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The Very Short Hydrogen Bond in the Pyridine *N*-Oxide – Trichloroacetic Acid Complex: An Inelastic Neutron Scattering and Computational Study

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Dedicated to Professor Dušan Hadži on the occasion of his 90th birthday

Abstract

We have investigated the dynamics of the very short hydrogen bond ($R_{O...O}$ = 2.430 Å) of the pyridine *N*-oxide trichloroacetic acid complex in the solid state by combining vibrational spectroscopy using inelastic neutron scattering with extensive computational studies and analysis of the vibrational spectra. The Density Functional Theory (DFT) computational models used ranged from the isolated gas phase cluster to three approaches with periodic boundary conditions, namely CRYSTAL, CPMD and VASP, all of which, however calculate frequencies in the harmonic approximation. While all but the gas phase calculation yield structural parameters for the hydrogen bond in reasonable agreement with experiment, only the periodic VASP and CPMD approaches resulted in INS spectra (calculated with the program a-climax) that adequately reproduced some of the key features of the experimental spectrum related to the in-plane and out-of-plane bending modes of the H-bond. No clear indication was found either in experiment or computational studies for OH stretching. More sophisticated and time-consuming calculations are therefore indicated to elaborate on the hydrogen bond dynamics including molecular dynamics simulations or the use of quantum dynamics on multidimensional potential energy surfaces.

Keywords: Short hydrogen bonding, vibrational dynamics, inelasting neutron scattering, periodic DFT calculations, harmonic analysis.

1. Introduction

The detailed understanding of the structure and dynamics of short hydrogen bonding is a long standing problem and continues to pose a significant challenge to experimental and computational investigations.[1,2] Short hydrogen bonding has also been implicated in a variety of physical or chemical processes, one of the most recent of which is crystalline croconic acid, the first reported single-phase hydrogen-bonded organic material, which exhibits ferroelectric properties. This functionality relies on a network of short hydrogen bonds in the crystalline structure.[3]

An improved understanding of the features of short hydrogen bonding has been greatly facilitated by studies of benchmark examples, which are typically small and stable molecules or adducts which can be readily characterized not only by a variety of experimental techniques, but also by accurate theoretical calculations. Such investigations offer profound, complementary and reliable information on many of the essential aspects of the structure and dynamics of this type of H-bond. Perhaps the best known family of benchmark intramolecular hydrogen-bonded systems are the enolized β-diketones,[4–16] which include a large set of compounds with diverse proton potential energy profiles (from symmetric double well to flat and asymmetric single well). Another set of promising benchmark systems for short O-H…O hydrogen bonding are complexes between carboxylic acids and pyridine *N*-oxide or its derivatives (or analogs).[17–19] These systems exhibit in most cases asymmetric and flat single well proton potentials, which result in large-amplitude proton dynamics with occurrences of frequent proton transfer. Examples of both intra- and intermolecular hydrogen bonds exist within this family, but most importantly, these systems were found in almost all cases to have extremely short O…O separation, barely above 2.40 Å (but rarely above 2.50 Å). The most prominent member of this family is picolinic acid *N*-oxide (PANO, Fig. 1), whose short intramolecular hydrogen bond has been extensively characterized by a variety of experimental and computational techniques and has been for long time at the focal point of our group's research activities, led and inspired by Prof. Hadži.[20–23]

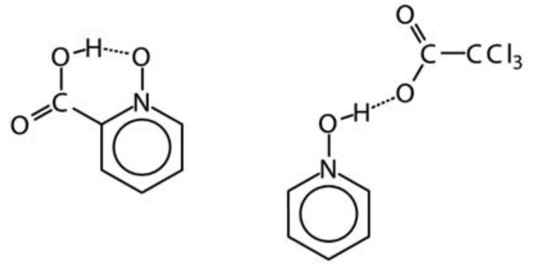

Figure 1. The structure of picolinic acid *N*-oxide (PANO) and pyridine *N*-oxide – trichloroacetic acid complex (PyO-TCA).

