

Joint Treatment Of Large-Amplitude Motions In Free Molecules Using Spectroscopic, Electron Diffraction And Ab Initio Data

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Abstract

Motivation. The analysis of molecules with large amplitude torsions or angle bending shows that methods based on harmonic vibration theory are inadequate for describing such molecules. In recent years, the interpretation of gas-phase electron diffraction data has been based on the separation of the large-amplitude coordinates and representation the molecule as a set of “pseudo-conformers” with different value of large-amplitude coordinates (for each “pseudo-conformer” the coordinate of large amplitude is considered to be frozen).

Method. In the given paper we describe the theoretical approach based on the adiabatic separation between large- and small-amplitude motions. The Hamiltonian developed gains versatility by directly proceeding from assumed model properties to energy levels and wavefunctions. A particular form of the Hamiltonian is specified by the system to be considered.

Results. Two molecules: C₂Cl₆ and B₂F₄ were selected for illustration of the large amplitude approach described below. Two different treatments (anharmonic small-amplitude vibrations and torsional large amplitude motion) were used to approximate experimental electron diffraction intensities for these molecules. For C₂Cl₆ both treatments give reasonable approximation for experimental electron diffraction intensities. For B₂F₄ the same treatments give very different results. The small amplitude model doesn't describe this molecule.

Conclusions. The results of present investigation show that the large amplitude model has to be applied in cases where the effective potential for the large amplitude motion is far from being quadratic. At the same time, anharmonic approximation based on the small vibrations approach remains applicable even for significantly large molecular deformations when the large amplitude potential is approximately harmonic. In this case, the two models have been shown to yield compatible results.

Keywords. Electron diffraction, large amplitude motion, C₂Cl₆, B₂F₄

1 INTRODUCTION

The large-amplitude motion is usually associated with low-frequency movement of certain molecular fragments around an equilibrium position. Such kind of motion can be described by the potential energy curve with a broad and shallow single or double minimum. The separation of the small- and large-amplitude motions, based on the sufficiently large difference between the periods

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of these motions, seems to be a very useful concept. In this approach, molecules undergoing large-amplitude motion are described as a set of quasistatic intermediate configurations (pseudo-conformers) with different value of the large-amplitude coordinate. These pseudo-conformers are usually treated as ordinary molecules undergoing small vibrations of their frames excluding the motion along the large-amplitude coordinate [1].

2 MATERIALS AND METHODS

The derivation of a molecular model in the case of large-amplitude motion can be formulated on the basis of adiabatic perturbation theory. The most important feature of different treatments is the separation of the small- and large-amplitude coordinates. Nuclear displacement vectors can be defined as a combination of translations, rotations and relative motion (described in internal coordinates). The internal coordinates are usually introduced as displacements of N nuclei from the equilibrium configuration $\{\mathbf{R}^0\} = \{\mathbf{R}_1^0, \dots, \mathbf{R}_N^0\}$. They are assumed to be small as compared to interatomic distances [2].

When large-amplitude motions are present, this approach has to be modified [3]. We explicitly introduce one or more coordinates describing large-amplitude motions (for example, torsional coordinates or angle bending coordinates) ρ_i ($i = 1, 2, \dots, m$). For each set of these coordinates, we introduce a pseudo-equilibrium molecular configuration $\{\mathbf{R}^0(\boldsymbol{\rho})\}$ that delivers a minimum to the potential function with respect to all remaining internal degrees of freedom. These remaining nuclear coordinates q_k ($k = 1, 2, \dots, n$), $n = 3N - 6 - m$ are chosen so as to describe deviations from pseudo-equilibrium configurations, representing small vibrations around them. On this way, we arrive at the coordinates transformation

$$\mathbf{R}'_i = \mathbf{R} + C(\boldsymbol{\theta})\mathbf{R}_i = \mathbf{R} + C(\boldsymbol{\theta})\left[\mathbf{R}_i^0(\boldsymbol{\rho}) + \sum_{k=1}^n \mathbf{A}_{ik}(\boldsymbol{\rho})q_k\right] \quad (1)$$

where \mathbf{R}'_i are nuclear coordinates in the fixed (laboratory) frame of reference, \mathbf{R}_i are the same coordinates in the molecular frame, \mathbf{R} is a radius-vector of center of mass of molecular nuclear system, $C(\boldsymbol{\theta})$ is a rotation matrix unambiguously defined by Euler angles $\boldsymbol{\theta} = \{\theta_1, \theta_2, \theta_3\}$ (nonlinear configuration is assumed).

