

## Relationship Between Atomic Polar Tensors and Bond Polar Parameters Formulations of Infrared Intensities

S. Ilieva, T. Dudev and B. Galabov

Department of Chemistry  
University of Sofia  
Sofia 1126, Bulgaria

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The mathematical and physical aspects of the relationship between the atomic polar tensors and bond polar parameters formulations of vibrational intensities in infrared spectra are discussed. The theoretical considerations are illustrated with parallel applications of the two approaches in analysing experimental intensity data for ethane, methyl chloride and H<sub>2</sub>O.

### INTRODUCTION

Vibrational intensities in infrared spectra are interpreted by transforming the measured integrated absorption intensities into molecular parameters characterizing the dynamics of the electric charges in a molecule with vibrational distortions. Several theoretical models for reduction of intensity data have been put forward.<sup>1-8</sup> Because of the diverse approaches applied in different laboratories to interpreting intensity data, it is essential to analyze and define the relationships between the theories developed. These efforts should, hopefully, contribute to a better understanding of the physical significance of the various intensity parameters employed. Several papers dealing with the problem appeared during the past decade.<sup>9-11</sup> In the present study we analyse the relationship between the atomic polar tensors (APT)<sup>3,4</sup> and bond polar parameters (BPP)<sup>7,8</sup> formulations of IR intensities. We first discuss some mathematical and physical correlations between the two theoretical approaches. In the following section, parallel applications of the two methods to analyzing the experimental IR intensity data for ethane, methyl chloride and water are presented.

### THEORETICAL CONSIDERATIONS

Atomic polar tensors are defined as:<sup>3,4</sup>

$$\mathbf{P}_x^{(a)} = \begin{pmatrix} \partial p_x / \partial x_\alpha & \partial p_x / \partial y_\alpha & \partial p_x / \partial z_\alpha \\ \partial p_y / \partial x_\alpha & \partial p_y / \partial y_\alpha & \partial p_y / \partial z_\alpha \\ \partial p_z / \partial x_\alpha & \partial p_z / \partial y_\alpha & \partial p_z / \partial z_\alpha \end{pmatrix} \quad (1)$$

$p_x$ ,  $p_y$  and  $p_z$  are the Cartesian components of the molecular dipole moment;  $\Delta x_\alpha$ ,  $\Delta y_\alpha$  and  $\Delta z_\alpha$  — cartesian displacement coordinates for atom  $\alpha$ . The atomic polar tensors matrix  $\mathbf{P}_X$  has the structure:

$$\mathbf{P}_X = (P_x^{(1)} \dots P_x^{(\alpha)} \dots P_x^{(N)}) \quad (2)$$

$N$  is the number of atoms in a molecule.

The elements of  $P_X$  are evaluated using the matrix expression<sup>3,4</sup>

$$\mathbf{P}_X = \mathbf{P}_Q \mathbf{L}_S^{-1} \mathbf{B}_S + \mathbf{P}_\beta \quad (3)$$

$\mathbf{P}_Q$  contains the experimental dipole moment derivatives with respect to normal coordinates.  $\mathbf{L}_S$  is the normal coordinate transformation matrix and  $\mathbf{B}_S$  is the matrix defining the relation between internal symmetry coordinates and atomic cartesian displacements.<sup>12</sup>  $\mathbf{P}_\beta$  is a rotational correction term.<sup>4</sup>

Bond polar parameters are derivatives of the Cartesian components of the molecular dipole moment with respect to linear and angular bond displacement coordinates:<sup>7,8</sup>

$$s_k = \begin{pmatrix} \partial p_x / \partial r_k \\ \partial p_y / \partial r_k \\ \partial p_z / \partial r_k \end{pmatrix} \quad d_k = \begin{pmatrix} \partial p_x / \partial \Theta_k & \partial p_x / \partial \varphi_k \\ \partial p_y / \partial \Theta_k & \partial p_y / \partial \varphi_k \\ \partial p_z / \partial \Theta_k & \partial p_z / \partial \varphi_k \end{pmatrix} \quad (4)$$

$\Delta r_k$  defines the change of bond length,  $\Delta \Theta_k$  and  $\Delta \varphi_k$  are changes of bond polar and azimuthal angles in a spherical polar coordinate system,  $k$  is a bond index.