An interesting intermolecular analog of PANO is the adduct between pyridine *N*-oxide and trichloroacetic acid (PyO-TCA, Fig. 1) with a extremely short donor-acceptor separation of 2.430 Å. The proton was found to be located nearer to the acceptor side of the hydrogen bond, namely closer to the PyO molecule (Fig. 1). The structure of this complex was obtained by X-ray diffraction in 1974[24] and subsequently by neutron diffraction in 1991.[18] A principal challenge for the characterization of this adduct is the fact that proton transfer is feasible, which in turn calls for characterization by means of vibrational spectroscopy supported by a variety of computational approaches, including vibrational analysis, multi-dimensional proton potential calculations, and molecular dynamics simulation. We also found it to be essential to explore the influence of the environment on the preferred location of the proton, as the proton potential and thus the equilibrium proton position depend substantially on the model used, particularly on the treatment of the condensed phase environment.[25] For example, gas-phase and solvent reaction field (SCRF)[26] calculations predict proton transfer to be energetically unfavorable, but the inclusion of a cluster of explicit neighboring PyO-TCA adducts, taken from the crystal structure was found to facilitate proton transfer.[25] The structure with the proton located on the acceptor side was also found by Balevičius et al. by using the PBE1PBE/6-311++G(d,p) level of theory in conjunction with the SCRF-IEFPCM approach with highly polar acetonitrile as solvent.[27–29] Thus, the PyO-TCA adduct is particularly interesting for its susceptibility to the effects of environment, in that the slight change in the model of the environment can result in a major displacement of the hydrogen atom, possibly accompanied by substantial changes of certain geometric parameters and charge redistribution. Both experimental and theoretical investigations are therefore essential to elaborate this problem.

Vibrational spectroscopy by inelastic neutron scattering is exceptionally well suited for the studies of hydrogen bonds in crystalline materials because of the sensitivity of neutrons to hydrogen, the utility of isotopic substitution of D for H in the hydrogen bond, and the fact that INS spectra can be readily calculated[30] using sets of frequencies and vibrational amplitudes obtained from any one of a considerable number of *ab-initio* computational methods.

The present study therefore is aimed at characterization of the structure and vibrational properties of the hydrogen bonding in the PyO-TCA complex by means of INS spectroscopy and DFT calculations. The calculations relied on various models of the environment, ranging from the bare (isolated) PyO-TCA adduct, a continuum model of the solvent reaction field, and explicit treatment of the crystal field based on periodic boundary conditions.

In its essence, this work demonstrates the complexity of the problem of adequately describing the hydrogen bond dynamics of such short hydrogen bonds even when spectroscopic and advanced computational methods are combined. This work may be regarded as an introductory part to the ongoing, more concise study of the PyO-TCA adduct in various phases by a large body of experimental and computational techniques.[31] In honor of our long-lasting collaboration with Prof. Hadži, we fully expect ourselves to be enlightened on this complex problem more profoundly in the near future.

2. Experimental Details

Stoichiometric amounts of the reagents (trichloroacetic acid and pyridine *N*-oxide) were mixed in methanol. The solution was stirred at room temperature for a few minutes. The solvent was then removed on a rotary evaporator at 0 °C. The material thus obtained was recrystallized in methanol and dried overnight under high vacuum (10^{-5} torr at 0 °C. Inelastic neutron scattering spectra were obtained on the inverse geometry Filter Difference Spectrometer[32] of the Lujan Center at Los Alamos National Laboraotory. Approximately 2 g of the material was loaded into an Al sample container under He atmosphere for data collection at 10 K. Data treatment was carried out with standard programs for the FDS spectrometer.

3. Computational Details

The isolated PyO-TCA complex was treated at the B3LYP/6-31+G(d,p) level of theory with the *Gaussian*

09[33] program package. Periodic models were built on the basis of the neutron diffraction data of Eichhorn[18] and strictly followed periodic boundary conditions within the $P2_1/c$ space group symmetry. Three different program packages (*Crystal 06,*[34] CPMD v. 3.13.2,[35] and VASP v. 4.6.28[36]) were used, and the following approaches for periodic DFT modeling were employed: (*i*) With the *Crystal 06* program the B3LYP functional was adopted, and the localized atomic basis set 6-31G(d,p) was used to build periodic crystalline orbitals. (*ii*) With CPMD, the BLYP functional was chosen, and the core electrons were approximated by either Goedecker[37] or Troullier-Martins[38] atomic pseudopotentials; a plane-wave basis set with kinetic energy cutoff of 120 and 80 Ry was used in conjunction with Goedecker and Troullier-Martins pseudopotentials, respectively (please note that the CPMD calculations are labeled "CPMD-SG" and "CPMD-TM", respectively, according to the type of pseudopotential). (*iii*) With VASP, the PAW-PBE pseudpotential[39] was used in conjunction with Vanderbilt ultrasoft pseudopotentials,[40] and a plane-wave kinetic energy cutoff of 29.40 Ry (400 eV). A 2 × 2 × 2 Monkhorst-Pack mesh of *k*-points was used with all periodic calculations. The density functionals used in this study are otherwise frequently used and proved on many examples to provide reliable description of electron density in molecular systems. Based on our previous experience, a 2 × 2 × 2 *k*-point mesh yields reasonably converged values of energies, forces and frequencies, and provides a good compromise between computational accuracy and cost, and similar is true of the employed cutoff values.