The treatment of pseudo-conformers as molecular systems with only a limited number of degrees of freedom (when large-amplitude coordinates are frozen) affects harmonic and anharmonic energy levels for pseudo-conformers. The coordinate transformation together with a corresponding

transformation for electronic coordinates $\mathbf{r}'_i = \mathbf{R} + C(\boldsymbol{\theta})\mathbf{r}_i$ in a Hamiltonian is executed using a standard technique for a Laplace operator. We can obtain that zero-order terms in Hamiltonian do not depend on the small-amplitude coordinates \mathbf{q} , but depend on the large-amplitude coordinates. Hamiltonian for this problem can be introduced as

$$\hat{H} = \sum_{i=4}^{\infty} \hat{T}^{(i)} + \hat{H}_{vib} \quad (2)$$

Solution to the problem $\hat{H}\psi = E\psi$ may be represented as

$$\psi(R, \theta, \rho, q, r) = \sum_{mv'} R_{mv'}(R, \theta, \rho) \psi_{mv'}(\rho, q, r) \quad (3)$$

Averaging this function over the electron and small-amplitude coordinates in the state $(0, v)$ we arrive at

$$\sum_{mv'} (\int \psi_{0v}^* [\hat{T}^{(4)} + \hat{T}^{(5)} + \dots] R_{mv'} \psi_{mv'} dq dr) + E_{0v}(\rho) R_{0v} = E R_{0v} \quad (4)$$

We shall be interested only in zero order approximation when the single nonvanishing function is $R_{0v}^{(0)}(R, \theta, \rho)$:

$$[\hat{T}_{00, vv}^{(4)}(\rho) + E_{0v}(\rho)] R_{0v}^{(0)} = E R_{0v}^{(0)} \quad (5)$$

where kinetic energy operator $\hat{T}^{(4)}$ is averaged over the electron and small-amplitude coordinates.

Eq. (5) includes terms for rotation and translation, as well as interactions between rotation and other models of motion. The final results depend on particular properties of the molecule. In general, there may be two sufficiently different cases.

If in a molecule the energies corresponding to the large-amplitude movement are much higher than rotational energies, we may proceed with splitting the terms of the last Hamiltonian into two orders of perturbation theory. In this way, one obtains equation with kinetic energy operator

$$\hat{T}_{0v}^{(4a)} = \frac{1}{2} [(\hat{\pi} - \hat{b})^* S^{(0)} (\hat{\pi} - \hat{b})]_v + F^{(0)}(\rho) = \frac{1}{2} \hat{\pi}^* S^{(0)} \hat{\pi} + F_{0v}^{(0)}(\rho) \quad (6)$$