The matrix of bond polar parameters has the structure:

$$\mathbf{P}_b = (s_1 d_1 s_2 d_2 \dots s_{N-1} d_{N-1}) \quad (5)$$

BPPs are evaluated using the matrix equation:

$$\mathbf{P}_S - \mathbf{R}_S = \mathbf{P}_b \mathbf{V} \mathbf{A}_{gS} \quad (6)$$

In expression (6),  $\mathbf{P}_S$  is an array containing dipole moment derivatives with respect to symmetry coordinates;  $\mathbf{R}_S$  — matrix of rotational correction terms.<sup>13</sup>  $\mathbf{V}$  defines the transformation between the bond coordinates  $\Delta r_k$ ,  $\Delta \Theta_k$ ,  $\Delta \varphi_k$  and the atomic coordinates  $\Delta x_\alpha$ ,  $\Delta y_\alpha$ ,  $\Delta z_\alpha$ ;<sup>8</sup>  $\mathbf{A}_{gS}$  ( $= \partial \mathbf{X} / \partial \mathbf{S}$ ) matrix refers to a heavy non-rotating isotope of the molecule, as proposed by van Straten and Smit.<sup>13</sup>

The infrared intensity formulations briefly presented above have similarities in several aspects. First, both theories employ as parameters derivatives of the total molecular dipole moment (Eqn. 1 and 4). Thus, the bond moment or point charge approximations, inherent in other intensity theories<sup>2,5,6</sup> are avoided. The validity of these approximations as applied to infrared intensity analysis has been already discussed in detail.<sup>14,15,16</sup>

A second essential feature of the two approaches is the equality between the number of parameters to be determined and the number of experimental observables. Hence, the inverse intensity problem is completely defined.

From a physical point of view the most significant difference between APT and BPP formulations is in the treatment of rotational effects on vibrational intensities. As it is known, for molecules that do not possess an equilibrium dipole moment, rotational motion does not affect infrared band

intensities. In these cases there is a simple matrix relation between APTs and BPPs

$$\mathbf{P}_X = \mathbf{P}_b \mathbf{V} \quad (7)$$

For molecules having a permanent dipole moment, however, there are rotational contributions to intensities, respectively dipole derivatives, for vibrations belonging to certain symmetry species.<sup>17</sup> Only after subtraction of the so called rotational corrections from the dipole moment derivatives, the latter may be regarded as intramolecular quantities. That is why, in the BPP formulation, the dipole gradients  $\partial p/\partial S_j$  forming matrix  $\mathbf{P}_s$  are corrected for rotational contributions by the  $\mathbf{R}_s$  matrix (Eqn. 6). The element of  $\mathbf{R}_s$  may be obtained by different methods.<sup>13,18</sup> In the BPP method, rotational corrections are evaluated following the heavy isotope method.<sup>13</sup> Further, the right-hand side of Eqn. (6) is also corrected for rotational effects as described earlier. Thus, both sides of the linear equations (6) are free of rotational contributions and, as a result, the elements of  $\mathbf{P}_b$ , the bond polar parameters, are also purely vibrational quantities. In the APT theory some elements of  $\mathbf{P}_X$  matrix originate from the term  $\mathbf{P}_\beta$ , and hence, from the equilibrium dipole moment. For this reason, the elements of  $\mathbf{P}_X$  may not be considered as purely vibrational quantities.

It should be noted that there is a relationship between the elements of the atomic polar tensors of a molecule expressed as<sup>4</sup>

$$\sum_{\alpha} \mathbf{P}_X^{(\alpha)} = \mathbf{O}_3 \quad (8)$$

where  $\mathbf{O}_3$  is  $(3 \times 3)$  zero matrix. In contrast, the elements of  $\mathbf{P}_b$  form a set of completely independent quantities.

Finally, it should be emphasized that mathematically it is definitely easier to evaluate atomic polar tensors — simply by matrix multiplication (Eqn. 3). Bond polar parameters, however, are determined by solving sets of linear equations (Eqn. 6). Molecular symmetry has to be accounted for in order to arrive at complete sets of linear equations. Computing programs implementing the BPP approach are available.<sup>19</sup>

#### EXAMPLES OF APPLICATIONS

In this part, the experimental gas-phase infrared intensity data for ethane,  $\text{CH}_3\text{Cl}$  and  $\text{H}_2\text{O}$  are transformed into local intensity parameters following the formalisms of the APT and BPP methods. The ethane molecule does not possess a dipole moment and, therefore, the applications of the APT and BPP methods are expected to result in rather similar, from the physical point of view, intensity parameters. The treatment of the polar molecules of  $\text{CH}_3\text{Cl}$  and  $\text{H}_2\text{O}$  should provide a deeper insight into the nature of the differences between the two infrared intensity formulations.

#### *Ethane*

The experimental  $\mathbf{P}_0$  matrix for ethane is taken from the work of Kondo and Saëki.<sup>20</sup>

The reference Cartesian system, numbering of atoms, bond directions and internal coordinates are defined in Figure 1. The symmetry coordinates

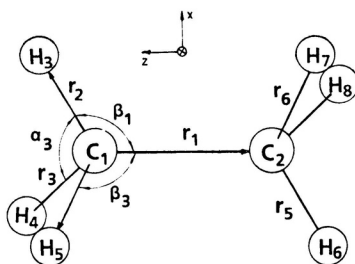


Figure 1. Definitions of internal coordinates, bond directions, cartesian reference system and numbering of atoms for ethane.

are given in Table I. Molecular geometry data used are as given in Ref. 21. The symmetrized normal coordinate transformation matrix  $L_S$  was calculated using the force field of Nakagawa and Shimanouchi.<sup>22</sup> The calculated elements of the  $P_S$  matrix for ethane are given in Table II. The sign convention for