In all cases a geometry optimization was performed first, which was followed by frequency calculation within the harmonic approximation, both of which are standard routines in all quantum chemistry programs. In the periodic calculations the unit cell was kept fixed during the optimization. While analytic second derivatives are available in *Gaussian 09*, a finite difference method was employed for numerical evaluation of second derivatives with CPMD and VASP, using displacement steps of 0.0052 Å (0.01 a.u.) and 0.015 Å, respectively.

The INS spectra were computed with the program a-Climax 5.5.0[41] with the harmonic frequencies and atomic displacements of the normal modes being used as input. All overtones up to 0 → 10 were included as well as the contribution of phonon wings to the spectra. Apart from the models described above we also used the previously optimized structure and normal modes of PyO-TCA provided by Balevičius et al.[27,29] Their calculation at the PBE1PBE/6-311++G(d,p) level of theory included the influence of a polar solvent (acetonitrile), represented by a self-consistent reaction field (SCRF) of Tomasi and coworkers,[26] featuring proton transfer from the donor to the acceptor site of the hydrogen bond.

4. Results and Discussion

A reasonable test for reliability of computational methodologies is a comparison of the structures derived from the geometry optimization with that determined by neutron diffraction.[18] Since the use of neutrons makes it possible to accurately determine of the location of the proton, the calculated proton position may readily be confronted with the experimental data. Table 1 lists the optimized and experimental characteristic hydrogen bond distances for PyO-TCA.

Table 1. Calculated and measured characteristic distances of the hydrogen bond in the PyO-TCA complex.

	$R_{O...O}$ [Å]	R_{O-H} [Å]	$R_{O...H}$ [Å]
Gaussian, isolated	2.570	1.022	1.562
Gaussian, SCRF*	2.438	1.361	1.080
CPMD, TM	2.459	1.364	1.097
CPMD, SG	2.475	1.378	1.100
Crystal	2.439	1.364	1.079
VASP	2.417	1.230	1.191
Experimental	2.430	1.284	1.148

* Taken from Refs. [27] and [29].

The gas-phase model was found to give results which differ significantly from the experimental structure with an O...O distance being notably too long (by 0.14 Å), and a proton position nearer the donor molecule (TCA). This is clearly in disagreement with the experimental structure. All the other models, however, are in quite reasonable agreement with experiment: the proton is located at the acceptor site of the hydrogen bond, and the O...O distance ranges from 2.417 to 2.475 Å, as compared to the experimental value of 2.430 Å. Moreover, while SCRF and periodic calculations correctly predict the angle between the planes of the PyO ring and that of the carboxylic group of TCA to be about 50 degrees, the gas-phase model has the PyO ring and the carboxylic group almost coplanar. Most of the SCRF and periodic calculations place the proton slightly farther from the midpoint of the O...O line than the experimental observation. The measured difference of the distance between hydrogen and donor oxygen ($R_{O–H}$ in Table 1) and the distance between hydrogen and acceptor oxygen ($R_{O...H}$) is 0.136 Å, while the calculated values are around 0.27 Å in most cases. An exception to this is the VASP calculation, where the proton is found to be located nearly at the midpoint of the hydrogen bond. While the gas-phase calculation is obviously less reliable, the SCRF and periodic models all correctly predict a structure of the complex with proton transfer and a very short donor-acceptor separation. We note that in a our attempts to induce the proton transfer by applying the SCRF, only the PBE1PBE/6-311++G(d,p)/SCRF approach originally used by Balevičius[27] was successful. As the equilibrium proton position is quite sensitive to the density functional and SCRF settings, one may expect that the energy difference between the structures with and without proton transfer calculated by the SCRF models, is very small: the PBE1PBE/6-311++G(d,p)/SCRF estimate is 0.17 kcal/mol.[29] This is consistent with the expected asymmetric, flat single-well or low-barrier double-well type of hydrogen bond in the PyO-TCA complex.

Vibrational spectra offer considerably more detailed information on the structure and dynamics of this system. Although most of the computational methodologies used in this work give fairly similar results when only the structure is considered, large differences appear when their calculated INS spectra (Fig. 2) are compared. Individual components of the spectra have been identified and peaks corresponding to the characteristic hydrogen bond modes (also called "protonic modes") are labeled accordingly.

