CROATICA CHEMICA ACTA CCACAA **61** (3) 569—587 (1988)

CCA-1812

YU ISSN 0011-1643
UDC 543.42
Author's Review

Bond Properties and Molecular Conformation from Vibrational Intensity Analysis

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Received February 1, 1988

Experimental vibrational intensities in infrared spectra can be transformed into quantities characterizing bond properties following the formalism of the bond polar parameters model. The theory is briefly presented. An optimized set of bond polar parameters for hydrocarbons is obtained following constraints derived from experimental spectral data and *ab initio* MO calculations. The set of intensity parameters together with transferable force constants is used in predicting the infrared spectra of individual conformers and equilibrium conformer mixtures of *n*-butane-d_0, *n*-pentane-d_0, *n*-pentane-d_{12} and *n*-hexane-d_{14}. The influence of rotational isomerism on infrared intensities in these systems is discussed.

INTRODUCTION

It has long been known that vibrational intensities in infrared and Raman spectra are molecular probes extremely sensitive to environmental changes. The measurement and interpretation of intensities have, therefore, a considerable potential in studying molecular structure and various intra- and intermolecular interactions. In spite of the well known difficulties and problems encountered usually in vibrational intensity analysis steady progress has been achieved in both theory and experiment especially during the past fifteen years[1-10]. Several theoretical models of vibrational intensities have been applied in analysing intensities to arrive at parameters characterizing details of molecular structure[1-10]. Successful quantitative predictions of vibrational intensities based on transferable intensity parameters have also been reported[1,10].

In this paper some theoretical aspects of the bond polar parameters model of infrared intensities[11,12] are reviewed. The utilization of vibrational intensity analysis in studying molecular structure is illustrated by computations of the infrared spectra of individual conformers of *n*-alkanes.

THEORY

Vibrational spectroscopy provides direct experimental evidence that chemical bonds may be regarded as separate physical entities. The isolated frequencies and local mode approaches[13,14] reflect the almost perfect interrelation between the electronic structure of individual valence bonds and the corresponding vibrational frequencies. Although the concept of »isolated vibrational intensities« associated with individual bonds has not yet been developed as a specific approach in studying the properties of valence bonds, some recent data on the Raman intensities of partially deuterated alkanes[15] show that it may have a sound pshysical basis. Generalizing, the molecular interpretation of vibrational intensities in terms of parameters associated with vibrational distortions of individual bonds apears physically plausible.

The intensity parameters in the bond polar parameters model[11,12] represent derivatives of the Cartesian components of the total molecular dipole moment with respect to coordinates describing vibrational distortions of valence bonds. These coordinates are: (1) changes in bond lengths, Δr_k, with k a bond index; (2) changes of the bond polar and azimuthal angles, $\Delta\Theta_k$ and $\Delta\varphi_k$, in a spherical polar coordinate system defined with respect to a space-fixed cartesian reference system. Bond polar parameters are, therefore, expressed as:

$$s_k = \begin{pmatrix} \partial p_x/\partial r_k \\ \partial p_y/\partial r_k \\ \partial p_z/\partial r_k \end{pmatrix} \qquad d_k = \begin{pmatrix} \partial p_x/\partial\Theta_k & \partial p_x/\partial\varphi_k \\ \partial p_y/\partial\Theta_k & \partial p_y/\partial\varphi_k \\ \partial p_z/\partial\Theta_k & \partial p_z/\partial\varphi_k \end{pmatrix} \tag{1}$$

The intensity parameters for all bonds in a molecule are elements of a matrix, P_b, with structure:

$$P_b = (s_1\, d_1\, s_2\, d_2 \ldots s_{N-1}\, d_{N-1}) \tag{2}$$

N-1 is the number of bonds in an N-atomic non-cyclic molecule.

It should be pointed out that with the definition (1) a clear separation between intensity parameters associated with intensities of stretching and deformation modes is achieved. This leads to simpler physical sense of the parameters. It is of interest to compare the angular coordinates $\Delta\Theta_k$ and $\Delta\varphi_k$ with the usual angular internal coordinates employed in vibrational analysis. An obvious advantage of the internal angular coordinates is that they are not associated with any specific direction in space. They are, therefore, quite appropriate in describing the internal vibrations of a molecule. These coordinattes cannot, however, be related to distortions of individual bonds. Even the simplest type of internal angular coordinates implies distortions of at least two bonds. Moreover, in a general case, the internal angular coordinates are not independent. The redundancy hampers the physical interpretation of any molecular quantity defined in terms of such coordinates. The coordinates $\Delta\Theta_k$ and $\Delta\varphi_k$ have the disadvantage of being associated with x, y and z directions of the reference Cartesian system. One should remember, however, that molecular dipole moments and dipole derivatives have also space-directional properties. It appears, therefore, natural to define intensity parameters in terms of variables associated with the directions in space. Besides, these coordinates form an independent set of variables and describe the change of spacial orientation of individual bonds with vibrational motion.

The elements of P_b are determined from the experimental integrated infrared band intensities in several steps. First, dipole moment derivatives with respect to normal coordinates are evaluated:

$$A_i = \frac{N_0 \pi}{3c^2} \left(\frac{\partial p}{\partial Q_i} \right)^2 \tag{3}$$

with

$$\left(\frac{\partial p}{\partial Q_i} \right)^2 = \left(\frac{\partial p_x}{\partial Q_i} \right)^2 + \left(\frac{\partial p_y}{\partial Q_i} \right)^2 + \left(\frac{\partial p_z}{\partial Q_i} \right)^2 \tag{4}$$

Individual band intensities may be determined experimentally for molecules of small and medium size possessing some reasonable symmetry. For such systems symmetry also allows one to evaluate the cartesian component of the dipole gradient $\partial p/\partial Q_i$. A knowledge of individual $\partial p_\xi/Q_i$ ($\xi = x,\ y,\ z$) components is a necessary condition for carrying further the intensity analysis. It is worth mentioning that if more than one rotational isomer of the molecule is present the separation of individual band intensities for the different conformers is almost impossible due to a strong band overlap in many parts of the spectrum.

