bar{\tau}_{\mu\nu}^A$ is the distance from the centroid of the hybrid orbital (μ, ν) to nucleus A, and the integral $\bar{\epsilon}_{\mu\nu}^{AB}$ is the distance from the center of charge to the midpoint of the chemical bond A-B, (μ belongs to A and ν belongs to B). The second and third terms in the eqn. (2) have already been discussed (ref. 3) and identified as the atomic dipole and homopolar dipole contributions to the dipole moment, respectively. The main interest in this way of partitioning the dipole moment comes from its invariance with respect to the choice of origin for the system. Taking the gradient of the eqn. (2), a general expression for the APT is obtained

$$\nabla_\alpha \mathbf{p} = q_\alpha \mathbf{E} + \sum_A (\nabla_\alpha q_A) \mathbf{R}_A - \sum_A \sum_{\mu < \nu} \nabla_\alpha (2P_{\mu\nu} \bar{\mathbf{R}}_{\mu\nu}^A) - \sum_{A < B} \sum_\mu \sum_\nu \nabla_\alpha (2P_{\mu\nu} \bar{\mathbf{R}}_{\mu\nu}^{AB}), \quad (3)$$

where \mathbf{E} is the identity matrix and \mathbf{R}_A the vector position of nucleus A whose components are ϵ_A . The first two terms on eqn. (3), are the charge and charge-flux and have already been well discussed before (refs 4,5). The last two terms, are called atomic and homopolar dipole flux, respectively, and can still be separated, each of them, in two parts if the rule for differentiation of products is used when taking the gradient of those terms in the parenthesis. The atomic dipole flux involves only intra-atomic off diagonal density matrix elements and the respective centers of charge of the hybrid orbitals. For the homopolar dipole flux, two different atoms of the molecule have being considered.

RESULTS

The APT results calculated for the hydrogen atom in some ROH molecules by SCF method using 4-31 G basis sets are presented in Table 1. The origin of the coordinate system is at the oxygen atom and the OH bond lies on the Z axis. R represents one of the following groups: H, CH₃, NH₂, OH and F. As noted before on (ref. 5), in all the cases, the charge flux contributions for the polar bond OH are quite small when compared with the charge tensor (for a homopolar bond they would be of nearly the same order of magnitude). The vectors $\partial \mathbf{p} / \partial \mathbf{r}_{\text{OH}} = (\partial p_x / \partial z_H, \partial p_y / \partial z_H, \partial p_z / \partial z_H)$ which are the third columns of the atomic dipole and homopolar dipole fluxes are plotted on Fig. 1. As one can see in the Fig. 1, for each atom, the atomic ($\partial \mathbf{p}^A / \partial \mathbf{r}_{\text{OH}}$) and homopolar ($\partial \mathbf{p}^h / \partial \mathbf{r}_{\text{OH}}$) dipole flux vectors are by far linearly independent which can be interpreted as if they are carrying independent informations supporting therefore the partition used.

A high negative value of the $\partial \mathbf{p}^A / \partial \mathbf{r}_{\text{OH}}$ on the atomic dipole flux is obtained

for all the molecules and this is mainly due to the change in the (2S,2P) hybridization, which implies that the atomic dipole contribution to the dipole moment has decreased as the chemical bond is stretched indicating a rearranging of negative charge on O atom. The heavy atom from the R group, also gives its contribution to the atomic dipole flux even though it is not significant. Comparing those values with the charge tensor, one can see that they

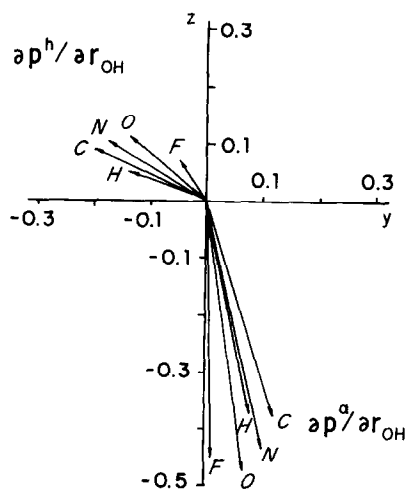


Fig. 1. Plot of the atomic dipole flux ($\partial p^a/\partial r_{OH}$) and homopolar dipole flux ($\partial p^h/\partial r_{OH}$) vectors.

