

Tensorial Properties via the Neuroevolution Potential Framework: Fast Simulation of Infrared and Raman Spectra

Nan Xu, Petter Rosander, Christian Schäfer, Eric Lindgren, Nicklas Österbacka, Mandi Fang, Wei Chen, Yi He,* Zheyong Fan,* and Paul Erhart*



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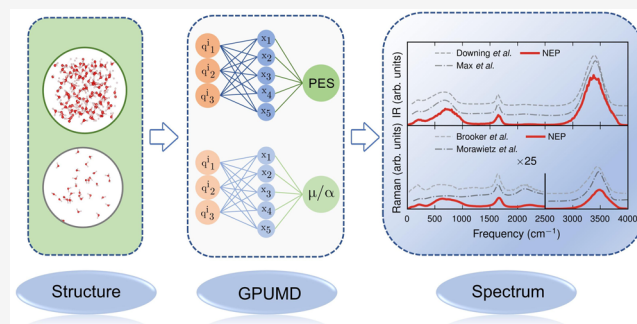
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ABSTRACT: Infrared and Raman spectroscopy are widely used for the characterization of gases, liquids, and solids, as the spectra contain a wealth of information concerning, in particular, the dynamics of these systems. Atomic scale simulations can be used to predict such spectra but are often severely limited due to high computational cost or the need for strong approximations that limit the application range and reliability. Here, we introduce a machine learning (ML) accelerated approach that addresses these shortcomings and provides a significant performance boost in terms of data and computational efficiency compared with earlier ML schemes. To this end, we generalize the neuroevolution potential approach to enable the prediction of rank one and two tensors to obtain the tensorial neuroevolution potential (TNEP) scheme. We apply the resulting framework to construct models for the dipole moment, polarizability, and susceptibility of molecules, liquids, and solids and show that our approach compares favorably with several ML models from the literature with respect to accuracy and computational efficiency. Finally, we demonstrate the application of the TNEP approach to the prediction of infrared and Raman spectra of liquid water, a molecule (PTAF⁻), and a prototypical perovskite with strong anharmonicity (BaZrO₃). The TNEP approach is implemented in the free and open source software package GPUMD, which makes this methodology readily available to the scientific community.



1. INTRODUCTION

Infrared (IR) and Raman spectroscopy are widely used techniques for the nondestructive characterization of the dynamics and to some extent chemistry of materials spanning the entire range from the gas phase to condensed matter.^{1–3} Over the years, various theoretical approaches have been developed for simulating IR and Raman spectra, including in particular methods based on *ab initio* molecular dynamics (MD) simulations.^{4–8} While these approaches are capable of reproducing experimental IR and Raman spectra of gases, liquids, and solids,^{5,7–9} they are severely limited with respect to the system sizes and time scales attainable for two main reasons:^{5,10} First, *ab initio* MD simulations rely on computationally demanding electronic structure calculations that scale strongly with system size in order to obtain energy and forces at every time step. Second, similarly expensive calculations of dipole moment (μ), polarizability (α), or electric susceptibility (χ) are required for at least many thousands of configurations to achieve numerical convergence of the underlying correlation functions.⁵

MD simulations can be accelerated by using classical force fields^{11–13} or empirical interatomic potentials,^{14,15} which approximate the potential energy surface (PES) with physically motivated yet constrained functions and few fitted parameters.

The accuracy of such approaches for general materials is, however, often limited, negatively affecting the prediction of IR and Raman spectra.¹⁶ Machine learning (ML) potentials are well suited to address this challenge as they bridge between the accuracy of quantum mechanical methods and the computational efficiency of classical force fields or empirical interatomic potentials.^{17–21} The power of this approach, in particular for capturing vibrational properties of materials, has been shown repeatedly, see, e.g., refs.^{22–26}

The calculation of μ , α , or χ can be accelerated using parametric models in a similar fashion. Considering only static charges, the dipole moment is given by $\mu = \sum_{i=1}^N Q_i r_i$, where Q_i and r_i are the charge and position of atom i . Many classical force fields^{11–13} assign fixed charges to atoms and thereby provide a convenient approach for calculating μ . Such fixed-charge models neglect, however, polarization effects, which can lead to large errors.²⁷ While this situation can in principle be