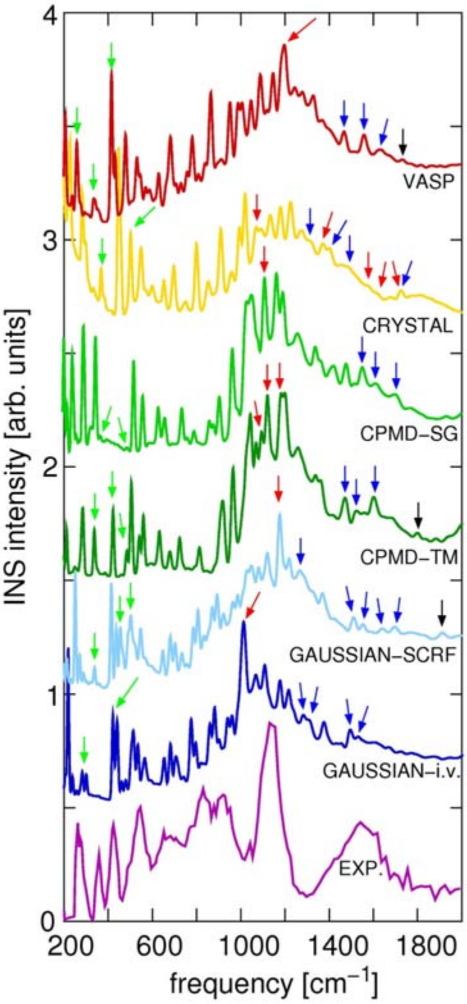

Figure 2. INS spectra of the PyO-TCA complex calculated by various approaches, and the experimental INS spectrum. Arrows denote the peaks which correspond to characteristic hydrogen bond ("protonic") modes. Black arrows: OH stretching; blue arrows: in-plane OH bending; red arrows: out-of-plane OH bending; green arrows: O...O (donor-acceptor) stretching.

The experimental INS spectrums exhibits two peaks that can readily be attributed to the hydrogen-bond proton, namely the in-plane and out-of-plane bending modes in the broad band at 1600 cm^{-1} and at 1130 cm^{-1}. The latter mode typically gives rise to the most intense band in the INS spectrum for such hydrogen bonds, as it has the largest amplitude and is relatively pure. In-plane bending, on the other hand, is often involved in several vibrational modes, so that the INS intensity is more widely distributed. The energy resolution of the spectrometer decreases with increasing energy, which is responsible for the poor spectral definition at higher energies along with the increasing prevalence of multiphonon excitations. We are unable to unambiguously assign ν_{OH} from the INS spectrum without assistance from the computational studies.

The most pronounced feature in all the calculated spectra is a broad area centered in most cases at about 1200 cm^{-1} and topped with individual peaks. Its most intense component is usually the out-of plane OH bending mode. Most of the INS intensity originating from the in-plane OH bending appears between 1400 and 1600 cm^{-1}, but the intensity of the peaks in this area is notably lower than of the out-of-plane bending mode. The OH stretching mode is barely (if at all) visible in both the experimental and calculated INS spectra of PyO-TCA. Even when its frequency falls into the range shown (Gaussian-SCRF, CPMD-TM, and VASP calculation), the OH stretching mode produces at best a peak of very low intensity. A possible explanation for this is that several other modes have in part OH stretching character, which lowers the intensity of the principal stretching mode. We also attempted to identify some low-frequency modes characteristic of the donor-acceptor stretching motion of the interacting PyO and TCA monomers ("O…O stretching"). As in our previous work,[20,22] these modes appear in the 300–500 cm^{-1} region, but their frequency and composition differ drastically among the computational models. In addition, unambiguous assignment of bands in the low frequency part of the experimental INS spectrum to the O…O stretching motion is quite a demanding task, as any associated proton motion is more likely to arise from protons on the ring than that in the H-bond for this symmetric mode. This renders any comparison between the calculated and experimental O…O stretching frequencies of very limited value.

The findings presented above suggest that most of the information on hydrogen bonding of the PyO-TCA complex that can be acquired from the experimental and calculated INS spectra is confined to the out-of-plane and in-plane bending modes, but regretfully very little (if at all) can be deduced about the OH stretching mode. Frequency calculations, even at the harmonic level, demonstrate that the frequency and composition of the OH stretching mode (and, to some extent, also of other protonic modes) is very sensitive to the level of modeling, and that the OH stretching mode is extremely prone to mixing with other degrees of freedom (*see below*).