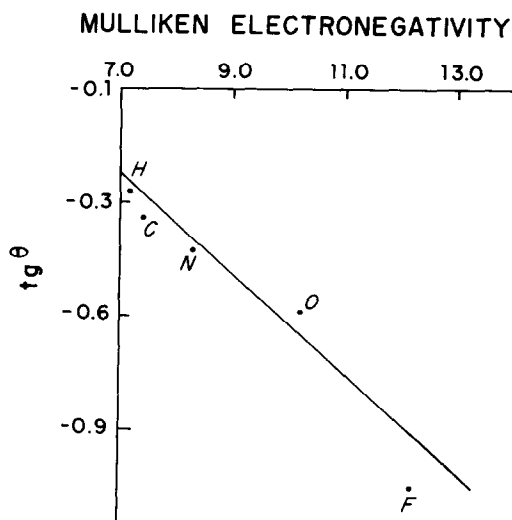


Fig. 2. Plot of the direction of $\partial p^a/\partial r_{OH}$ vector given by the tangent of its angle (θ) with the y axis versus Mulliken's electronegativity of the R group for ROH molecules.

nearly cancel each other, and so the total $\partial p/\partial r_{OH}$ is made up from small contributions. The homopolar dipole flux $\partial p^h/\partial r_{OH}$, which is related to all bonds in the molecule is small, particularly for H_2O and FOH molecules. That shows that the APT of H atom, has strong atomic characteristics which suggest it to be transferable to other molecules with similar behavior for prediction of infrared intensities.

The relationship between the direction of the homopolar dipole flux vectors and the Mulliken electronegativity of the R group is plotted on Fig. 2. There is a good linear correlation except for the FOH molecule which can be justified by the small magnitude of the $\partial p^h/\partial r_{OH}$ vector since any fluctuation can cause a large variation on the vector direction (if FOH is taken out, the correlation coefficient is 0.99 and if the H atom is also excluded the correla-

TABLE 1

Polar Tensor of H atom for ROH molecules^a. R = H, CH₃, NH₂, HO, F^b.

	Charge			Charge flux			Atomic dipole flux			Homopolar dipole flux			Total			Experimental ^c		
HOH	0.39	0	0	0	0	0	0.33	0	0	-0.26	0	0	0.46	0	0	0.33	0	0
	0	0.39	0	0	-0.08	0.03	0	0.16	0.08	0	-0.14	-0.14	0	0.34	-0.03	0	0.25	-0.06
	0	0	0.39	0	-0.06	0.03	0	-0.13	-0.38	0	0.09	0.05	0	-0.10	0.09	0	-0.05	0.13
CH ₃ OH	0.40	0	0	-0.03	0	0	0.32	0	0	-0.24	0	0	0.45	0	0	0.26	0	0
	0	0.40	0	0	-0.18	0.05	0	0.21	0.12	0	-0.15	-0.20	0	0.28	-0.03	0	0.16	0.02
	0	0	0.40	0	0.04	0.04	0	-0.19	-0.38	0	0.12	0.09	0	-0.04	0.15	0	-0.07	0.14
NH ₂ OH	0.42	0	0	-0.03	0	0	0.30	0	0	-0.23	0	0	0.46	0	0			
	0	0.42	0	0	-0.19	0.02	0	0.17	0.10	0	-0.13	-0.18	0	0.27	-0.06			
	0	0	0.42	0	0.07	0.11	0	-0.32	-0.44	0	0.21	0.10	0	-0.04	0.19			
HOOH	0.43	0	0	-0.02	-0.01	-0.02	0.29	-0.05	0.02	-0.24	0.06	-0.01	0.47	0	-0.01			
	0	0.43	0	0	-0.19	-0.01	0	0.12	0.07	0	-0.12	-0.14	0	0.24	-0.08			
	0	0	0.43	-0.01	0.06	0.15	0	-0.29	-0.47	0	0.20	0.11	-0.01	-0.03	0.21			
FOH	0.45	0	0	0	0	0	0.29	0	0	-0.24	0	0	0.50	0	0			
	0	0.45	0	0	-0.18	-0.04	0	0.07	0.01	0	-0.09	-0.05	0	0.25	-0.08			
	0	0	0.45	0	0.05	0.17	0	-0.23	-0.45	0	0.15	0.07	0	-0.03	0.24			

a) The Oxygen atom is at the origin of the coordinate system and the OH bond lies on the Z axis. The heavy atom of R lies on the YZ plane.

b) Atomic units (e).

c) From ref. 5.

tion coefficient goes to 0.999).

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