Dependence of Potential Energy on Inter-bond Angles in Simple Molecules

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Z. Naturforsch. **47a**, 765–767 (1992); received February 29, 1992

A method is developed to investigate the variation of potential energy contributions (V_{stretch}, V_{bend}, $V_{\text{stretch-bend}}$ and $V_{\text{stretch-stretch}}$) in simple molecules when their inter-bond angles θ are varied arbitrarily. Applied to XY_2 bend symmetric systems, the $V-\theta$ plots suggest that the actual equilibrium configuration in these molecules lies in the premises of minimum V_{bend} and zero $V_{\text{stretch-bend}}$.

In terms of internal symmetry coordinates, the average potential energy of a vibrating molecule may be written as [1]

$$\langle 2V \rangle = \sum F_{ij} \Sigma_{ij} . \tag{1}$$

Here the matrices F and Σ define the intramolecular force field and the mean square amplitudes of vibration, respectively. They are given by

$$F = \tilde{L}^{-1} \Lambda L^{-1} , \tag{2}$$

$$\Sigma = L \Delta \tilde{L} . \tag{3}$$

The elements Λ_i and Δ_i of the diagonal matrices Λ and Δ can easily be calculated from the values of the vibrational frequencies. The elements of the L matrix are significant in the sense that they relate the normal coordinates Q_i to the internal symmetry coordinates S_i in the form $S = LQ$. The evaluation of the L matrix is a basic problem in molecular dynamics, since one has to determine n^2 elements using the n vibrational frequencies as the input data. One most useful condition in this context has been provided by Wilson [2] as

$$L\tilde{L} = G , \tag{4}$$

where G is the inverse kinetic energy matrix obtainable from the molecular geometry and atomic masses. Thus the potential energy of a vibrating molecule depends on its vibrational frequencies and geometry.

It will be of fundamental interest to investigate the variation of the potential energy with the geometry of a molecule since every molecule has its own preferential geometry for stability. A mathematical formalism for this kind of investigation is developed here. As an illustration, the method is applied to XY_2 bend symmetric systems. A parametric approach developed by Ananthakrishnan et al. [3–6] to analyse vibrational problems in molecules basically involves splitting up of the L matrix into the form

$$L = L_0 C . \tag{5}$$

Here L_0 is written in the lower triangular form and is easily calculated using (4). C is an orthogonal matrix of the $n(n-1)/2$ parameters associated with each vibrational species of order n. Many simple molecules of types XY_2 bend symmetric, XY_3 planar, XY_3 pyramidal and XY_4 tetrahedral possess vibrational species of order $n = 2$, and in such cases the orthogonal matrix C of (5) can be written as

$$C = \frac{1}{\sqrt{1+c^2}} \begin{pmatrix} 1 & c \\ -c & 1 \end{pmatrix} . \tag{6}$$

Along with (5), the invariance of the F matrix under isotopic substitution enables us to write (2) as

$$\tilde{L}_0^{-1} C \Lambda \tilde{C} L_0^{-1} = \tilde{L}_{0*}^{-1} C_* \Lambda_* \tilde{C}_* L_{0*}^{-1} . \tag{7}$$

Here the asterisk refers to the case after isotopic substitution. Since C_* is orthogonal,

$$\operatorname{Trace}(\tilde{L}_{0*} \tilde{L}_0^{-1} C \Lambda \tilde{C} L_0^{-1} L_{0*}) = \operatorname{Trace} \Lambda_* . \tag{8}$$