From the set of experimental dipole moments $\partial p/\partial Q_i$ the dipole moment derivatives with respect to symmetry vibrational coordinates are usually obtained. This stage requires an accurate normal coordinate transformation matrix L_S. Using matrix notation we have

$$P_S = P_Q L_S^{-1} - R_S \tag{5}$$

P_S has the structure:

$$P_S = \begin{pmatrix} \partial p_x/\partial S_1 & \partial p_x/\partial S_2 \ldots & \partial p_x/\partial S_{3N-6} \\ \partial p_y/\partial S_1 & \partial p_y/\partial S_2 \ldots & \partial p_y/\partial S_{3N-6} \\ \partial p_z/\partial S_1 & \partial p_z/\partial S_2 \ldots & \partial p_z/\partial S_{3N-6} \end{pmatrix} \tag{6}$$

R_S is the matrix containing rotational correction terms[16].

Finally, bond polar parameters are determined from the set of dipole moment derivatives with respect to symmetry coordinates following the matrix expression[12]

$$P_S = P_b\, V\, A_S \tag{7}$$

Matrix V contains derivatives of the variables Δr_k, $\Delta \Theta_k$ and $\Delta \varphi_k$ with respect to atomic Cartesian displacements[12], while A_S defines the relation between Cartesian and symmetry vibrational coordinates[17]. In the cases of molecules possessing a permanent dipole moment, rotational contributions to the dipole gradients with respect to symmetry coordinates are present for vibrations belonging to some symmetry species. In these cases both sides of Eq. (7) have to be corrected for rotational effects. This is achieved by determining the elements of R_S (Eq. 5) and by using a heavy, non-rotating isotope in the evaluation of the A_S matrix[16]. The elements of P_b are evaluated from the sets of linear equations for each symmetry class.

To compare bond polar parameter values evaluated from the band intensities in different molecules, a further transformation is necessary. The initial set of parameters is converted into values referring to local bond Cartesian reference system.[18,19] In the bond axis system, usually marked by (x_o, y_o, z_o), the x_o axis passes through the bond. One of the other Cartesian axis lies in any existing plane of symmetry with respect to the bond site symmetry. The direction of the third axis is chosen to form a right-handed system. These transformations are

$$s_k^o = T_x s_k \tag{8}$$

$$d_k^o = T_x d_k T_\alpha \tag{9}$$

T_x is a standard transformation matrix between two Cartesian systems, while T_α gives the relation between the angular intensity coordinates defined with respect to molecular and bond reference systems. The transition from molecular to local bond system is essential in computations aimed at predicting intensities by transfer of parameters between molecules having similar structural fragments. The entire intensity analysis is carried out using a package of computer programs[10].

The intramolecular charge reorganizations accompanying vibrational motion that determine band intensities in infrared spectra are extremely complex[7,20,21]. A detailed *ab initio* MO study of Wiberg and Wendoloski[7] showed that bending of a valence bond results in charge density fluctuations in the immediate vicinity of the bond that can be expressed in terms of the point-charge approach as follows: (1) purely geometrical displacements of the equilibrium charges associate with the atoms; (2) charge flux effects; (3) creation of a bent bond moment arising from incomplete orbital following. It is evident, therefore, that direct interrelation between IR intensity parameters and equilibrium bond polarity cannot be expected. We should add here that bond polarity cannot, in principle, be defined in a unique and unambiguous way. It may, of course, be quite useful in qualitative descriptions of chemical properties. It follows, that the local intensity parameters may only be qualitatively related to bond polarity. These quantities are, in general terms, determined by:

(1) the difference in the equilibrium net electric charges on the bonded atoms; (2) charge fluctuations in the immediate vicinity of the bond undergoing vibrational displacements; (3) more distant charge flows if conjugation or other long distance effects are present.

Bond polar parameter values derived from gas-phase infrared intensities for various molecules have been compared in a recent review[10]. Some distinct trends of changes have been found. The interpretation of all parameter values in terms of simple intramolecular polarization effects is not, however, straightforward. As discussed earlier, this is mainly due to the very complex nature of the charge fluctuations determining vibrational intensities.

It is, perhaps, of greater interest to analyse the possible transferability of local infrared intensity parameters between molecules having the same bonds in a similar environment. The results obtained[10] showed that the comparable C—H parameters in methane and ethane, for example, are distinctly different and, therefore, not transferable. The same is also the case with the C—H bond polar parameters in the methyl halide series. For other molecules, however, such as ethane and propane, acetylene and methylacetylene, ethylene and benzene, the respective parameter values are quite close and transferable.

A possibility arises, therefore, to use these quantities for quantitative predictions of vibrational intensities. Combined with transferable force constants bond polar parameters may be used to compute and simulate the entire infrared spectra. In the following section these avenues are exploited in computing vibrational spectra and analyzing the molecular conformations in the *n*-alkanes.

CONFORMATION OF *n*-ALKANES AND INFRARED INTENSITIES

In a recent study[22] we calculated the infrared spectral curves of *n*-butane, *n*-pentane and *n*-hexane using the transferable force field for hydrocarbons developed by Shimanouchi *et al.*[23] and C—H and C—C bond polar parameters determined from experimental gas phase IR intensities of ethane and propane[24]. The computation of intensities involved a number of inaccuracies that had to be necessarily introduced. Firstly, the accuracy of the experimental dipole moment derivatives for propane used in evaluating methylene C—H bond polar parameters was not very high. This question is discussed in detail by Kondo and Saëki[24] and the problems arise from difficulties in resolving overlapping bands in several parts of the spectrum. In the second place, identical sets of methylene C—H bond polar parameters were used for *s-trans* and *gauche* structures, due to lack of any experimental data. As mentioned, these parameters were derived from the experimental $\partial p/\partial S_j$ derivatives for propane. Finally, any changes in the electronic structure of the C—H and C—C bonds, hence on the respective intensity parameters, upon extending the hydrocarbon chain were neglected. The latter appears to be a reasonable approximation[20].