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ameliorated by fluctuating-charge models,^{28,29} the latter tend to lack robustness and can be difficult to generalize.^{10,30}

Both α and χ describe the dielectric response to an applied electric field. For α or χ , the bond polarizability model is one of the most frequently used parametric ones and has for example been applied to alkanes^{31,32} and zeolites³³ as well as carbon nanotubes.³⁴ However, this simple model often suffers from unsatisfactory transferability when used in different environments.³⁵ POLI2VS³⁶ and MB-pol³⁷ are two other parametric models that can be used for predicting μ and α but are limited to molecular systems such as water.¹⁰

The successful applications of ML potentials have inspired the development of ML dipole, polarizability, and susceptibility models.^{22,38–41} For μ , a rank-1 tensor, both partial-charge and the partial-dipole ML models have been developed.³⁰ The objective of the partial-charge models is to assign proper partial charges for atoms in order to fit the total dipole moment.^{22,30,42} Here, one concern is the balance between the fitting quality of μ and the reproducibility of total charges.^{22,30} By contrast partial-dipole models such as symmetry-adapted Gaussian process regression (SA-GPR),³⁸ tensorial embedded-atom neural network (T-EANN),³⁹ and deep potential (DP)⁴⁰ treat μ as a sum of vectors^{30,38} that can be determined from atom-centered chemical environments.

While this approach works for μ , which is a rank-1 tensor, it does not transfer to the construction of ML models for α or χ , which are rank-2 tensors. This has motivated the pioneering development of the SA-GPR method for tensorial properties³⁸ as well as later the T-EANN^{39,43} and DP models.¹⁰

The combination of ML potentials with ML models for μ , α , or χ enables the simulations of IR and Raman spectra. This approach has been used to predict, e.g., the IR spectra of methanol, *n*-alkanes, and a peptide,²² IR and Raman spectra of liquid water,^{10,20,39,44} or the Raman spectra of various solid materials.⁴⁵ While these earlier studies have established the usefulness of ML models for predicting IR and Raman spectra, there is still ample room for improvement of current models for μ , α , or χ in terms of computational and data efficiency^{30,39} as well as the accessibility of these techniques in order to lower the threshold for the widespread adoption of such approaches.

This situation motivates the present work, in which we introduce accurate as well as computationally and data efficient ML models for rank-1 and rank-2 tensors based on the NEP framework.^{21,46,47} We demonstrate the efficacy and efficiency of the resulting TNEP approach by training models for μ , α , and χ and combining these with models for the PES to predict IR and Raman spectra for a molecule (PTAF⁻), a liquid (water), and a solid (BaZrO₃; Figure 1). We make this methodology available via the GPUMD package,⁴⁷ enabling comprehensive simulations of high-quality IR and Raman spectra with limited user effort.

2. METHODOLOGY

2.1. NEP Models for the PES. Since the ML models for μ and α that we introduce below are based on the NEP framework for modeling PESs,^{21,46,47} we first provide a brief review of the latter. Originally NEPs are ML potentials that model the high-dimensional PES of finite or extended systems, in the spirit of the neural network potential model proposed by Behler and Parrinello.⁴⁸ In this formalism, the total energy of the system is given by the sum of atomic site energies $U = \sum_i U_i$. The site energy U_i for a given atom i depends on the local environment of the atom, which is represented by an