TABLE I

*Symmetry coordinates for ethane*

$A_{2u}$

$$S_5 = 1/\sqrt{6} (\Delta r_2 + \Delta r_3 + \Delta r_4 - \Delta r_5 - \Delta r_6 - \Delta r_7)$$

$$S_6 = 1/\sqrt{2} a [\Delta a_1 + \Delta a_2 + \Delta a_3 - \Delta a_4 - \Delta a_5 - \Delta a_6] - b (\Delta \beta_1 + \Delta \beta_2 + \Delta \beta_3 - \Delta \beta_4 - \Delta \beta_5 - \Delta \beta_6)$$

$E_u$

$$S_{10a} = (1/2 \sqrt{3}) (2\Delta r_2 - \Delta r_3 - \Delta r_4 - 2\Delta r_5 + \Delta r_6 + \Delta r_7)$$

$$S_{11a} = (1/2 \sqrt{3}) (2\Delta a_1 - \Delta a_2 - \Delta a_3 - 2\Delta a_4 + \Delta a_5 + \Delta a_6)$$

$$S_{12a} = (1/2 \sqrt{3}) (2\Delta \beta_1 - \Delta \beta_2 - \Delta \beta_3 - 2\Delta \beta_4 + 2\Delta \beta_5 + \Delta \beta_6)$$

$$S_{10b} = 1/2 (\Delta r_3 - \Delta r_4 - \Delta r_6 + \Delta r_7)$$

$$S_{11b} = 1/2 (\Delta a_2 - \Delta a_3 - \Delta a_5 + \Delta a_6)$$

$$S_{12b} = 1/2 (\Delta \beta_2 - \Delta \beta_3 - \Delta \beta_5 + \Delta \beta_6)$$

$$a = 0.414957$$

$$b = 0.401428$$

dipole moment derivatives throughout this study is: a shift of a negative charge in the positive direction of a Cartesian axis corresponds to a negative dipole derivative.

TABLE II

$\Gamma_S$  matrix for ethane

$$A_{2u} \begin{matrix} P_5 = -1.1436 \\ P_6 = -0.3647 \end{matrix}$$

$$E_u \begin{matrix} P_{10} = -1.1956 \\ P_{11} = 0.2511 \\ P_{12} = -0.2974 \end{matrix}$$

Atomic polar tensors were calculated from the relation  $P_X = P_O L_S^{-1} B_S$ . The rotational polar tensor  $P_{\alpha\beta}$  (Eqn. 3) has zero elements. The entire  $P_X$  matrix for ethane is given below (in units  $D/\text{\AA}$ ).

$$\mathbf{P}_X = \left\{ \begin{array}{cc}
 \begin{array}{c} C_1 \\ \begin{pmatrix} 0.626 & 0 \\ 0 & 0.626 \\ 0 & 0 & -0.042 \end{pmatrix} \end{array} & \begin{array}{c} C_2 \\ \begin{pmatrix} 0.626 & 0 \\ 0 & 0.626 \\ 0 & 0 & -0.042 \end{pmatrix} \end{array} \\
 \\
 \begin{array}{c} H_3 \\ \begin{pmatrix} -0.611 & 0 & -0.333 \\ 0 & 0.194 & 0 \\ -0.508 & 0 & 0.014 \end{pmatrix} \end{array} & \begin{array}{c} H_4 \\ \begin{pmatrix} -0.008 & 0.348 & 0.167 \\ 0.349 & -0.409 & -0.288 \\ 0.254 & -0.439 & 0.014 \end{pmatrix} \end{array} \\
 \\
 \begin{array}{c} H_5 \\ \begin{pmatrix} -0.008 & -0.348 & 0.167 \\ -0.349 & -0.409 & 0.288 \\ 0.254 & 0.439 & 0.014 \end{pmatrix} \end{array} & \begin{array}{c} H_6 \\ \begin{pmatrix} -0.611 & 0 & -0.333 \\ 0 & 0.194 & 0 \\ -0.508 & 0 & 0.014 \end{pmatrix} \end{array} \\
 \\
 \begin{array}{c} H_7 \\ \begin{pmatrix} -0.008 & 0.348 & 0.167 \\ 0.349 & -0.409 & -0.288 \\ 0.254 & -0.439 & 0.014 \end{pmatrix} \end{array} & \begin{array}{c} H_8 \\ \begin{pmatrix} -0.008 & -0.348 & 0.167 \\ -0.349 & -0.409 & 0.288 \\ 0.254 & 0.439 & 0.014 \end{pmatrix} \end{array} \end{array} \right\} \quad (9)$$

The calculated values of the elements of the bond polar parameters matrix  $P_b$  are presented below. The elements  $s_k$  and  $d_k$  are in units  $D/\text{\AA}$  and  $D/\text{rad}$ , respectively.