In this section we report results on the calculations of infrared spectral curves of *n*-butane and *n*-pentane, the integrated IR intensities of *n*-pentane-d_{12} and *n*-hexane-d_{14} using optimized set of bond polar parameters for hydrocarbons. The set of intensity parameters is determined using constraints derived from experimental data and 6—31G** *ab initio* MO calculations[25].

The optimized set of bond polar parameters for C—H and C—C bonds in *n*-alkanes used in the present calculations is as follows:

a. Methyl C—H bonds

$$s_o^{\mathrm{C-H}} = \begin{pmatrix} -0.790 \\ 0 \\ 0.103 \end{pmatrix} D/\text{Å}; \qquad d_o^{\mathrm{C-H}} = \begin{pmatrix} -0.005 & 0 \\ 0 & 0.340 \\ -0.100 & 0 \end{pmatrix} D/\mathrm{rad} \qquad (10)$$

b. Methylene C—H bonds

s-trans

$$s_o = \begin{pmatrix} -0.805 \\ -0.072 \\ 0 \end{pmatrix} D/\text{Å}; \qquad d_o = \begin{pmatrix} 0.020 & 0.070 \\ -0.050 & 0.100 \\ 0.090 & 0 \end{pmatrix} D/\mathrm{rad} \qquad (11)$$

gauche

$$s_o = \begin{pmatrix} -0.815 \\ -0.075 \\ 0 \end{pmatrix} D/\text{Å}; \qquad d_o = \begin{pmatrix} -0.040 & 0.120 \\ -0.050 & 0.150 \\ 0.130 & 0 \end{pmatrix} D/\mathrm{rad} \qquad (12)$$

c. C—C bonds

$$s_o = \begin{pmatrix} -0.070 \\ 0 \\ 0.180 \end{pmatrix} D/\text{Å}; \qquad d_o = \begin{pmatrix} -0.100 & 0 \\ 0 & 0 \\ -0.030 & 0 \end{pmatrix} D/\text{rad} \tag{13}$$

These values refer to the local bond Cartesian reference system defined in Figure 1.

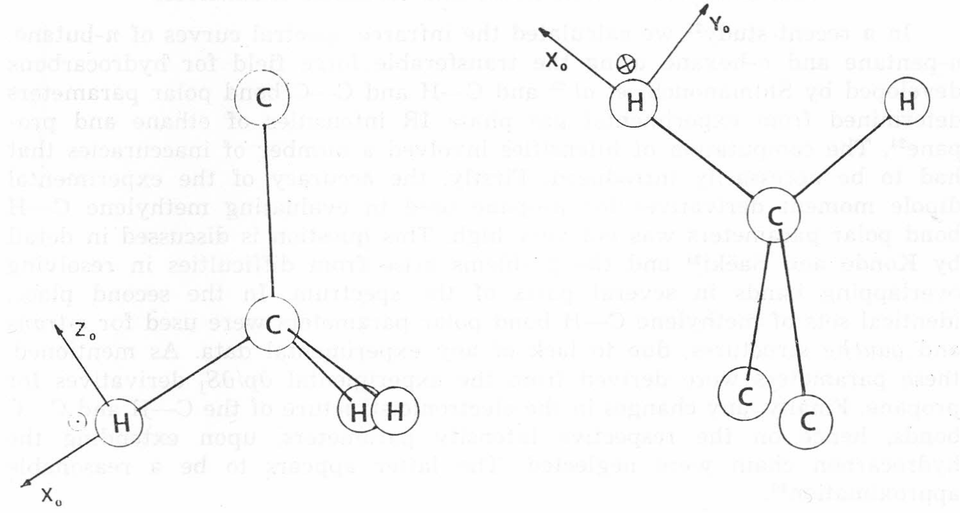

Figure 1. Definitions of local bond cartesian reference systems for methyl and methylene C—H bonds.

Some parameter values for both methyl and methylene C—H bonds differ significantly from the purely experimental estimates[22]. In Table I methylene C—H bond polar parameters derived from experimental intensity data for propane, from 6—31G** *ab initio* MO calculations and the set of optimized values are juxtaposed. Significant differences between comparable parameters are detected. For instance, the experimental parameter $\partial p_{x_o} / \partial r_{C-H}$ is much too low. This is reflected in seriously underestimated intensities for the methylene stretching bands in *n*-butane, *n*-pentane and *n*-hexane[22]. The inaccuracy of the experimental $\partial p_{x_o} / \partial r_{C-H}$ values may also be seen by comparing the respective values for methyl and methylene C—H bonds. They differ by more than 40% in the set of parameters derived from experimental dipole gradients. The *ab initio* MO calculations do not support such substantial differences. The theoretical values for $\partial p_{x_o} / \partial r_{C-H}$ are —1.026 D/Å (CH_3), —1.062 *D*/Å (CH_2 in a *trans*-structure) and —1.109 D/Å (CH_2 in a *gauche*-structure)[25]. As already mentioned, the inaccuracies in the experimental estimates should be attributed to incorrectly resolved overlapping bands in the C—H stretching region. Distinct differences between parameter values for methylene C—H bonds in *trans* and *gauche* structures are detected only in the elements of the d_o matrices.

