



# Hydrogen bonded pyridine *N*-oxide/trichloroacetic acid complex in polar media: 2D potential energy surface and O–H···O vibration analysis using exact vibrational Hamiltonian



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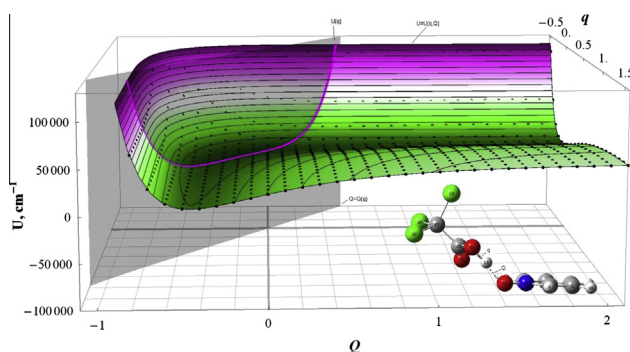
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## HIGHLIGHTS

- Exact form of kinetic energy operator for 1D and 2D vibrational Hamiltonian was derived.
- Numerical solution of 2D Schrödinger equation using Fourier series was realized.
- 1D and 2D PES for PyO/TCA complex in acetonitrile were obtained.
- The wave numbers were calculated and compared with experiment.
- Comparison of results obtained using various sets of vibrational coordinates was made.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The analysis of O–H···O stretching vibrations of the pyridine *N*-oxide/trichloroacetic acid (PyO/TCA) H-bond complex in acetonitrile solution was carried out. 1D and 2D potential energy surfaces associated with the variation of valence coordinates of hydroxyl and hydrogen bonds were calculated for this purpose in the B3LYP/cc-pVTZ approximation. The exact form of kinetic energy operator was obtained using these coordinates and Wilson's vectors. The numerical solution of 2D Schrödinger equation using Fourier series was realized and the wave numbers of O–H and O···H vibrations were calculated and compared with the results obtained using different sets of vibrational coordinates. The values of the O–H···O stretching frequencies obtained as a result of the matrix diagonalization were discussed and compared with the experimental data, the results of harmonic- and anharmonic computations as well as with the results of 3D computations of potential energy surfaces of the PyO/TCA complex using simplified form of kinetic energy operator.

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## 1. Introduction

The complexes of carboxylic acids with pyridine *N*-oxide (PyO) are the promising benchmark systems for the studies of short- and

very short O–H···O hydrogen bonding [1–3]. These systems exhibit asymmetric and flat single well potential energy surfaces (PES), which result in large-amplitude proton motion with frequent proton transfer. The interest in H-bonding and proton dynamics is significantly gained by its importance in modern material science, understanding fine features of organic and enzymatic reactions, transition state, vibrationally enhanced catalysis, etc. [4–7].

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The PyO/TCA (trichloroacetic acid) is a peculiar complex in this series having an extremely short donor–acceptor separation of 2.430 Å [1]. Recently we have performed for the title complex (PyO/TCA) the calculations of 1D and 2D PES and O–H vibrations frequencies *in vacuo* [8], 3D calculations *in vacuo* [9], 3D and anharmonic calculations in polar media (acetonitrile) [10]. It was shown that the accuracy prediction of the O–H stretching frequency increases while going from 1D to 3D model. Carrying out these 1D–3D calculations [8–10] we have used a slightly simplified Hamiltonian and the set of Cartesian coordinates of the hydroxyl hydrogen atom necessary to describe its motion. It is quite obvious that predictive ability of the calculations should increase enlarging the dimensionality of the vibrational problem as well as improving the precision of presentation of kinetic and potential energy operators in the Hamiltonian. On the other hand, it seems that the results of calculations should not depend on the choice of vibrational coordinates. Therefore the purposes of the present work were: (i) to derive the exact expression for kinetic energy operator in the Hamiltonian, which describes the vibrational motion of the hydroxyl hydrogen atom using several natural (internal) coordinates; (ii) to apply it solving 2D Schrödinger equation by using of Fourier series; (iii) to calculate 1D and 2D potential energy surfaces and the frequencies of O–H and O...H stretching vibrations in PyO/TCA complex in acetonitrile solution and to compare them with the available experimental data.