$$\mathbf{P}_b = \left\{ \begin{array}{cc}
 \begin{array}{c} s_1 \\ \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \end{array} & \begin{array}{c} d_1 \\ \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \end{array} & \begin{array}{c} s_2 \\ \begin{pmatrix} -0.690 \\ 0 \\ -0.467 \end{pmatrix} \end{array} & \begin{array}{c} d_2 \\ \begin{pmatrix} 0.094 & 0 \\ 0 & 0.198 \\ -0.218 & 0 \end{pmatrix} \end{array} \\
 \\
 \begin{array}{c} s_3 \\ \begin{pmatrix} 0.345 \\ -0.598 \\ -0.467 \end{pmatrix} \end{array} & \begin{array}{c} d_3 \\ \begin{pmatrix} -0.047 & -0.171 \\ 0.081 & -0.099 \\ -0.218 & 0 \end{pmatrix} \end{array} & \begin{array}{c} s_4 \\ \begin{pmatrix} 0.345 \\ 0.598 \\ -0.467 \end{pmatrix} \end{array} & \begin{array}{c} d_4 \\ \begin{pmatrix} -0.047 & 0.171 \\ -0.081 & -0.099 \\ -0.218 & 0 \end{pmatrix} \end{array} \\
 \\
 \begin{array}{c} s_5 \\ \begin{pmatrix} 0.690 \\ 0 \\ 0.467 \end{pmatrix} \end{array} & \begin{array}{c} d_5 \\ \begin{pmatrix} 0.094 & 0 \\ 0 & -0.198 \\ -0.218 & 0 \end{pmatrix} \end{array} & \begin{array}{c} s_6 \\ \begin{pmatrix} -0.345 \\ 0.598 \\ 0.467 \end{pmatrix} \end{array} & \begin{array}{c} d_6 \\ \begin{pmatrix} -0.047 & 0.171 \\ 0.081 & 0.099 \\ -0.218 & 0 \end{pmatrix} \end{array} \\
 \\
 \begin{array}{c} s_7 \\ \begin{pmatrix} -0.345 \\ -0.598 \\ 0.467 \end{pmatrix} \end{array} & \begin{array}{c} d_7 \\ \begin{pmatrix} -0.047 & -0.171 \\ -0.081 & 0.099 \\ -0.218 & 0 \end{pmatrix} \end{array} \end{array} \right\} \quad (10)$$

The elements of the  $\mathbf{V}$  matrix (Eqn. 6) are calculated using formulas given in Ref. 8. Matrix multiplication showed that the equality  $\mathbf{P}_b \mathbf{V} = \mathbf{P}_X$  holds perfectly.

### Methyl Chloride

The experimental intensity data used in the present comparative study are taken from the work of Kondo *et al.*<sup>23</sup> In the calculations we employed internal and symmetry coordinates and molecular geometry, as defined in Ref. 23.

The normal coordinate transformation matrix  $\mathbf{L}_S$  is also as given by Kondo *et al.* (23). The Cartesian reference system, numbering of atoms and bond directions are defined in Figure 2. The dipole moment derivatives with respect to symmetry coordinates are given in Table III.

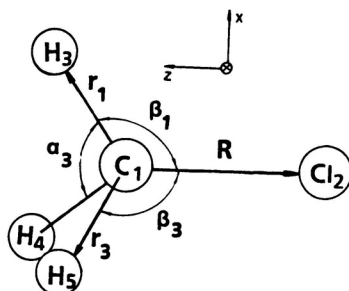


Figure 2. Definitions of internal coordinate, bond directions, cartesian reference system and numbering of atoms for methyl chloride.

TABLE III

Dipole moment derivatives with respect to symmetry coordinates for methyl chloride

$A_1 \mathbf{P}_1 = -0.6250$	$E \mathbf{P}_4 = -0.3857$
$\mathbf{P}_2 = 0.1819$	$\mathbf{P}_5 = 0.2848$
$\mathbf{P}_3 = 2.2373$	$\mathbf{P}_6 = -0.1659$

<sup>a</sup> Calculated from experimental intensity data of Kondo, Koga, Nakanaga and Sasaki<sup>23</sup> and force field of Duncan, Allan and McKean<sup>24</sup>.

The calculated atomic polar tensors matrix are the following (in units D/Å):

$$\mathbf{P}_X = \left\{ \begin{array}{cc}
 \begin{array}{ccc} \text{C} & & \\ \left( \begin{array}{ccc} 0.565 & 0 & 0 \\ 0 & 0.565 & 0 \\ 0 & 0 & 2.950 \end{array} \right) & & \begin{array}{ccc} \text{Cl} & & \\ \left( \begin{array}{ccc} -0.847 & 0 & 0 \\ 0 & -0.847 & 0 \\ 0 & 0 & -2.237 \end{array} \right) & & \\ & & \\ & & \\ \begin{array}{ccc} \text{H}_3 & & \\ \left( \begin{array}{ccc} -0.214 & 0 & -0.171 \\ 0 & 0.402 & 0 \\ -0.302 & 0 & -0.238 \end{array} \right) & & \begin{array}{ccc} \text{H}_4 & & \\ \left( \begin{array}{ccc} 0.248 & 0.267 & 0.086 \\ 0.267 & -0.060 & -0.148 \\ 0.151 & -0.262 & -0.238 \end{array} \right) & & \\ & & \\ \begin{array}{ccc} \text{H}_5 & & \\ \left( \begin{array}{ccc} 0.248 & -0.267 & 0.086 \\ -0.267 & -0.060 & 0.148 \\ 0.151 & 0.262 & -0.238 \end{array} \right) & & \end{array} \end{array} \right\} \quad (11)$$