The optimized set of local intensity parameters is obtained by taking into account the ratios and relative signs suggested by the *ab initio* results and altered to best fit the observed intensities and spectral profile for *n*-butane[25]. These parameters were used in the present work to calculate absolute IR intensities for the thermodynamically allowed conformers of *n*-butane, *n*-pentane, *n*-pentane-d_{12} and *n*-hexane-d_{14}. It should be noted that Jona, Gussoni and Zerbi[26] have carried out computations on the vibrational spectra of a series of *n*-alkanes using transferable force fields suggested by Snyder[27] and by Shimanouchi *et al.*[23] The intensity computations are based on the use of the valence optical theory. Transferable electro-optical parameters are determined and used to calculate the intensities of C_4—C_7 *n*-alkanes. The *trans*-planar structures have, however, been considered only for these molecules[26].

n-*Butane*

The computed infrared intensities for all IR active vibrational modes of *s-trans* and *gauche* *n*-butane are presented in Table II. The calculated overall intensities for a conformer mixture of 54% *s-trans* and 46% *gauche* *n*-butane are also given and compared to the experimental values reported by Finkel[28]. This rotamer ratio corresponds to an enthalpy difference between *gauche* and *trans* forms of 500 cal/mol[29]. As mentioned before, calculations of *n*-butane served as basis to obtain the optimized set of intensity parameters for C—H and C—C bonds. The agreement between the observed and calculated intensities is quite good. There are, however, two spectral intervals where the agreement is not as satisfactory, at least with the available experimental data. Such is the case of the bands in the 1487—1451 cm^{-1} region, due to methylene scissoring and methyl asymmetric deformational modes, with the methyl bands having much greater contributions to the overall intensity (Table II). If bond polar parameters governing intensities of these bands are altered to fit better the experimental intensities the spectral curve would be greatly distorted in other parts of the spectrum, especially the band near 1380 cm^{-1} which is due to methyl symmetric deformational modes. The best compromise for the elements of d_o matrices is as shown in expressions (10)—(13). In the case of *n*-pentane, as it will be seen later, the agreement between the calculated and observed intensities in the interval 1500—1450 cm^{-1} is quite satisfactory. We may assume, therefore, that the set of bond polar parameter values given by expressions (10)—(13) represents correctly the charge reorganizations accompanying vibrational distortions of C—H and C—C bonds in *n*-alkanes.

The computed frequencies and intensities of the two rotational forms of *n*-butane as well as an equilibrium mixture of conformers lead to simulated spectral curves presented in Figure 2. A band halfwidth of 30 cm^{-1} was used in the calculations. The computed spectrum of the conformer mixture compares satisfactorily with the experimental gas-phase spectrum. It should be pointed out that the force field of Shimanouchi *et al.*[23] is optimized to fit liquid phase frequencies of *n*-alkanes. As a result, some computed frequencies deviate significantly from those observed in the gas phase. In such cases the visual comparison between the simulated and observed spectral curves is not as good. A notable example in this respect is the band position of the methylene antisymmetric stretching modes with calculated frequencies in the 2910—2905 cm^{-1} range and the observed maximum at about 2935 cm^{-1}.

TABLE I

Methylene C—H Bond Polar Parameters (in Units D $Å^{-1}$ and D rad^{-1})

From exp. data for propane[a]		From 6—31G** *ab initio* calc.[b]		Optimized set	
		s-trans[c]		*s-trans*[d]	
s_o	d_o	s_o	d_o	s_o	d_o
$\begin{pmatrix} -0.570 \\ -0.113 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.102 & 0.121 \\ -0.079 & 0.153 \\ 0 & 0 \end{pmatrix}$	$\begin{pmatrix} -1.062 \\ -0.122 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.065 & 0.061 \\ -0.052 & 0.076 \\ 0.072 & 0 \end{pmatrix}$	$\begin{pmatrix} -0.805 \\ -0.072 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.020 & 0.070 \\ -0.050 & 0.100 \\ 0.090 & 0 \end{pmatrix}$
		gauche[d]		*gauche*[c]	
		s_o	d_o	s_o	d_o
		$\begin{pmatrix} -1.109 \\ -0.137 \\ 0 \end{pmatrix}$	$\begin{pmatrix} -0.039 & 0.102 \\ -0.048 & 0.128 \\ 0.129 & 0 \end{pmatrix}$	$\begin{pmatrix} -0.815 \\ -0.075 \\ 0 \end{pmatrix}$	$\begin{pmatrix} -0.040 & 0.120 \\ -0.050 & 0.150 \\ 0.130 & 0 \end{pmatrix}$

[a] From refs. 22, 24.

[b] From ref. 25.

[c] Methylene groups in *s-trans* and *gauche* *n*-butane.

[d] Methylene groups in *s-trans* and *gauche* structures in *n*-alkanes.