describing only the large-amplitude motion. Hence, we arrive at the equation

$$[\hat{T}_{0v}^{(4a)} + E_{0v}(\rho)] R_{vw} = E_{vw} R_{vw} \quad (7)$$

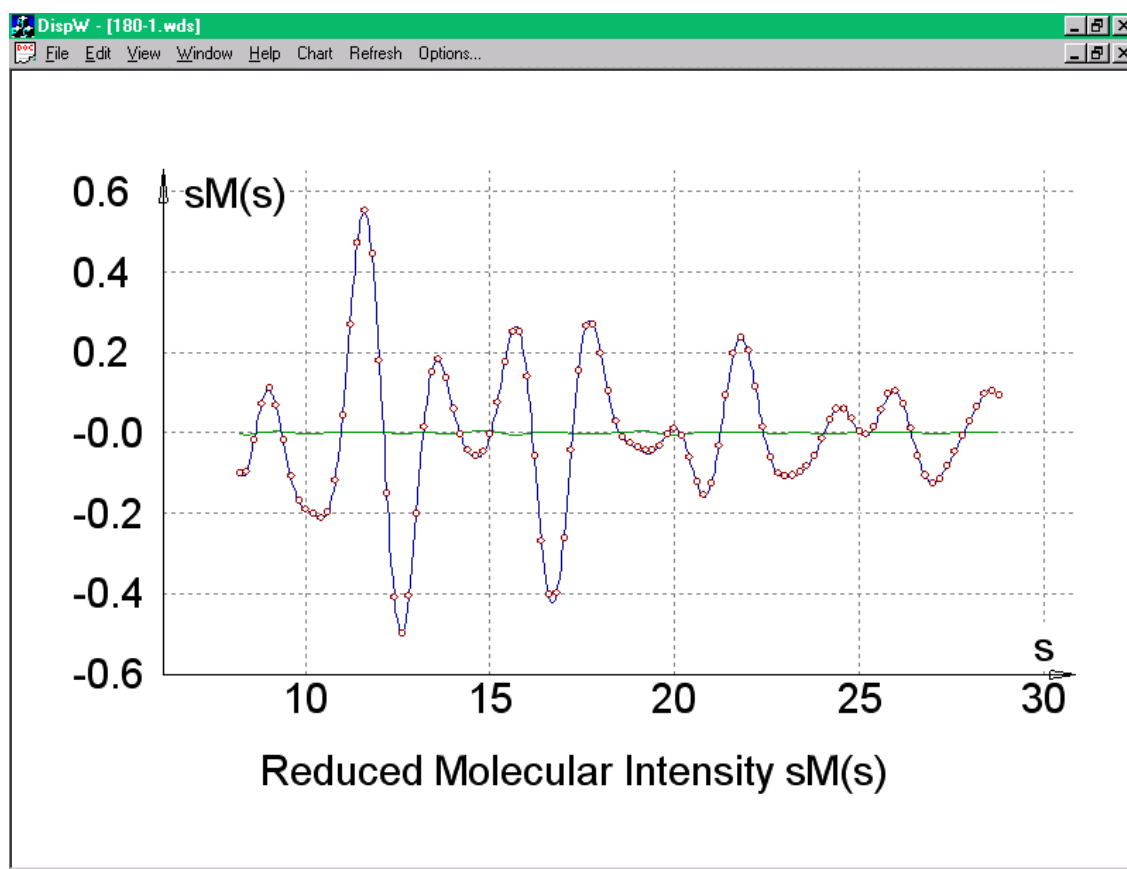
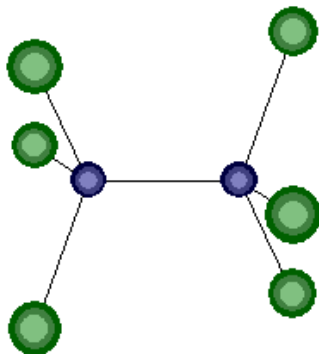
where index w is used to enumerate large-amplitude motion states. If necessary, rotation and other effects can be treated in the next order of perturbation theory.

Another case is when we can not separate large-amplitude motion. This may be in case of free internal rotation (with energies less than 1 cm^{-1}), or for linear molecules when bending can not be analyzed separately from the rotation around the molecular axis. The latter case yields

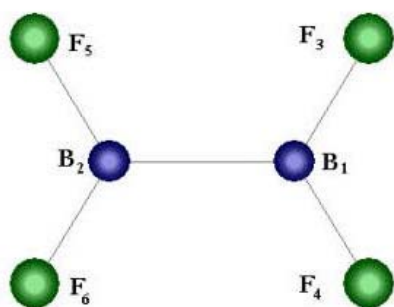
$$\hat{T}_v^{(4a)} = \frac{1}{2} \hat{\pi}^* S^{(0)} \hat{\pi} + \frac{1}{2} \hat{M}_z \sigma_{zz}^{(0)} \hat{M}_z + F_{0v}^{(0)}(\rho) \quad (8)$$

where additional effects may be considered, if necessary, at the next level of approximation.