$\mathbf{P}_X$  is the sum of two terms — vibrational polar tensor ( $= \mathbf{P}_S \mathbf{B}_S$ ) and rotational polar tensor ( $\mathbf{P}_\rho \beta$ ). The rotational polar tensor is evaluated using formulas given in Ref. 4 and an equilibrium dipole moment value of  $-1.87$  D.<sup>13</sup> The  $\mathbf{P}_S \mathbf{B}_S$  and  $\mathbf{P}_\rho \beta$  matrices are given below.

$$\mathbf{P}_s \mathbf{B}_s = \left\{ \begin{array}{cc} \text{C} & \text{Cl} \\ \begin{pmatrix} -0.162 & 0 & 0 \\ 0 & -0.162 & 0 \\ 0 & 0 & 2.950 \end{pmatrix} & \begin{pmatrix} 0.114 & 0 & 0 \\ 0 & 0.114 & 0 \\ 0 & 0 & -2.237 \end{pmatrix} \\ \\ \text{H}_3 & \text{H}_4 \\ \begin{pmatrix} -0.292 & 0 & -0.120 \\ 0 & 0.324 & 0 \\ -0.302 & 0 & -0.238 \end{pmatrix} & \begin{pmatrix} 0.170 & 0.267 & 0.060 \\ 0.267 & -0.138 & -0.104 \\ 0.151 & -0.262 & -0.238 \end{pmatrix} \\ \\ \text{H}_5 \\ \begin{pmatrix} 0.170 & -0.267 & 0.060 \\ -0.267 & -0.138 & 0.104 \\ 0.151 & 0.262 & -0.238 \end{pmatrix} \end{array} \right\} \quad (12)$$

$$\mathbf{P}_e \beta = \left\{ \begin{array}{cc} \text{C} & \text{Cl} \\ \begin{pmatrix} 0.727 & 0 & 0 \\ 0 & 0.727 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} -0.961 & 0 & 0 \\ 0 & -0.961 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ \\ \text{H}_3 & \text{H}_4 \\ \begin{pmatrix} 0.078 & 0 & -0.052 \\ 0 & 0.078 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0.078 & 0 & 0.026 \\ 0 & 0.078 & -0.045 \\ 0 & 0 & 0 \end{pmatrix} \\ \\ \text{H}_5 \\ \begin{pmatrix} 0.078 & 0 & 0.026 \\ 0 & 0.078 & -0.045 \\ 0 & 0 & 0 \end{pmatrix} \end{array} \right\} \quad (13)$$

Bond polar parameters for methyl chloride are as follows (in units D/Å and D/rad):

$$\mathbf{P}_b = \left\{ \begin{array}{cccc} s_R & d_R & s_1 & d_1 \\ \begin{pmatrix} 0 \\ 0 \\ 2.237 \end{pmatrix} & \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} & \begin{pmatrix} -0.257 \\ 0 \\ -0.361 \end{pmatrix} & \begin{pmatrix} 0.106 & 0 \\ 0 & 0.418 \\ 0.145 & 0 \end{pmatrix} \\ \\ s_1 & d_1 & s_3 & d_3 \\ \begin{pmatrix} 0.128 \\ -0.222 \\ -0.361 \end{pmatrix} & \begin{pmatrix} -0.053 & -0.362 \\ 0.092 & -0.209 \\ 0.145 & 0 \end{pmatrix} & \begin{pmatrix} 0.128 \\ 0.222 \\ -0.361 \end{pmatrix} & \begin{pmatrix} -0.053 & 0.362 \\ -0.092 & -0.209 \\ 0.145 & 0 \end{pmatrix} \end{array} \right\} \quad (14)$$

The matrix  $\mathbf{V}$  for methyl chloride is presented in Table IV. The matrix product  $\mathbf{P}_b \mathbf{V}$  is given below. The elements of  $\mathbf{P}_b \mathbf{V}$  are in units D/Å.