## 2. The exact form of kinetic energy operator in the Schrödinger equation

Let us to restrict the dimension of the current problem to 1D and 2D cases and to use the lengths of O–H and O...H bonds as the vibrational coordinates (denoted  $q$  and  $Q$ , respectively). Considering a restricted dimensionality of the current problem it is clear that there are three atoms in the bridge O–H...O that participate in the vibrational motion, while in the previously used models [8–10] the positions of all atoms in the H-bond complex were fixed, except the bridge hydrogen. The Schrödinger equation in the Born–Oppenheimer approximation can be written as

$$\begin{aligned} & -\frac{\hbar^2}{2M_A} \left[ \frac{\partial^2}{\partial^2 x_A} + \frac{\partial^2}{\partial^2 y_A} + \frac{\partial^2}{\partial^2 z_A} \right] \Psi - \frac{\hbar^2}{2M_B} \left[ \frac{\partial^2}{\partial^2 x_B} + \frac{\partial^2}{\partial^2 y_B} + \frac{\partial^2}{\partial^2 z_B} \right] \Psi \\ & - \frac{\hbar^2}{2M_C} \left[ \frac{\partial^2}{\partial^2 x_C} + \frac{\partial^2}{\partial^2 y_C} + \frac{\partial^2}{\partial^2 z_C} \right] \Psi + U(x_A \dots) \Psi \\ & = E\Psi, \end{aligned} \quad (1)$$

where A, B, C are understood as O, H, O, respectively,  $x_i, y_i$  and  $z_i$  are the Cartesian coordinates of  $i$ -th atom,  $M_A, M_B, M_C$  are the masses of corresponding atoms. We are interested in two internal coordinates, namely:  $q = l_{AB} - l_{AB}^0$  and  $Q = L_{BC} - L_{BC}^0$ , where  $l_{AB}$  and  $L_{BC}$  are the lengths of the corresponding bonds and  $l_{AB}^0, L_{BC}^0$  are the values of these lengths in the equilibrium configuration.

The transitions from the Cartesian to internal coordinates in the Schrödinger equation are usually based on the Podolsky transform [11]. This was realized in some recent works [12–15] as well as in the program package [16]. In the present work trying to get the exact expression of the kinetic energy operator in the  $q(Q)$  space we use the chain rule approach [17–19]. It is expected the operator in such a form to be more convenient for the computing and can be applied without any additional simplifying assumptions. The derivation consists of the following steps.

Since  $x_A$  affects only  $q$  we obtain:

$$\frac{\partial^2}{\partial^2 x_A} = \frac{\partial}{\partial x_A} \frac{\partial q}{\partial x_A} \frac{\partial}{\partial q} = \frac{\partial^2 q}{\partial x_A^2} \frac{\partial}{\partial q} + \left( \frac{\partial q}{\partial x_A} \right)^2 \frac{\partial^2}{\partial q^2}. \quad (2)$$

The similar expressions can be constructed for  $y_A$  and  $z_A$ , respectively. However,  $x_B$  affects on both  $q$  and  $Q$ . Therefore:

$$\begin{aligned} \frac{\partial^2}{\partial^2 x_B} &= \frac{\partial^2 q}{\partial x_B^2} \frac{\partial}{\partial q} + \frac{\partial^2 Q}{\partial x_B^2} \frac{\partial}{\partial Q} + \left( \frac{\partial q}{\partial x_B} \right)^2 \frac{\partial^2}{\partial q^2} + \left( \frac{\partial Q}{\partial x_B} \right)^2 \frac{\partial^2}{\partial Q^2} \\ &+ 2 \frac{\partial q}{\partial x_B} \frac{\partial Q}{\partial x_B} \frac{\partial^2}{\partial q \partial Q}. \end{aligned} \quad (3)$$

The analogous formulas can be obtained for  $y_B$  and  $z_B$ . Hence,

$$\begin{aligned} & -\frac{\hbar^2}{2M_B} \left[ \frac{\partial^2}{\partial^2 x_B} + \frac{\partial^2}{\partial^2 y_B} + \frac{\partial^2}{\partial^2 z_B} \right] \Psi \\ &= -\frac{\hbar^2}{2M_B} \left[ \frac{\partial^2 Q}{\partial x_B^2} + \frac{\partial^2 Q}{\partial y_B^2} + \frac{\partial^2 Q}{\partial z_B^2} \right] \frac{\partial}{\partial Q} \Psi - \frac{\hbar^2}{2M_B} \left[ \left( \frac{\partial Q}{\partial x_B} \right)^2 + \left( \frac{\partial Q}{\partial y_B} \right)^2 \right. \\ &+ \left. \left( \frac{\partial Q}{\partial z_B} \right)^2 \right] \frac{\partial^2}{\partial Q^2} \Psi - \frac{\hbar^2}{2M_B} \left[ \frac{\partial^2 q}{\partial x_B^2} + \frac{\partial^2 q}{\partial y_B^2} + \frac{\partial^2 q}{\partial z_B^2} \right] \frac{\partial}{\partial q} \Psi \\ &- \frac{\hbar^2}{2M_B} \left[ \left( \frac{\partial q}{\partial x_B} \right)^2 + \left( \frac{\partial q}{\partial y_B} \right)^2 + \left( \frac{\partial q}{\partial z_B} \right)^2 \right] \frac{\partial^2}{\partial q^2} \Psi \\ &- \frac{\hbar^2}{2M_B} 2 \left[ \frac{\partial q}{\partial x_B} \frac{\partial Q}{\partial x_B} + \frac{\partial q}{\partial y_B} \frac{\partial Q}{\partial y_B} + \frac{\partial q}{\partial z_B} \frac{\partial Q}{\partial z_B} \right] \frac{\partial^2}{\partial q \partial Q} \Psi, \end{aligned}$$