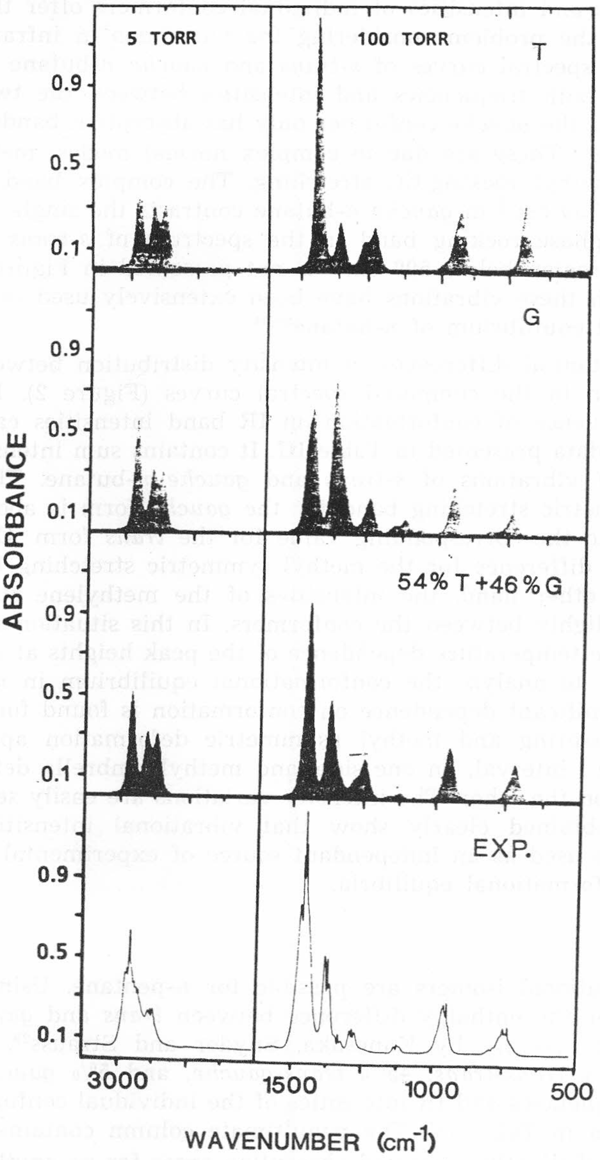

Figure 2. Simulated infrared spectral curves for *s-trans* *n*-butane (T), *gauche* *n*-butane (G), conformer mixture and experimental survey gas-phase spectrum of *n*-butane.

Of particular interest in studying vibrational spectra of *n*-alkanes is the problem of how molecular conformation affects spectral parameters, and vibrational intensities in particular. As it is well known vibrational spectra provide the most extensive experimental information on the conformational equilibria in alkanes[29–31]. So far, however, only frequencies have been used in analyzing the conformational state of these molecules. The computed spectral curves and intensities of individual conformers offer the opportunity to investigate the problem considering the variations in infrared intensities. The computed spectral curves of *s-trans* and *gauche n*-butane reveal distinct differences in both frequencies and intensities between the two forms. It is easily seen that the *gauche* conformer only has absorption bands in the 1200—1050 cm^{-1} range. These are due to complex normal modes: methylene/methyl rocking and methyl rocking/CC stretching. The complex band structure between 830 and 750 cm^{-1} in *gauche n*-butane contrasts the single infrared active methylene in-phase rocking band in the spectrum of *s-trans n*-butane. The CCC bending region below 500 cm^{-1} is not presented in Figure 2. The bands associated with these vibrations have been extensively used in studies of the conformational equilibrium of *n*-butane[30,31].

Very substantial differences in intensity distribution between conformers are easily seen in the computed spectral curves (Figure 2). In quantitative terms the influence of conformation on IR band intensities can be analyzed following the data presented in Table III. It contains sum intensities for particular types of vibrations of *s-trans* and *gauche n*-butane. The intensity of methyl asymmetric stretching band for the *gauche* form is about 30% higher as compared to the corresponding value for the *trans* form. Even more substantial is the difference for the methyl symmetric stretching band near 2880 cm^{-1}. On the other hand, the intensities of the methylene stretching bands only change slighly between the conformers. In this situation it becomes feasible to use the temperature dependence of the peak heights at about 2965 cm^{-1} and 2880 cm^{-1} to analyze the conformational equilibrium in *n*-butane. Similarly, very significant dependence on conformation is found for the band pair methylene scissoring and methyl asymmetric deformation appearing in the 1500—1450 cm^{-1} interval, on one side, and methyl umbrella deformation band at 1380 cm^{-1}, on the other. The intensity variations are easily seen in Figure 2. The results obtained clearly show that vibrational intensities in infrared spectra can be used as an independant source of experimental information in analysing conformational equilibria.

n-*Pentane*

Three rotational isomers are possible for *n*-pentane. Using the value of 500 cal/mol for the enthalpy difference between *trans* and *gauche* structures, as determined recently by Kanesaka, Snyder and Strauss[29], the conformer ratios are 50% *trans-trans*, 45% *trans-gauche*, and 5% *gauche-gauche*. The computed frequencies and IR intensities of the individual conformers of *n*-pentane are given in Table IV. The penultimate column contains the calculated intensities for distinctly separated absorption areas for an equilibrium mixture of the three rotameric forms. These are compared to the recently determined absolute gas-phase IR intensities for *n*-pentane[22]. The computed intensities are in good agreement with the experimental data. The visual comparison between experimental and simulated spectral curves, as presented in Figure 3, is also satisfactory. However, the intensity distribution of some overlapping bands is not always predicted correctly. Such is the case of the bands around 850 cm^{-1} due to methyl and methylene rocking modes. Other visual differences between the calculated and observed spectra result from incorrect calculations

TABLE II

Observed and Calculated Infrared Band Intensities for n*-Butane and Calculated Intensities for Individual Conformers*

s-trans-n-butane		*gauche-n*-butane		*n*-butane	
ν_i^{calc} (cm^{-1})	A_i^{calc} (km mol^{-1})	ν_i^{calc} (cm^{-1})	A_i^{calc} (km mol^{-1})	ΣA_i^{calc} (km mol^{-1})	ΣA_i^{obs}[a] (km mol^{-1})
		A 2964	0.89	283.79	287.43
		B 2963	65.28		
A_u 2963	55.68	B 2963	53.94		
B_u 2963	59.28	A 2963	28.54		
A_u 2910	72.09	A 2908	21.89		
B_u 2881	26.35	B 2905	51.83		
B_u 2866	61.07	A 2881	3.02		
		B 2881	5.38		
		A 2871	36.16		
		B 2867	27.81		
		A 1483	3.18	14.04	21.71
B_u 1487	0.05	B 1476	0.69		
A_u 1464	5.92	A 1463	0.69		
B_u 1451	10.98	B 1463	2.54		
		A 1459	0.44		
		B 1452	3.43		
		A 1382	3.18	8.02	7.84
B_u 1378	3.31	B 1379	7.53		
		B 1347	1.92		
		A 1342	0.50		
B_u 1295	1.74	A 1278	0.49	3.79	2.11
A_u 1258	2.91	B 1257	2.29		
		A 1173	0.53	0.72	—
		B 1133	1.03		
B_u 1012	0.36	A 1080	0.33	5.22	5.23
B_u 976	2.14	A 977	0.50		
A_u 952	3.62	B 963	2.80		
		B 955	0.53		
		A 829	0.28	3.44	3.48
A_u 729	4.61	A 789	0.24		
		B 757	1.55		
B_u 265	0.23	B 422	0.37		
		A 336	0.10		

[a] From Ref. 28.

of frequencies, as in the case of *n*-butane. Examples in this respect are the methylene antisymmetric stretching band and the methylene rocking band at about 730 cm^{-1}.