The comparison between the INS spectra displayed in Fig. 1 allows us to briefly comment on the agreement between the calculated and experimental spectra and on their selected features. Clearly, the gas-phase model ("Gaussian-gas") fails to predict the two crucial features associated with the in-plane and out-of-plane bending modes to the correct frequencies. The out-of-plane mode is calculated at a notably lower frequency (about 1015 cm^{-1}) than with any other model, which clearly indicates that the hydrogen bond is weaker and the force constant for the out-of-plane hydrogen displacement is significantly lower because of the overestimated O...O distance. The same is true of the in-plane bending components of the spectrum. The SCRF model[27] yields notable improvement in the location of these modes, but the intensity of the in-plane bending contributions is rather weak in comparison to the experimental spectrum. While the latter is also true for the solid-state models, the in-plane bending features of their INS spectra are somewhat more pronounced and thus in better agreement with the experimental spectrum. Particularly the CPMD-TM and VASP calculations are in quite reasonable qualitative agreement with the observed INS features of the hydrogen bond. CRYSTAL, on the other hand, gives results that are more difficult to understand as the out-of-plane bending mode, calculated to 1070 cm^{-1}, is rather weak when compared to neighboring modes and the out-of-plane component persists in modes to much higher frequency, up to 1670 cm^{-1} and exhibits coupling to the in-plane bending mode. These unusual features are not supported by any previous observation, and are likely to originate from artifacts of the model, and require further attention.[30]

The complexity of vibrational modes of PyO-TCA can be further demonstrated by a qualitative comparison of the OH stretching modes among the various computational models. The calculated OH stretching frequencies are displayed in Table 2 together with other internal degrees of freedom that are also involved in the (so called) OH stretching mode. Note that in the models that include only one PyO-TCA pair there is only one OH stretching mode, whereas in periodic models four such modes appear; their range is given instead.

Table 2. Ranges of calculated OH stretching modes (harmonic approximation) and their mixing with other internal degrees of freedom.

Approach	Range of OH stretching modes [cm^{-1}]	mixing
Gaussian, isolated	2792	virtually none
Gaussian, SCRF*	1908	slightly with $\nu_{C=O}$
CPMD, TM	1794–1833	significantly with $\nu_{C=O}$
CPMD, SG	2041–2222	slightly with $\nu_{C=O}$, significantly with $\delta_{N\text{-}O}$
Crystal	2139–2185	slightly with $\nu_{C=O}$ and ring $\delta_{C\text{-}H}$
VASP	1725–1739	significantly with $\nu_{C=O}$

* Taken from Refs. [27] and [29].

The gas phase model gives by far the highest OH stretching frequency, and this mode is comprised almost exclusively of the longitudinal motion of the proton along the OH bond line as would be expected. In all the other models the force constant for the stretching motion of the proton is considerably lower, which is not surprising because of the very short O...O distance. The resulting frequency is red shifted to ~2000 cm^{-1} or less, which effectively brings this mode close to the frequency region of other modes to facilitate extensive coupling with internal degrees of freedom other than OH stretching. In all cases the carbonyl (C=O) stretching component becomes mixed with OH stretching, so that the intensity of the $\nu_{C=O}$ component increases with a decrease of the OH frequency. While the $\nu_{C=O}$ component in the OH stretching mode is quite weak in the Crystal and CPMD/SG calculation because the OH stretching frequencies are still higher than 2000 cm^{-1}, the intensity of the carbonyl stretching mode becomes very pronounced in the CPMD/TM calculation and even more so in the VASP calculation, where the OH stretching frequency is red shifted to about 1730 cm^{-1}. This coupling between OH and carbonyl stretching is well known from other examples of short hydrogen bonds and can to a certain extent be generalized to such systems.[23] OH stretching modes calculated by CPMD/SG also include some in-plane N-O bending motion and the Crystal calculation shows the OH stretching modes to include some C-H ring deformation motion of PyO. While the detailed mechanism and significance of such coupling is unclear, its presence demonstrates the high complexity of the vibrational dynamics of the short hydrogen bonding in PyO-TCA. The in-plane bending mode exhibits a similarly complex coupling mechanism, particularly since there are a number of modes in the 1400–1600 cm^{-1} frequency range available for coupling, most of which include ring vibrations of PyO.