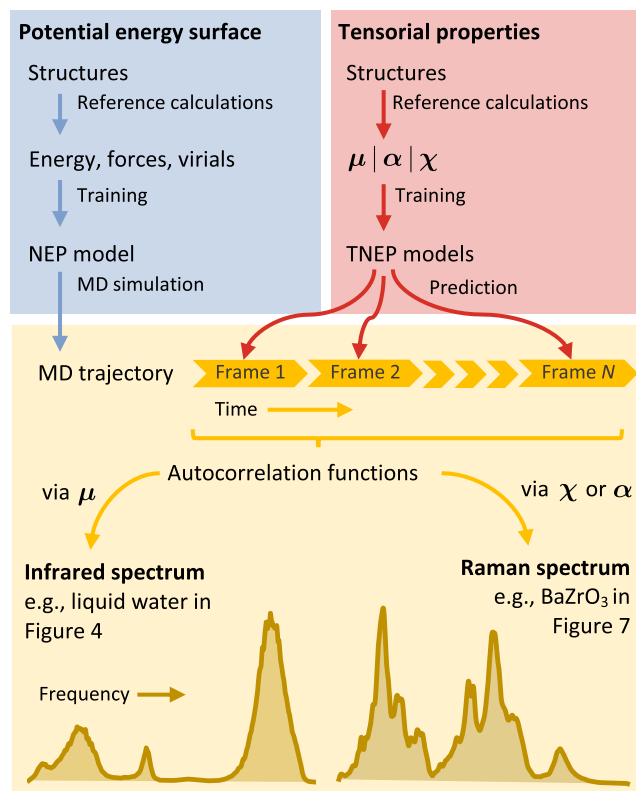


Figure 1. Workflow for simulations of IR and Raman spectra using NEP models for the PES and TNEP models for the dipole moment μ , the polarizability α , or the susceptibility χ .

abstract vector q_i^ν with a number of components indexed by ν . The function mapping from the descriptor to the site energy is represented by a feed-forward neural network (also known as a multilayer perceptron) with typically a single hidden layer. The input layer of the neural network is thus the descriptor vector, and the output layer consists of a single node whose value is the site energy U_i of the considered atom i , which can be formally expressed as

$$U_i = U_i(q_i^\nu) \quad (1)$$

From the energy, we can derive the rank-2 virial tensor that serves as the foundation for the dipole and polarizability models developed in the present work. For a given structure with N atoms, the virial tensor can be expressed as⁴⁷

$$W^{\nu\nu} = - \sum_i \sum_{j \neq i} r_{ij}^\nu \frac{\partial U_i}{\partial r_{ij}^\nu} \quad (2)$$

where r_{ij}^ν is the ν -component of the vector $\mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i$, and \mathbf{r}_i is the position of atom i . We refer to the term $\partial U_i / \partial r_{ij}^\nu$ as the partial force, explicit expressions for which have been presented in the original works developing the NEP approach.^{21,47}

2.2. TNEP Rank-1 Tensor Models. To develop an ML model for predicting μ , we first note that it is a rank-1 tensor commonly expressed as a vector, in contrast to the energy, which is a rank-0 tensor (i.e., a scalar). The partial force in eq 2 is a vector, but the summation of it over the whole structure would be zero as a result of Newton's third law. To obtain a vector representation that does not vanish for a general structure, we note that the quantity defined in eq 2 is a rank-2

tensor that can adopt both positive and negative values (as it is the virial tensor in the context of PES models). We can thus obtain an expression for a vector quantity by contracting this rank-2 tensor with a vector. A natural choice for the vector to be contracted is r_{ij} , which yields the following expression for rank-1 tensors such as the dipole moment

$$\boldsymbol{\mu} = -\sum_i^N \sum_{j \neq i} r_{ij} \left(r_{ij} \otimes \frac{\partial U_i}{\partial \mathbf{r}_{ij}} \right) = -\sum_i^N \sum_{j \neq i} r_{ij}^2 \left(\frac{\partial U_i}{\partial \mathbf{r}_{ij}} \right) \quad (3)$$

where $r_{ij}^2 = \mathbf{r}_{ij} \cdot \mathbf{r}_{ij}$ is the distance squared between atoms i and j . We note that U_i here should have the dimension of charge instead of energy. Crucially this goes to show that the NEP formalism for PESs can be directly used to construct an ML model for rank-1 tensors such as the dipole moment. Below we refer to eq 3 as the TNEP dipole model.