$$\mathbf{P}_b \mathbf{V} = \left\{ \begin{array}{cc} \text{C} & \text{Cl} \\ \begin{pmatrix} -0.282 & 0 & 0 \\ 0 & -0.282 & 0 \\ 0 & 0 & 2.951 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -2.237 \end{pmatrix} \end{array} \right\}$$

$$\begin{pmatrix} -0.214 & 0 & -0.172 \\ 0 & 0.402 & 0 \\ -0.302 & 0 & -0.238 \end{pmatrix} \begin{matrix} H_3 \\ \\ \end{matrix} \quad \begin{pmatrix} 0.248 & 0.266 & 0.086 \\ 0.267 & -0.060 & -0.149 \\ 0.151 & -0.262 & -0.238 \end{pmatrix} \begin{matrix} H_4 \\ \\ \end{matrix} \quad (15)$$

$$\left. \begin{pmatrix} 0.248 & -0.266 & 0.086 \\ -0.267 & -0.060 & 0.149 \\ 0.151 & 0.262 & -0.238 \end{pmatrix} \right\} \begin{matrix} H_5 \\ \\ \end{matrix}$$

It may be seen the  $\mathbf{P}_b\mathbf{V}$  for  $\text{CH}_3\text{Cl}$  does not equal  $\mathbf{P}_x$  (Eqn. 11).

### Water

The analysis of IR band intensities in the gas-phase for  $\text{H}_2\text{O}$  illustrates, perhaps most clearly, the differences between the APT and BPP theories. The experimental intensities are from the work of Clough *et al.*,<sup>25</sup> while the normal coordinate transformation matrix is obtained using a force field of Mills.<sup>26</sup> Molecular geometry parameters used are as follows:  $r_{\text{OH}} = 0.9572 \text{ \AA}$ ,  $\angle_{\text{HOH}} = 104.5^\circ$ .<sup>27</sup> The equilibrium dipole moment value used is  $-1.85 \text{ D}$ .<sup>13</sup> The Cartesian reference system and internal coordinates for  $\text{H}_2\text{O}$  are defined in Figure 3. The symmetry coordinates have the usual form:

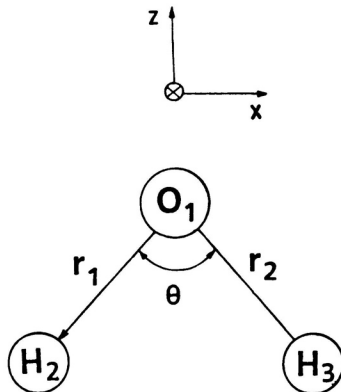


Figure 3. Cartesian reference system and internal coordinates for  $\text{H}_2\text{O}$ .

$$\begin{aligned}
 A_1 \quad S_1 &= (\Delta r_1 + \Delta r_2) / \sqrt{2} \\
 S_2 &= \Delta \theta \\
 B_1 \quad S_3 &= (\Delta r_1 - \Delta r_2) / \sqrt{2}
 \end{aligned} \quad (16)$$

The signs of the experimental  $\delta p / \delta Q_i$  gradients are as given by Zilles and Person:<sup>28</sup>  $A_1 (+ -)$ ,  $B_1 (-)$ . The  $\mathbf{P}_s$  and  $\mathbf{P}_s^{\text{corr}}$  matrices for  $\text{H}_2\text{O}$  are as follows (in units  $\text{D/\AA}$  and  $\text{D/rad}$ ):

$$\mathbf{P}_s = \begin{pmatrix} 0 & 0 & -0.9918 \\ 0 & 0 & 0 \\ -0.2341 & 0.7259 & 0 \end{pmatrix} \quad (17)$$



TABLE IV  
*V* matrix for methyl chlorida

	C <sub>1</sub>		Cl <sub>2</sub>		H <sub>3</sub>		H <sub>4</sub>		H <sub>5</sub>						
	$\Delta x_1$	$\Delta y_1$	$\Delta z_1$	$\Delta x_2$	$\Delta y_2$	$\Delta z_2$	$\Delta x_3$	$\Delta y_3$	$\Delta z_3$	$\Delta x_4$	$\Delta y_4$	$\Delta z_4$	$\Delta x_5$	$\Delta y_5$	$\Delta z_5$
$\Delta r_1$	0	0	0	0	0	-1	0	0	0	0	0	0	0	0	0
$\Delta \theta_1$	-0.562	-0.562	0	0.562	0.562	0	0	0	0	0	0	0	0	0	0
$\Delta \rho_1$	0	-0.562	0	0	0.562	0	0	0	0	0	0	0	0	0	0
$\Delta r_2$	-0.951	0	-0.310	0	0	0	0.951	0	0.310	0	0	0	0	0	0
$\Delta \theta_2$	-0.283	0	0.868	0	0	0	0.283	0	-0.868	0	0	0	0	0	0
$\Delta \rho_2$	0	-0.913	0	0	0	0	0	0.913	0	0	0	0	0	0	0
$\Delta r_3$	0.475	-0.823	-0.310	0	0	0	0	0	0	-0.475	0.823	0.310	0	0	0
$\Delta \theta_3$	0.142	-0.245	0.868	0	0	0	0	0	0	-0.142	0.245	-0.868	0	0	0
$\Delta \rho_3$	0.791	0.457	0	0	0	0	0	0	0	-0.791	-0.457	0	0	0	0
$\Delta r_4$	0.475	0.823	-0.310	0	0	0	0	0	0	0	0	0	-0.475	-0.823	0.310
$\Delta \theta_4$	0.142	0.245	0.868	0	0	0	0	0	0	0	0	0	-0.142	-0.245	-0.868
$\Delta \rho_4$	-0.791	0.457	0	0	0	0	0	0	0	0	0	0	0.791	-0.457	0

$$\mathbf{P}_s^{\text{cor}} = \begin{pmatrix} 0 & 0 & -0.9145 \\ 0 & 0 & 0 \\ -0.2341 & 0.7259 & 0 \end{pmatrix} \quad (18)$$