In the next steps of this treatment we get:

$$\begin{aligned} & -\frac{\hbar^2}{2M_A} \left[ \frac{\partial^2}{\partial^2 x_A} + \frac{\partial^2}{\partial^2 y_A} + \frac{\partial^2}{\partial^2 z_A} \right] \Psi - \frac{\hbar^2}{2M_B} \left[ \frac{\partial^2}{\partial^2 x_B} + \frac{\partial^2}{\partial^2 y_B} + \frac{\partial^2}{\partial^2 z_B} \right] \Psi \\ & - \frac{\hbar^2}{2M_C} \left[ \frac{\partial^2}{\partial^2 x_C} + \frac{\partial^2}{\partial^2 y_C} + \frac{\partial^2}{\partial^2 z_C} \right] \Psi \\ &= \left[ -\frac{\hbar^2}{2M_A} \left[ \frac{\partial^2 q}{\partial x_A^2} + \frac{\partial^2 q}{\partial y_A^2} + \frac{\partial^2 q}{\partial z_A^2} \right] - \frac{\hbar^2}{2M_B} \left[ \frac{\partial^2 q}{\partial x_B^2} + \frac{\partial^2 q}{\partial y_B^2} + \frac{\partial^2 q}{\partial z_B^2} \right] \right] \frac{\partial}{\partial q} \Psi \\ &+ \left[ -\frac{\hbar^2}{2M_B} \left[ \frac{\partial^2 Q}{\partial x_B^2} + \frac{\partial^2 Q}{\partial y_B^2} + \frac{\partial^2 Q}{\partial z_B^2} \right] - \frac{\hbar^2}{2M_C} \left[ \frac{\partial^2 Q}{\partial x_C^2} + \frac{\partial^2 Q}{\partial y_C^2} + \frac{\partial^2 Q}{\partial z_C^2} \right] \right] \frac{\partial}{\partial Q} \Psi \\ &+ \left[ -\frac{\hbar^2}{2M_A} \left[ \left( \frac{\partial q}{\partial x_A} \right)^2 + \left( \frac{\partial q}{\partial y_A} \right)^2 + \left( \frac{\partial q}{\partial z_A} \right)^2 \right] \right. \\ &- \left. \frac{\hbar^2}{2M_B} \left[ \left( \frac{\partial q}{\partial x_B} \right)^2 + \left( \frac{\partial q}{\partial y_B} \right)^2 + \left( \frac{\partial q}{\partial z_B} \right)^2 \right] \right] \frac{\partial^2}{\partial q^2} \Psi \\ &+ \left[ -\frac{\hbar^2}{2M_B} \left[ \left( \frac{\partial Q}{\partial x_B} \right)^2 + \left( \frac{\partial Q}{\partial y_B} \right)^2 + \left( \frac{\partial Q}{\partial z_B} \right)^2 \right] \right. \\ &- \left. \frac{\hbar^2}{2M_C} \left[ \left( \frac{\partial Q}{\partial x_C} \right)^2 + \left( \frac{\partial Q}{\partial y_C} \right)^2 + \left( \frac{\partial Q}{\partial z_C} \right)^2 \right] \right] \frac{\partial^2}{\partial Q^2} \Psi \\ &+ \frac{\hbar^2}{M_B} \left[ \frac{\partial q}{\partial x_B} \frac{\partial Q}{\partial x_B} + \frac{\partial q}{\partial y_B} \frac{\partial Q}{\partial y_B} + \frac{\partial q}{\partial z_B} \frac{\partial Q}{\partial z_B} \right] \frac{\partial^2}{\partial q \partial Q} \Psi. \end{aligned} \quad (4)$$

Using formalism of Wilson's  $\vec{s}$  vectors [20] one can obtain:

$$\begin{aligned} \text{grad}_{r_A}(q) &= \frac{\partial q}{\partial x_A} + \frac{\partial q}{\partial y_A} + \frac{\partial q}{\partial z_A} = \vec{s}_{r_A}^q, \\ \left( \frac{\partial q}{\partial x_A} \right)^2 + \left( \frac{\partial q}{\partial y_A} \right)^2 + \left( \frac{\partial q}{\partial z_A} \right)^2 &= (\vec{s}_{r_A}^q)^2, \end{aligned} \quad (5)$$

$$\frac{\partial^2 q}{\partial x_B^2} + \frac{\partial^2 q}{\partial y_B^2} + \frac{\partial^2 q}{\partial z_B^2} = \text{div} \vec{s}_{r_B}^q. \quad (6)$$

and substituting (5) and (6) to (4) we get

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