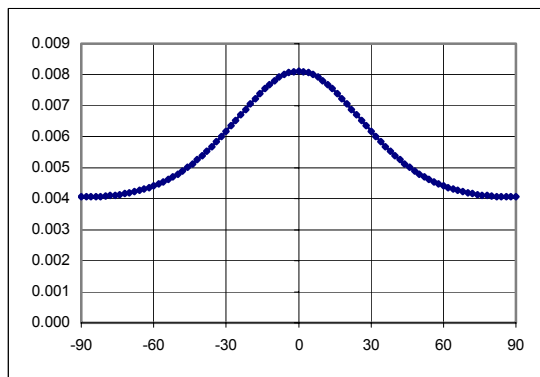
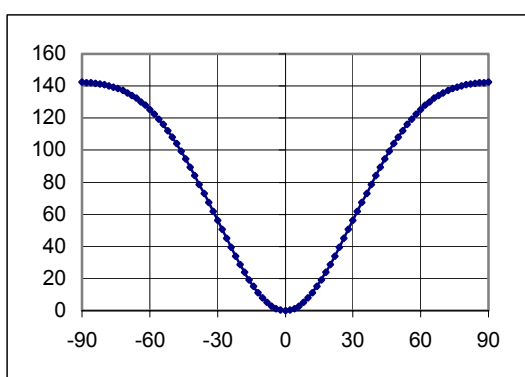
2.1 Chemical Data



Both treatments (anharmonic small-amplitude vibrations [2] and torsional large amplitude motion [3,4]) give reasonable approximation for experimental electron diffraction intensities.

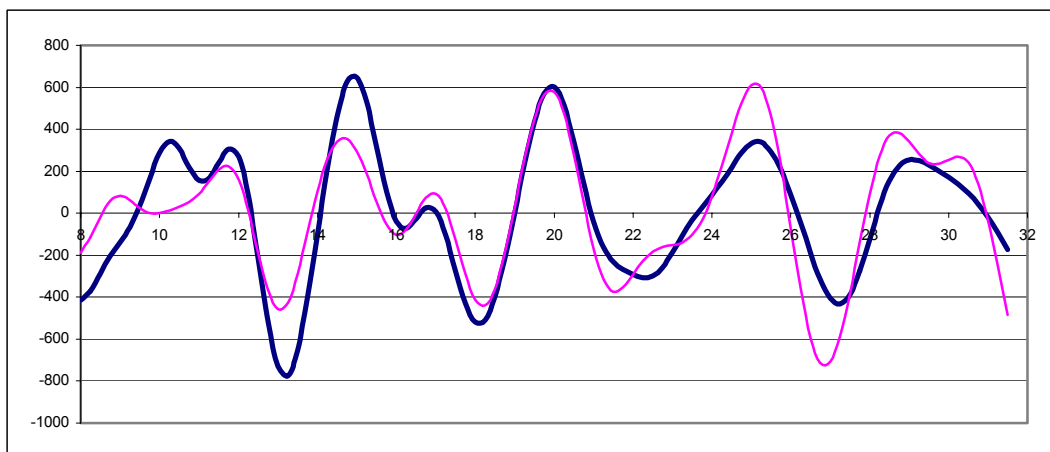


Planar equilibrium configuration



**Potential function of the internal rotation
(cm^{-1})**

**Angular distribution density
for torsion**



Molecular intensity calculated with large-amplitude model (thick curve) and within the approximation of small vibrations (thin curve).

3 RESULTS AND DISCUSSION

Two molecules: C₂Cl₆ and B₂F₄ were selected for illustration of the large amplitude approach described below. Two different treatments (anharmonic small-amplitude vibrations and torsional large amplitude motion) were used to approximate experimental electron diffraction intensities for these molecules. For C₂Cl₆ both treatments give reasonable approximation for experimental electron diffraction intensities. For B₂F₄ the same treatments give very different results. The small amplitude model doesn't describe this molecule.

4 CONCLUSIONS

The results of present investigation show that the large amplitude model has to be applied in cases where the effective potential for the large amplitude motion is far from being quadratic. At the same time, anharmonic approximation based on the small vibrations approach remains applicable even for significantly large molecular deformations when the large amplitude potential is approximately harmonic. In this case, the two models have been shown to yield compatible results.

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