The  $\mathbf{P}_b$  matrix for  $\text{H}_2\text{O}$  evaluated by applying Eqn. 6 has the form (the elements of  $\mathbf{P}_b$  are in units  $\text{Å}/\text{Å}$  and  $\text{D}/\text{rad}$ ):

$$\left\{ \begin{array}{cc} s_1 & d_1 \\ \begin{pmatrix} -0.6467 \\ 0 \\ -0.1656 \end{pmatrix} & \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ -0.7259 & 0 \end{pmatrix} \end{array} \right\} \left\{ \begin{array}{cc} s_2 & d_2 \\ \begin{pmatrix} -0.6467 \\ 0 \\ -0.1656 \end{pmatrix} & \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ -0.7259 & 0 \end{pmatrix} \end{array} \right\} \quad (19)$$

The matrix product  $\mathbf{P}_b\mathbf{V}$  yields (in units  $\text{D}/\text{Å}$ ):

$$\mathbf{P}_b\mathbf{V} = \left\{ \begin{array}{cc} O_1 & H_3 \\ \begin{pmatrix} -1.0227 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1.4020 \end{pmatrix} & \begin{pmatrix} 0.5113 & 0 & -0.3959 \\ 0 & 0 & 0 \\ 0.3333 & 0 & 0.7010 \end{pmatrix} \end{array} \right\} \quad (20)$$

$$\left\{ \begin{array}{cc} H_2 \\ \begin{pmatrix} 0.5113 & 0 & 0.3595 \\ 0 & 0 & 0 \\ -0.3333 & 0 & 0.7010 \end{pmatrix} \end{array} \right\}$$

The two submatrices forming the atomic polar tensors matrix are (in units  $\text{D}/\text{Å}$ ):

$$\mathbf{P}_s\mathbf{B}_s = \left\{ \begin{array}{cc} O_1 & H_2 \\ \begin{pmatrix} -1.1090 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1.4019 \end{pmatrix} & \begin{pmatrix} 0.5545 & 0 & 0.4294 \\ 0 & 0 & 0 \\ -0.3334 & 0 & 0.7009 \end{pmatrix} \end{array} \right\} \quad (21)$$

$$\left\{ \begin{array}{cc} H_3 \\ \begin{pmatrix} 0.5545 & 0 & -0.4294 \\ 0 & 0 & 0 \\ 0.3334 & 0 & 0.7009 \end{pmatrix} \end{array} \right\}$$

$$\mathbf{P}_p\beta = \left\{ \begin{array}{cc} O_1 & H_2 \\ \begin{pmatrix} -1.0968 & 0 & 0 \\ 0 & 3.1568 & 0 \\ 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0.5484 & 0 & -0.7975 \\ 0 & 1.5785 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{array} \right\} \quad (22)$$

$$\left\{ \begin{array}{cc} H_3 \\ \begin{pmatrix} 0.5484 & 0 & 0.7975 \\ 0 & 1.5785 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{array} \right\}$$

Finally, the  $\mathbf{P}_X$  matrix evaluated as a sum of  $\mathbf{P}_s\mathbf{B}_s$  (vibrational polar tensor) and  $\mathbf{P}_p\beta$  (rotational polar tensor) has the structure:

$$\mathbf{P}_X = \left\{ \begin{array}{cc} O_1 & H_2 \\ \begin{pmatrix} -2.2058 & 0 & 0 \\ 0 & -3.1568 & 0 \\ 0 & 0 & -1.4019 \end{pmatrix} & \begin{pmatrix} 1.1029 & 0 & -0.3681 \\ 0 & 1.5785 & 0 \\ -0.3334 & 0 & 0.7009 \end{pmatrix} \end{array} \right\} \quad (23)$$

$$\left\{ \begin{array}{cc} H_3 \\ \begin{pmatrix} 1.1029 & 0 & 0.3681 \\ 0 & 1.5785 & 0 \\ 0.3334 & 0 & 0.7009 \end{pmatrix} \end{array} \right\}$$

$\mathbf{P}_b\mathbf{V}$  does not, as expected, equal  $\mathbf{P}_X$ . It is easily seen that some elements of  $\mathbf{P}_X$ , e.g. all second row elements ( $\mathbf{P}_{yy}$ ), come directly from the rotational polar tensor  $\mathbf{P}_\rho\beta$ . Since the nonzero elements of  $\mathbf{P}_\rho\beta$  contain the Cartesian components of the equilibrium dipole moment, it is evident that the final  $\mathbf{P}_X$  matrix also contains such non-vibrational contributions.