Figure 3 and the data presented in Table V illustrate the effect of conformation on vibrational intensities. For this molecule the methylene C—H stretching bands appear more sensitive to conformational variations. Changes of the sum intensity of the CH$_2$ antisymmetric stretching band are of order

TABLE III

Conformational Effects on Infrared Band Intensities in n-*Butane*

Approximate description	*trans*		*gauche*	
	Freq. range[a]	ΣA_i[b]	Freq. range[a]	ΣA_i[b]
CH_3 antisymmetric stretch	2963	114.96	2964—2963	148.65
CH_2 antisymmetric stretch	2910	72.09	2908—2905	73.72
CH_3 symmetric stretch	2881	26.35	2881	8.40
CH_2 symmetric stretch	2866	61.07	2871—2868	63.97
CH_2 scissors	1487	0.05	1483—1476	3.87
CH_3 antisymmetric deformation	1464—1451	16.60	1463—1452	7.10
CH_3 symmetric deformation	1378	3.31	1382—1379	10.71
CH_2 wag	1295	1.74	1347—1342	2.42
CH_2 twist	1258	2.91	1278—1257	2.78
C—C stretch, CH_2 and CH_3 rock	—	—	1173—1133	1.56
C—C stretch, CH_2 wag	—	—	1080	0.33
C—C stretch	1012	0.36	—	—
CH_3 rock	952	3.62	963	2.80
C—C strech, CH_3 rock	—	—	829—789	0.52
CH_2 rock	729	4.61	757	1.55
CCC bend	265	0.23	422—336	0.47

[a] Frequency range in cm^{-1}.

[b] Sum of intensities in km mol^{-1}.

of 70%. Like in the case of *n*-butane the bands in the 1500—1450 cm^{-1} interval due to methylene scissoring and methyl asymmetric deformation modes vary significantly between the three rotamers (Figure 3, Table V). Most dramatic is the intensity change for the *gauche-gauche n*-pentane. The intensity of the methyl symmetric deformation band at 1380 cm^{-1} is three to four times greater as compared to the *trans-trans* and *trans-gauche* forms. Because of the low presence of this isomer at ambient temperature, however, the effect of these intensity variations on the spectrum of the conformer mixture is small. The spectral curves of the three conformers are notably different in the region of the methylene rocking modes at around 730 cm^{-1}. Of particular interest is the band near 1000 cm^{-1} due to methyl rocking modes with a very different intensity for the *trans-trans* and *trans-gauche* conformers of *n*-pentane. In most of the cases discussed so far the frequencies of the corresponding modes are quite constant for all rotamers and do not provide a possibility to study the conformational state. We may conclude that the data for the infrared intensity distribution in the spectra of the three conformers of *n*-pentane offer, as in the case of *n*-butane, avenues for studies of the rotational isomerism.

n-*Pentane*-d_{12} *and* n-*Hexane*-d_{14}

To supplement the available spectroscopic data for *n*-alkanes we determined the absolute infrared intensities of the fully deuterated isotopomers of *n*-pentane and *n*-hexane in the gas-phase. Integrated IR intensities for well separated band areas were measured on a Perkin-Elmer model 983G ratio

TABLE IV

Observed and Calculated Infrared Band Intensities for n-*Pentane and Calculated Intensities for Individual Conformers*

TT-*n*-pentane		TG-*n*-pentane		GG-*n*-pentane		*n*-pentane	
ν_i^{calc} (cm^{-1})	A_i^{calc} (km mol^{-1})	ν_i^{calc} (cm^{-1})	A_i^{calc} (km mol^{-1})	ν_i^{calc} (cm^{-1})	A_i^{calc} (km mol^{-1})	$\Sigma A_i^{calc\,a}$ (km mol^{-1})	$\Sigma A_i^{obs\,b}$ (km mol^{-1})
		2964	38.23	B 2964	62.16	336.09	355.42
A_1 2964	47.55	2963	27.18	A 2964	10.78		
B_1 2964	23.47	2963	53.27	A 2963	33.62		
B_2 2963	61.75	2963	21.70	B 2963	23.88		
B_2 2912	95.65	2911	52.25	B 2909	35.07		
B_2 2900	2.60	2906	24.16	A 2907	42.24		
A_1 2881	0.77	2901	1.09	B 2903	35.38		
B_1 2881	12.71	2881	6.30	A 2881	6.41		
A_1 2875	3.06	2881	13.37	B 2881	7.38		
B_1 2869	0.70	2874	1.65	A 2872	12.30		
A_1 2865	82.77	2870	19.48	B 2869	60.81		
		2866	82.82	A 2868	8.00		
A_1 1486	0.15	1488	0.40	A 1489	1.95	17.02	19.45
B_1 1478	0.29	1478	1.24	B 1477	0.21		
B_2 1464	2.71	1466	1.53	A 1470	0.24		
A_1 1458	8.33	1464	7.71	B 1464	1.42		
B_1 1455	0.07	1462	1.62	A 1463	1.87		
A_1 1447	3.85	1454	3.58	B 1456	2.12		
		1452	3.41	A 1451	3.22		
		1381	2.73			6.89	6.64
B_1 1379	0.87	1379	1.38	B 1382	7.11		
A_1 1379	1.85	1363	0.96	A 1379	5.35		
B_1 1367	1.68	1344	1.50	B 1356	2.43		
A_1 1332	0.18	1301	1.28	B 1343	0.70		
		1295	0.52	A 1341	1.01		

Table IV continued.