2.3. TNEP Rank-2 Tensor Models. To develop ML models for predicting $\boldsymbol{\alpha}$ or $\boldsymbol{\chi}$, we first note that these are rank-2 tensors. Clearly, the quantity defined in eq 2 is an ideal candidate. However, using only eq 2 to represent $\boldsymbol{\alpha}$ or $\boldsymbol{\chi}$ does not lead to high regression accuracy because the diagonal terms of $\boldsymbol{\alpha}$ or $\boldsymbol{\chi}$ are usually much larger than the off-diagonal ones. We therefore represent $\boldsymbol{\alpha}$ (and equivalently $\boldsymbol{\chi}$) as a combination of eqs 1 and 2 as follows

$$\alpha^{\nu\mu} = \sum_i^N U_i \delta^{\nu\mu} - \sum_i^N \sum_{j \neq i} r_{ij}^{\nu} \frac{\partial U_i}{\partial r_{ij}^{\mu}} \quad (4)$$

where $\delta^{\nu\mu}$ is the Kronecker delta. Note that both the first and second terms on the right-hand side contribute to the diagonal elements of $\alpha^{\nu\mu}$, but only the second term contributes to the off-diagonal elements. U_i here has the dimension of polarizability instead of energy, yet the entire NEP formalism can be reused. Below we refer to eq 4 as the TNEP polarizability or susceptibility model.

2.4. Loss Functions. The NEP approach is named after the underlying ML model (a neural network) and the separable natural evolution strategy used as the training algorithm.⁴⁹ The latter is a principled real-valued black-box optimization method that is very well suited for training the weight and bias parameters in the neural network, of which there are typically a few thousand. The optimization is driven by the minimization of a loss function that is given by the weighted sum of the root-mean-square error (RMSE) of physical quantities as well as \mathcal{L}_1 and \mathcal{L}_2 regularization terms. For the construction of PES models, the physical quantities included in the loss function are the energies, forces, and virial tensors of the structures in the training set

$$L(\mathbf{z}) = \lambda_e \Delta U(\mathbf{z}) + \lambda_f \Delta F(\mathbf{z}) + \lambda_v \Delta W(\mathbf{z}) + \text{regularization terms} \quad (5)$$

where $\Delta U(\mathbf{z})$, $\Delta F(\mathbf{z})$, and $\Delta W(\mathbf{z})$ are the RMSEs of energies, forces, and virials calculated using a set of trainable parameters \mathbf{z} , and λ_e , λ_f , and λ_v are the corresponding relative weights. Explicit expressions for the regularization terms can be found in ref 47. For the construction of dipole TNEP models, the loss function is defined in terms of the RMSE of the dipole $\Delta\boldsymbol{\mu}(\mathbf{z})$

$$L(\mathbf{z}) = \Delta\boldsymbol{\mu}(\mathbf{z}) + \text{regularization terms} \quad (6)$$

For the construction of polarizability TNEP models, the loss function is defined in terms of the RMSE of the polarizability $\Delta\boldsymbol{\alpha}(\mathbf{z})$

$$L(\mathbf{z}) = \Delta\boldsymbol{\alpha}(\mathbf{z}) + \text{regularization terms} \quad (7)$$

2.5. Dielectric Response. It is instructive to recall some relations that describe the response of finite systems (such as molecules) and extended systems (such as solids and liquids) to an applied electric field.

If a molecule is subjected to an electric field \mathbf{E} , the resulting displacement of nuclei and electrons induces a dipole, which is given by⁵⁰

$$\boldsymbol{\mu}_{\text{ind}} = \boldsymbol{\alpha}\mathbf{E}$$

where $\boldsymbol{\alpha}$ is the *molecular polarizability*.

For an extended system such as a solid or a liquid, one considers equivalently the dipole moment per unit volume, i.e., the polarization

$$\mathbf{P} = \epsilon_0 \boldsymbol{\chi}\mathbf{E}$$

where $\boldsymbol{\chi}$ is the *electric susceptibility*. In the context of bulk liquids, the latter has also been referred to as the bulk polarizability. For clarity in the following, we use the term polarizability only to refer to molecular polarizability. There are different conventions for expressing $\boldsymbol{\mu}$, $\boldsymbol{\alpha}$, and $\boldsymbol{\chi}$ leading to different units (Sect. S7). Here, we use e-bohr for $\boldsymbol{\mu}$ and bohr³ for $\boldsymbol{\alpha}$, whereas $\boldsymbol{\chi}$ is unitless.

We note that under certain conditions, one can approximately connect the molecular polarizability and the electric susceptibility via the Clausius-Mossotti relation, which is based on a mean-field treatment of local field effects (see Sect. S8 in the Supporting Information).