This reduces to a simple quadratic equation of the form

$$p c^2 + q c + r = 0 . \tag{9}$$

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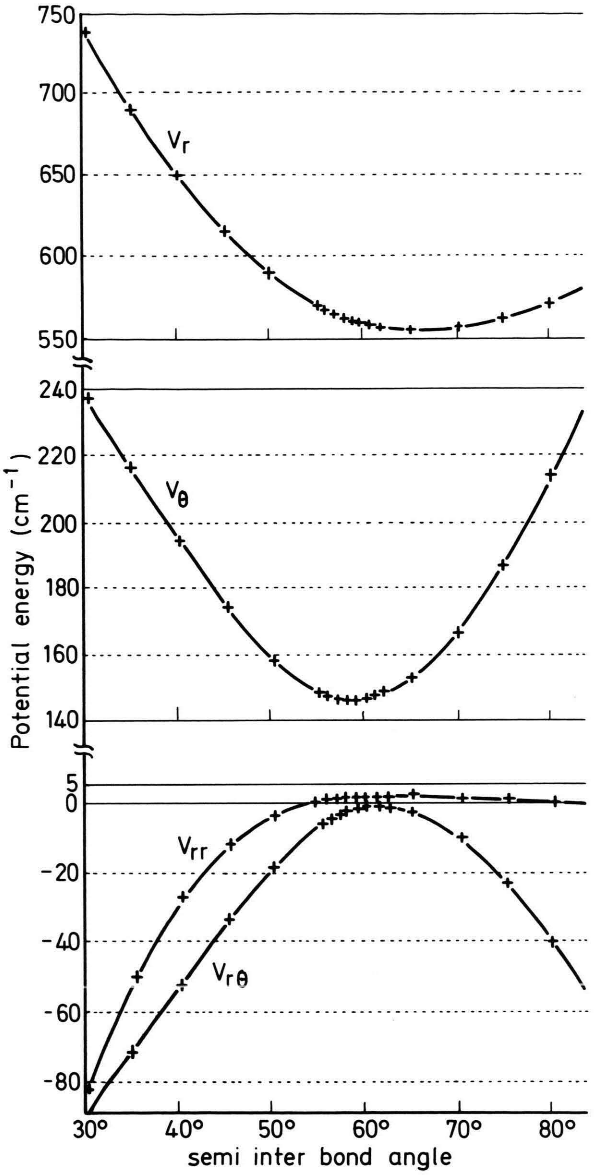

Fig. 1. Variation of potential energy with semi interbond angle in ClO_2.

Evidently, the p, q, r terms depend on molecular geometry and frequencies of the normal and isotopic molecules. Equation (9) leads to unique fixing of c and hence L.

The XY_2 bend-symmetric type molecules belong to C_{2v} symmetry and have the vibrational representation $T = 2A_1 + B_1$. The potential energy contributions for such a molecule are

$$V = V_r + V_{rr} + V_\theta + V_{r\theta}\,, \qquad (10)$$

Table 1. Semi interbond angle determined from energy considerations.

Molecule	Semi interbond angle based on		Experimental value [7–9]
	$V_{\theta\,\mathrm{minimum}}$	$V_{r\theta}=0$	
$^{95}ClO_2$ $^{97}ClO_2$	58.8°	58.8°	58.8° ± 0.5°
$^{14}NO_2$ $^{15}NO_2$	66.8°	66.8°	67.04°
H_2O D_2O	55°	55°	52.26°
H_2S D_2S	48.1°	48.1°	46.1°
H_2Se D_2Se	47.5°	47.5°	45.28°

where the four terms represent pure stretch, stretch-stretch, pure bend and stretch-bend interaction, respectively. A standard recipe for plotting the potential energy contributions as functions of interbond angle is as follows:

First fix the interbond angle at any arbitrary value and then evaluate c and L using (6)–(9). The F_{ij} and Σ_{ij} elements corresponding to vibrational species A_1 can then be determined using (2) and (3). Being a problem of order $n = 1$, the F and Σ elements corresponding to B_1 species are uniquely determined. The process is repeated for different values of interbond angle and the various contributions to V in (1) are separated out.

The molecules ClO_2, NO_2, H_2O, H_2S and H_2Se have been selected as examples. The force fields in these molecules are unambiguously fixed as the vibrational frequencies of their isotopic substituents are also readily available [7–9].

Figure 1 shows the plots of V_r, V_{rr}, V_θ and $V_{r\theta}$ against the semi interbond angle $\theta/2$ for a typical case, viz. ClO_2. Interestingly, the V_θ plot shows that the minimum of bending energy corresponds to a semi interbond angle 58.8°, whereas the value obtained from experimental data [7] is 58.8° ± 0.5°. Another important observation is that the stretch-bend interaction energy $V_{r\theta}$ becomes almost zero at the same angle. Extrema are observed in V_r and V_{rr} but the corresponding angles are far away from the equilibrium value and no physical significance can be attributed to them. Results obtained for all the molecules studied are summarised in Table 1.

A glance at the table shows that the agreement between the theoretical and experimental values is fine in the case of non-hydrides. However in the case of hydrides an error of about 4% to 5% is noticed. This is quite natural as anharmonic effects are more pronounced in hydrides and the parameter *c* of (6) is very sensitive to the vibrational frequencies of normal and isotopic molecules [6].

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