TT-*n*-pentane		TG-*n*-pentane		GG-*n*-pentane		*n*-pentane	
ν_i^{calc} (cm^{-1})	A_i^{calc} (km mol^{-1})	ν_i^{calc} (cm^{-1})	A_i^{calc} (km mol^{-1})	ν_i^{calc} (cm^{-1})	A_i^{calc} (km mol^{-1})	$\Sigma A_i^{calc\,a}$ (km mol^{-1})	$\Sigma A_i^{obs\,b}$ (km mol^{-1})
				A 1279	0.68	2.51	1.17
B_2 1288	0.50	1264	1.09	B 1259	0.48		
B_1 1265	2.49	1237	0.85	A 1232	1.70		
B_2 1177	1.80	1167	0.73	B 1159	1.29	1.45	1.30
A_1 1148	0.19	1138	0.05	A 1134	0.77		
B_1 1068	0.31	1082	0.37	B 1092	0.16	0.33	0.42
		1028	0.44	A 1016	0.72	1.94	1.34
A_1 1043	0.54	1014	2.36	B 1006	1.72		
B_1 1021	0.07	988	0.46	A 987	0.86		
B_1 927	0.07	908	1.16	B 896	2.31	2.06	2.53
A_1 868	0.48	862	0.08	B 852	3.58		
B_2 857	0.96	846	0.74	A 846	2.34		
B_2 726	1.17	766	2.50	A 773	0.77	2.51	2.73
		732	1.61	B 733	0.66		
B_1 404	0.17	468	0.75	A 469	0.44		
A_1 400	0.01	336	0.26	B 385	1.18		

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[a] Calculated intensity for a mixture of 50% TT, 45% TG and 5% GG conformers.

[b] From Ref. 22.

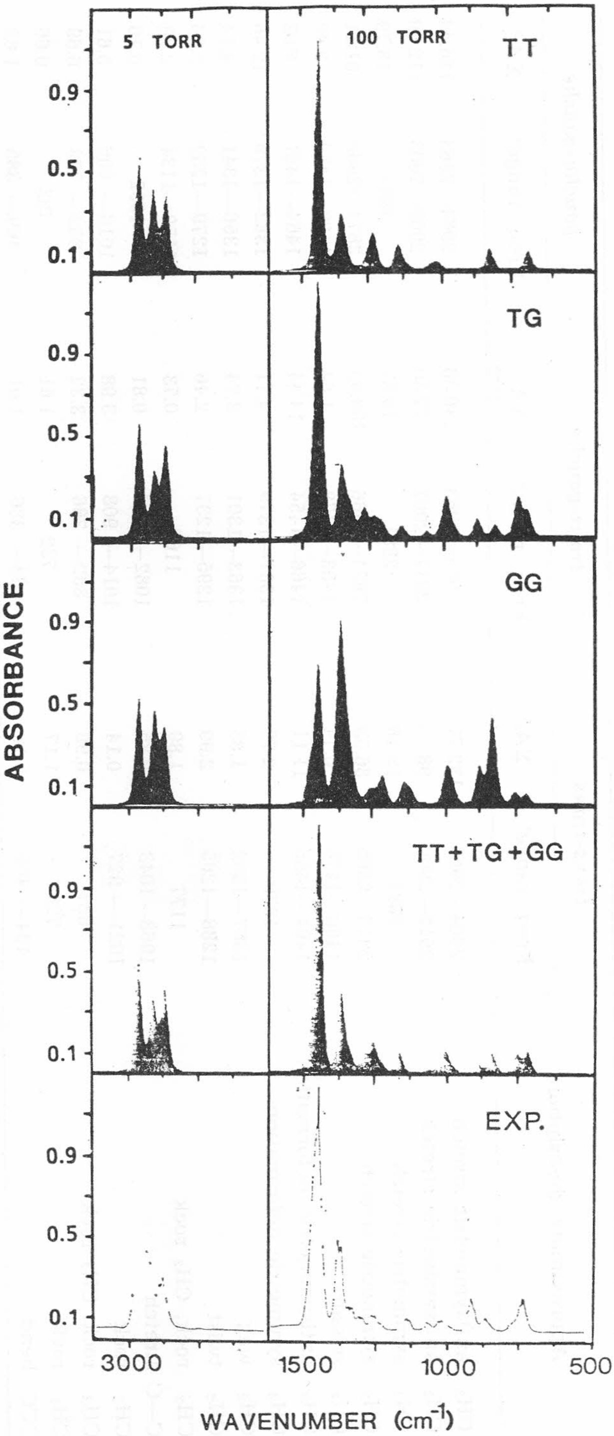

Figure 3. Simulated spectral curves for *trans-trans* (TT), *trans-gauche* (TG), *gauche-gauche* (GG), an equilibrium mixture of the three conformers (see text) and experimental survey gas-phase infrared spectrum of *n*-pentane.

TABLE V

Conformational Effects on Infrared Intensities of Some Characteristic Bands in n-*Pentane*