2.6. The IR Intensity. The IR absorption cross section is given by⁵⁰

$$\sigma(\omega) = \frac{4\pi^2}{\hbar c n} \omega (1 - e^{-\beta\hbar\omega}) M(\omega) \quad (8)$$

where n is the refractive index of the material, c is the speed of light, $\beta = 1/k_B T$, and $M(\omega)$ is the absorption line shape given by the Fourier transform of the autocorrelation function (ACF) of the (total) dipole moment $\boldsymbol{\mu}$

$$M(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle (\hat{\boldsymbol{\epsilon}} \cdot \boldsymbol{\mu}(0)) (\hat{\boldsymbol{\epsilon}} \cdot \boldsymbol{\mu}(t)) \rangle e^{-i\omega t} dt$$

where $\langle \dots \rangle$ indicates the average over time origins, and $\hat{\boldsymbol{\epsilon}}$ is the polarization of the light.⁵⁰ For an isotropic sample, the time correlation should be averaged over the three directions, i.e., the line shape reduces to one-third of the trace of the dipole time correlation. Since the line shape is sampled classically, we make a classical approximation for the prefactor by expanding the Boltzmann factor to first order, which gives

$$\sigma(\omega) \propto \omega^2 M(\omega) \quad (9)$$

2.7. The Raman Intensity. The differential Raman cross-section for Stokes scattering is given by⁵⁰⁻⁵²

$$\frac{\partial^2 \sigma}{\partial \omega_{\text{out}} \partial \Omega} = \left(\frac{\omega_{\text{in}} - \omega}{c} \right)^4 \sum_{\gamma\delta\mu\nu} \hat{n}_\gamma \hat{n}_\mu L_{\gamma\delta\mu\nu}(\omega) \hat{\boldsymbol{\epsilon}}_\delta \hat{\boldsymbol{\epsilon}}_\nu \quad (10)$$

where \hat{n} is the polarization of observed light, $\hat{\boldsymbol{\epsilon}}$ is the polarization of the incoming light, and Ω is a solid angle. Here, it is assumed that the frequency of the incoming light ω_{in} is significantly larger than the Raman shift ω and significantly smaller than the band gap, i.e., far from any electronic excitations. $L(\omega)$ is the Raman line shape given by the Fourier transform of the time-dependent polarizability $\boldsymbol{\alpha}(t)$ (finite

systems) or susceptibility $\chi(t)$ (extended systems), e.g., in the case of the former

$$L_{\gamma\delta\mu\nu}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \alpha_{\gamma\delta}(0) \alpha_{\mu\nu}(t) \rangle e^{-i\omega t} dt \quad (11)$$

Note that the elements of the polarizability (or susceptibility) tensor are selected by the polarization of the incoming and outgoing light as indicated in eq 10. Polarized Raman measurements can be directly related to eq 10 by combinations of the Raman line shape $L(\omega)$. One can also calculate an average spectrum for isotropic samples.⁵⁰ The polarizability tensor (and equivalently the susceptibility tensor) can also be written as $\alpha = \gamma I + \beta$ where $\gamma = \text{Tr}(\alpha)/3$, and β is a traceless tensor to obtain the isotropic (polarized) and anisotropic (depolarized) spectrum. This leads to the decomposition

$$L_{\text{iso}}(\omega) \propto \int_{-\infty}^{\infty} \langle \gamma(0) \gamma(t) \rangle e^{-i\omega t} dt$$

$$L_{\text{aniso}}(\omega) \propto \int_{-\infty}^{\infty} \langle \text{Tr}[\beta(0)\beta(t)] \rangle e^{-i\omega t} dt \quad (12)$$

The electric susceptibility (Sect. 2.5) can be separated into an electronic and an ionic contribution

$$\chi = \chi_{\text{ion}}(\omega) + \chi_{\text{e}}(\omega)$$

where the general frequency dependence of these terms is emphasized. For the prediction of Raman spectra, we only need to consider the electronic contribution $\chi_{\text{e}}(\omega)$. Furthermore, we limit ourselves to nonresonant Raman spectroscopy. This means that we require the electric susceptibility in the ion-clamped static limit, i.e., $\chi_{\text{e}}(0)$, and do not have to consider the frequency dependence of $\chi_{\text{e}}(\omega)$, which arises from electronic transitions.