Apart from the complications arising from the coupling between internal degrees of freedom, another important and even critical factor is the presence of a substantial degree of anharmonicity in the potential energy surface. The fundamental underlying assumption of the harmonic frequency calculation – that the potential can be approximated by a quadratic function of the respective coordinates – is of very limited validity in short hydrogen bonds. Hence advanced numerical techniques based on the solving of the vibrational Schrödinger equation are required to overcome this drawback,[42–47] but the extreme computational costs often make such a treatment prohibitive.

A challenging aspect of the present study is related to the established correlations between hydrogen bond characteristics and acid-base properties of its constituents. Namely, a spontaneous proton transfer phenomenon is far from being a common event, particularly since both TCA and PyO are rather weak acid and weak base, respectively. It would be a challenge for our future work to consider the gas-phase acidity and basicity of the constituents and confront them with the proposed criteria for spontaneous proton transfer.[48,49] Acid-base properties of partners involved in hydrogen bonding were shown to be crucial factors determining the strength of these interactions and eventual subsequent proton transfer reaction.[50] Also, it was recently demonstrated that apart from its significant biological role, an *N*-oxide group can exhibit quite a remarkable acidifying effect on the neighboring protons,[51] which is comparable to the acidifying effect of very strong electron-withdrawing groups, like for example the cyano group.

The present experimental and computational INS characterization of short hydrogen bond of the title compound demonstrates the high degree of complexity of the vibrational dynamics as well as high sensitivity to the type and level of modeling used. In many aspects the present preliminary study leaves more questions open than it is able to answer, but it does point into the direction of what is required for an improved theoretical analysis of such vibrational spectra, namely the application of a variety of advanced and complementary experimental and computational techniques, which are already part of our extensive collaboration with Prof. Hadži.[30]

5. Conclusions

The present work demonstrates that the vibrational dynamics of the hydrogen-bonded complex between PyO and TCA in the crystalline solid state is extremely complex and cannot be sufficiently elaborated by the experimental and the computational techniques used in this study. The observable hydrogen bond features in the experimental INS spectrum are mostly limited to the out-of-plane and in-plane OH bending modes and virtually no direct information on the OH stretching mode is discernible. Among the various computational approaches, those using periodic boundary conditions as implemented into the CPMD and VASP program packages, show good agreement of the optimized geometry with the previously published neutron diffraction study,[18] and the qualitative agreement of the out-of-plane and in-plane INS spectral features with the measured ones is reasonable. Nevertheless, the present study is unable to address the most important problems of vibrational dynamics of the hydrogen bond, particularly those related to OH stretching. At the experimental level the collected dataset on the spectral features, particularly "protonic" bands, is rather small and limited by the experimental resolution, which requires the use of additional experimental techniques, such as infrared, Raman and NMR spectroscopy. At the computational level, the problem of the extensive anharmonicity of the potential energy surface and the coupling of the proton motion to the fluctuating environment needs to be considered, along with a real-time dynamics of the system. The required experimental and computational work, aimed at the improved understanding of the structure and dynamics of short hydrogen bonding, is in progress in the framework of our collaboration with Prof. Hadži and coworkers.[30]

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Povzetek

Z metodo neelastične nevtronske vibracijske spektroskopije (INS) ter računskimi metodami smo proučevali dinamiko kratke vodikove vezi (R_{OO} = 2.430 Å) v kompleksu piridin *N*-oksida in triklorocetne kisline v trdnem kristaliničnem stanju. Uporabili smo računske metode, ki temeljijo na teoriji gostotnih funkcionalov, in sistem obravnavali na več nivojih (glede na kompleksnost okolice), od izoliranega kompleksa do polnega periodičnega modela. Uporabili smo tri programe za periodično modeliranje (CRYSTAL, CPMD in VASP) ter z njimi izračunali vibracijske frekvence v harmonskem približku; INS spektre smo izračunali na podlagi harmonskih frekvenc z uporabo programa a-cilmax. Medtem ko vsi modeli z izjemo izoliranega dobro opišejo strukturo kompleksa, pa je ujemanje izračunanega spektra z izmerjenim (v delih, povezanih z upogibnimi nihanji protona v vodikovi vezi) zadovoljivo le pri programih CPMD in VASP. V izmerjenem spektru prispevek valenčnega nihanja protona ni opazen, račun pa kaže, da je njegova intenziteta zelo nizka. Za primerno računsko obravnavo dinamike vodikove vezi v tem sistemu je nujna uporaba bolj zahtevnih tehnik, kot so metode molekulske dinamike ter kvantne dinamike na multidimenzionalni potencialni ploskvi.