Approximate description	*trans-trans*		*trans-gauche*		*gauche-gauche*	
	Freq. range[a]	ΣA_i[b]	Freq. range[a]	ΣA_i[b]	Freq. range[a]	ΣA_i[b]
CH_3 antisymmetric stretch	2964—2963	132.77	2964—2963	140.38	2964—2963	130.44
CH_2 antisymmetric stretch	2912—2900	98.25	2911—2901	77.50	2909—2903	112.69
CH_3 symmetric stretch	2881	13.48	2881	19.67	2881	13.79
CH_2 symmetric stretch	2875—2865	86.53	2874—2866	103.95	2872—2868	81.11
CH_2 scissors	1486—1478	0.44	1488—1478	1.64	1489—1470	2.40
CH_3 antisymmetric deformation	1464—1455	11.11	1466—1454	14.44	1464—1451	8.63
CH_3 symmetric deformation	1379	2.72	1381—1379	4.11	1382—1379	12.46
CH_2 wag	1367—1332	1.86	1363—1301	3.74	1356—1341	4.14
CH_2 twist	1288—1265	2.99	1295—1237	2.46	1279—1232	2.86
CH_2 rock, CH_3 rock	1177	1.80	1167	0.73	1159—1134	2.06
C—C stretch	1068—1043	0.85	1082—1028	0.81	1092	0.16
CH_3 rock	1021— 927	0.14	1014— 908	3.98	1016— 896	5.61
CH_2 rock, CH_3 rock	857	0.96	862— 766	3.32	852— 773	6.69
CH_2 rock	726	1.17	732	1.61	733	0.66
CCC bend	404— 400	0.18	468— 336	1.01	469— 385	1.62

[a] Infrared frequency range in cm^{-1}.

[b] Sum of calculated intensities in km mol^{-1}.

recording spectrometer at 700 torr total pressure. This pressure was sufficient to obtain straight lines on the Beer's law plots for all band areas. The integration was carried out using the standard software provided with the Perkin-Elmer 3600 data station. The absolute intensities were determined from the slopes of the Beer's law plots. Each plot was defined by 10 to 15 individual points reflecting the dependence Apl/pl, where A is absolute IR intensity, p — the partial pressure of the hydrocarbon, and l — the path length. Each point on the plot was determined from the averaged values of A and p of three independent measurements. The samples of *n*-pentane-d_{12} and *n*-hexane-d_{14} were obtained from Cambridge Isotope Laboratories Inc., and used as purchased. The stated purity of *n*-pentane-d_{12} is higher than 98%, and of *n*-hexane-d_{14} — higher than 99%. In the measurements the spectra of non-deuterated *n*-pentane and *n*-hexane were subtracted from the observed spectrum to secure no absorption in the 3000—2800 cm^{-1} region. The experimental intensities obtained are given in Tables VI and VII.

TABLE VI

Infrared Absorption Intensities in n-*Pentane*-d_{12}

Interval of integration (cm^{-1})	A_{obs} (km mol^{-1})	A^{a}_{calc} (km mol^{-1})
2296—2009	197.84	183.22
1268—1021	18.28	12.60
1021— 917	1.23	3.34
917— 826	0.30	0.42
802— 669	1.66	1.63
669— 620	0.13	0.46
620— 501	1.88	1.37

[a] Calculated intensities for a conformer mixture of 50% *trans-trans*, 45% *trans-gauche* and 5% *gauche-gauche* *n*-pentane-d_{12}.

TABLE VII

Infrared Absorption Intensities in n-*Hexane*-d_{14}

Interval of integration (cm^{-1})	A_{obs} (km mol^{-1})	A^{a}_{calc} (km mol^{-1})
2296—2009	230.25	195.34
1260—1019	23.61	16.08
1019— 920	1.82	3.16
920— 838	0.59	0.48
798— 654	2.99	2.97
654— 501	2.12	2.01

[a] Calculated intensities for an equilibrium conformer mixture consisting of *trans-trans-trans* (18%), *trans-trans-gauche* (31%), *trans-gauche-trans* (16%), *trans-gauche-gauche* (14%), *gauche-trans-gauche* (7%) and *gauche-trans-gauche* (14%).

Using the set of bond polar parameters as given in expressions (10)—(13) and the force field of Shimanouchi *et al.*[23] we calculated the frequencies and intensities of all thermodynamically possible conformers of *n*-pentane-d_{12}

and *n*-hexane-d_{14}. These are the three conformers of *n*-pentane as discussed in the previous section and the following rotameric forms of *n*-hexane-d_{14}: *trans-trans-trans* (18$^{0}/_{0}$), *trans-trans-gauche* (31$^{0}/_{0}$), *trans-gauche-trans* (16$^{0}/_{0}$), *trans-gauche-gauche* (14$^{0}/_{0}$), *gauche-trans-gauche* (7$^{0}/_{0}$) and *gauche-trans-gauche* (14$^{0}/_{0}$).

The conformers ratios correspond to an enthalpy difference between *trans* and *gauche* structures of 500 cal/mol[29]. The computed overall intensities for separated band areas are given in Tables VI and VII and compared to the corresponding experimental values. The agreement is reasonable, though less satisfactory when compared with the result for non-deuterated alkanes. A detailed analysis of the various factors which can influence the final results is needed in order to arrive at definite conclusions about the origin of the worsened correlation between the observed and computed intensities. We should, however, mention that anharmonicity effects are quite different in the deuterated and non-deuterated alkanes and that intensity distribution in some parts of the spectra may be substantially affected by Fermi resonances[24,26]. On the basis of the intensity results it does seem that some assignments in the infrared spectra of the deuterated species may have to be altered.

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SAŽETAK

Svojstva veza i molekulska konformacija iz analize vibracijskih intenziteta

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Eksperimentalni vibracijski intenziteti u infracrvenim spektrima mogu se transformirati u veličine koje karakteriziraju svojstva veza, slijedeći formalizam modela polarnih parametara veze. Ukratko je prikazana metoda. Sažeti su i razmotreni rezultati primjene na raznim molekulskim sustavima. Dobiven je optimizirani niz polarnih parametara veza za ugljikovodike, slijedeći ograničenja izvedena iz eksperimentalnih spektralnih podataka i 6-31G** *ab initio* MO proračuna. Niz parametara intenziteta, zajedno s prenosivim konstantama sila, upotrijebljen je za predviđanje infracrvenih spektara pojedinih konformera i ravnotežnih konformerskih smjesa za *n*-butan-d_0, *n*-pentan-d_0, *n*-pentan-d_{12} i *n*-heksan-d_{14}. Raspravlja se o utjecaju rotacijske izomerije na infracrvene intenzitete tih sustava.