2.8. Workflow for Simulations of IR and Raman Spectra. By combining a NEP model for the PES with TNEP models for dipole, polarizability, or susceptibility, one obtains a simple yet general workflow for the computation of IR and Raman spectra (Figure 1). Starting from a NEP PES model, large-scale MD simulations are performed to sample the PES via the GPUMD package, typically for a few hundred picoseconds. TNEP dipole, polarizability, or susceptibility models are then employed to predict $\mu(t)$, $\alpha(t)$, or $\chi(t)$ along the trajectory. Finally, IR or Raman spectra are obtained via Fourier transformation of the respective ACFs via eq 9 or 10.

3. PERFORMANCE EVALUATION

In this section, we evaluate the performance of the TNEP dipole, polarizability, and susceptibility models in comparison with models from the literature with respect to both regression accuracy and computational speed. The comparison includes the molecules H_2O , $(\text{H}_2\text{O})_2$, and H_5O_2^+ (the Zundel cation), as well as a set of configurations representing liquid water. Structures with dipole, polarizability, and/or susceptibility data were retrieved from the repository maintained by the developers of the SA-GPR models^{38,53} (see Sect. S1 in the Supporting Information for details). The data set for each of these systems comprises 1000 configurations, half of which were used for training, while the other half were used for validation. The hyperparameters used in the training of the TNEP models are presented in Tables S1 and S2. In the case of the SA-GPR method, the results for liquid water were computed using a publicly available model,⁵⁴ while the models for the molecules were trained by us (see Sect. S3 for details).

In the case of the T-EANN method, we only use those data available in the literature.³⁹

3.1. Dipole Moment. The TNEP dipole models can achieve very high precision when predicting μ for both molecules and liquid water with very low RMSEs (Table 1) and coefficients of determination (R^2) very close to one (Figure S2).

Table 1. RMSEs (in e·bohr) and RRMSEs (unitless) for μ for the Validation Sets Using NEP Rank-1 Tensor Models^a

System	RMSE	RRMSE
H_2O	2×10^{-4}	0.069%
$(\text{H}_2\text{O})_2$	105×10^{-4}	1.681%
H_5O_2^+	14×10^{-4}	0.371%
liquid water	17×10^{-4}	0.852%

^aFor liquid water, the dipole moment is given per water molecule.

As a further, more intuitive measure, one can also consider the root-mean-square-error relative to standard deviation (RRMSE),³⁹ defined as the RMSE divided by the standard deviation of the reference data (Figure 2a). For the water

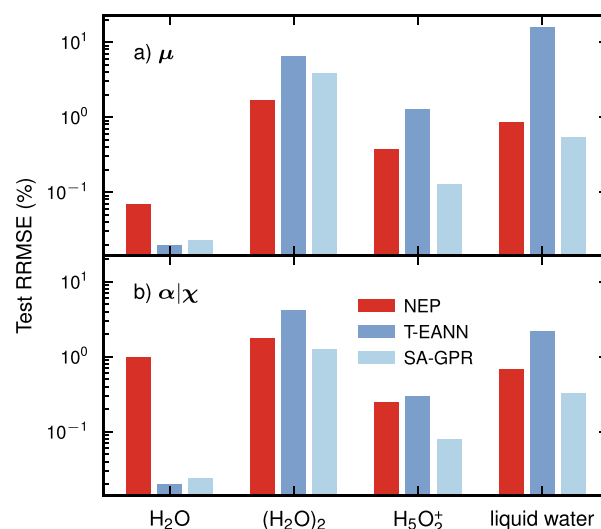


Figure 2. RRMSEs for the validation sets according to TNEP, T-EANN, and SA-GPR models for water systems for (a) μ as well as (b) α and χ/ρ . Validation RRMSEs for liquid water from T-EANN³⁹ were reported for the averaged molecular polarizability obtained via the Clausius-Mossotti relation (S8). The validation RRMSEs for χ/ρ should be somewhat higher than that for the averaged molecular polarizability (also see Table S5).