The physical interpretation of APT values is associated with the evaluation of quantities called effective atomic charges. These are found to be transferrable between structurally related molecules.<sup>29</sup> The trends of changes of BPP values in different molecules are discussed in a recent review.<sup>19</sup> Successful quantitative predictions of IR intensities for some hydrocarbons with the aid of transferred bond polar parameters were also reported.<sup>30</sup>

#### CONCLUSIONS

The results obtained show that the application of APT and BPP theories to analyzing vibrational intensities of non-polar molecules leads to parametric values related by simple transformation. In the general case of molecules having a permanent dipole moment, the interpretation of IR intensities using APT and BPP formulations results in local intensity parameters that have a distinctly different physical significance.

Bond polar parameters are purely vibrational quantities. The elements of atomic polar tensors are determined by both vibrational and rotational contributions.

#### REFERENCES

1. M. V. Volkenstein, *Dokl. Akad. Nauk SSSR* **30** (1941) 784.
2. L. A. Gribov, *Intensity Theory for Infrared Spectra of Polyatomic Molecules*, Consultant Bureau, New York 1964.
3. J. F. Biorge, J. Herranz, and J. Morcillo, *An. Quim. Ser. A* **57** (1961) 81.
4. W. B. Person and J. Newton, *J. Chem. Phys.* **61** (1974) 1040.
5. J. C. Decius, *J. Mol. Spectrosc.* **57** (1975) 348.
6. A. J. Van Straten and W. M. A. Smit, *J. Mol. Spectrosc.* **62** (1976) 297.
7. B. Galabov, *J. Chem. Phys.* **74** (1981) 1599.
8. B. Galabov, B. Niklova, and W. J. Orville-Thomas, *J. Mol. Struct.* **114** (1984) 475.
9. A. Rupprecht, *J. Mol. Spectrosc.* **89** (1981) 356.
10. A. J. Van Straten and M. A. Smit, *J. Mol. Spectrosc.* **65** (1977) 202.
11. M. Gussoni and S. Abbate, *J. Chem. Phys.* **65** (1976) 3439.
12. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York 1955.
13. A. J. Van Straten and W. M. A. Smit, *J. Mol. Spectrosc.* **56** (1975) 484.
14. B. Galabov, B. Nikolova, and W. J. Orville-Thomas, *Croat. Chem. Acta* **57** (1984) 1145.
15. Th. Kooops and W. M. A. Smit, *J. Mol. Struct.* **113** (1984) 25.
16. K. B. Wiberg and J. J. Wendoloski, *J. Phys. Chem.* **88** (1984) 586.
17. J. Overend, M. Davies (Ed.), *Infrared Spectroscopy and Molecular Structure*, Elsevier, 1963, p. 345.
18. B. L. Crawford, Jr., *J. Chem. Phys.* **20** (1952) 997.
19. B. Galabov, T. Dudev, J. R. Durig, and W. J. Orville-Thomas, *J. Mol. Struct.* **173** (1988) 111.
20. S. Kondo and S. Saeki, *Spectrochim. Acta* **29A** (1973) 735.
21. K. Kuchitsu, *J. Chem. Phys.* **49** (1968) 4456.
22. I. Nakagawa and T. Shimanouchi, *J. Mol. Spectrosc.* **39** (1971) 255.
23. S. Kondo, I. Koga, T. Nakanaga, and S. Saeki, *Bull. Chem. Soc. Jpn.* **56** (1983) 416.

24. L. J. Duncan, A. Allan, and D. C. McKean, *Mol. Phys.*, **18** (1970) 289.
25. S. Clough, Y. Beers, G. Kleinand, and L. Rothman, *J. Chem. Phys.* **59** (1973) 2254.
26. I. M. Mills, in: *Infrared Spectroscopy and Molecular Structure*, M. Davies (Ed.), Elsevier, New York 1963.
27. W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.* **24** (1956) 1139.
28. B. Zilles and W. Persson, *J. Chem. Phys.* **79** (1983) 65.
29. W. B. Persson and G. Zerbi (Eds.), *Vibrational Intensities in Infrared and Raman Spectroscopy*, Elsevier, Amsterdam 1982.
30. B. Galabov, T. Dudev, and J. R. Durig, *Croat. Chem. Acta.* **61** (1988) 569.

#### SAŽETAK

#### Odnos između tenzora atomske polarnosti i polarnih parametara veze temeljnih na IR intenzitetima

*S. Ilieva, T. Dudev i B. Galabov*

S matematičkog i fizikalnog gledišta uspoređeni su proračuni vibracijskih intenziteta s pomoću polarnih tenzora s proračunom zasnovanim na polarnim parametrima veze. Teorijska analiza ilustrirana je usporednom primjenom obaju pristupa, na eksperimentalnim podacima za etan, klorometan i vodu.