monomer (H_2O), all three methods yield extremely small RRMSEs below 0.1%. For the other three systems, including liquid water, the TNEP and SA-GPR models achieve comparable accuracy, while the T-EANN models perform systematically worse. This behavior is particularly pronounced for liquid water and might arise since the T-EANN model uses the positions relative to the center of mass as input, which are not well-defined in periodic systems.^{55,56}

Neutral Molecules. The μ of neutral molecules such as H_2O or $(\text{H}_2\text{O})_2$ is uniquely defined. In the TNEP approach, μ is calculated by summing over atomic contributions which, in contrast to, e.g., the T-EANN approach, does not require

choosing a reference point. Therefore, the TNEP dipole models are naturally suitable for neutral molecules.

In this context, we note that we also trained and validated a model for the QM7B data set containing thousands of neutral organic molecules,^{57,58} for which we make similar observations (Sect. S4). The TNEP model yields a very low RMSE for the validation set of 1.80×10^{-3} e-bohr atom⁻¹ and a very high R^2 score for the validation set of about 0.998.

Charged Molecules. The μ of charged molecules is nonunique and depends on the choice of the reference point.^{4,59} For charged molecules, one should therefore employ the relative permanent dipole μ_r , defined with respect to the center of mass when training TNEP dipole models. The reference μ values in the H_5O_2^+ data set^{38,53} have already been transformed to μ_r . Therefore, the absolute dipole moment of H_5O_2^+ including the movement of the center of mass should be $\mu = \mu_r + e \cdot r_{\text{COM}}$. The same procedure was applied to the PTAF⁻ molecule below (Sect. 4.3).

Periodic Systems. Traditional methods for calculating μ cannot be applied to periodic systems since the position operator is not uniquely defined.^{56,60} This issue is overcome via the modern theory of polarization,^{38,60,61} which provides a rigorous definition for the polarization of periodic systems and established a methodology for calculating μ . It was therefore used in the present work to obtain μ for periodic systems including water (Sect. S1) and $\alpha\text{-Fe}_2\text{O}_3$ (Sect. S5). The TNEP model for $\alpha\text{-Fe}_2\text{O}_3$ yields a very high R^2 score for the validation set close to one.

3.2. Polarizability and Susceptibility. The RMSEs for the diagonal and off-diagonal elements of α of (H_2O) , $(\text{H}_2\text{O})_2$, and H_5O_2^+ are quite small (Table 2), indicating the high

Table 2. RMSEs (in bohr³) and RRMSEs (unitless) for α (Molecules) and χ/ρ (Liquid Water) for the Validation Sets Using TNEP Rank-2 Tensor Models^a

System	diagonal elements		off-diagonal elements	
	RMSE	RRMSE	RMSE	RRMSE
H_2O	85×10^{-3}	5.89%	4×10^{-3}	1.22%
$(\text{H}_2\text{O})_2$	227×10^{-3}	8.82%	137×10^{-3}	12.59%
H_5O_2^+	23×10^{-3}	1.20%	17×10^{-3}	1.06%
liquid water	54×10^{-3}	16.28%	37×10^{-3}	20.38%

^aFor liquid water, χ/ρ is given per water molecule.

accuracy of the TNEP polarizability model. The coefficients of determination are larger than 0.98 mirroring this trend (Figure S7 and Figure S8). For liquid water, we consider χ/ρ , which has the unit of polarizability per atom. The RMSEs for χ/ρ are on the same order of magnitude as the RMSEs for α (Table 2).

The NEP models achieve an accuracy that is comparable to that of the T-EANN and SA-GPR models for the polarizability of $(\text{H}_2\text{O})_2$ and H_5O_2^+ as well as the susceptibility of liquid water (Figure 2b). While the performance for the water monomer H_2O is worse, the TNEP model still yields a validation RRMSE of less than 1%.

As a further test, we constructed a TNEP polarizability model for the QM7B data set (Sect. S4). The RMSE values for the validation set are 4.64×10^{-2} bohr³ atom⁻¹ and 2.58×10^{-2} bohr³ atom⁻¹ for the diagonal and off-diagonal elements of α , respectively. For comparison, Wilkins et al.⁶² reported a higher RMSE value of 5.50×10^{-2} bohr³ atom⁻¹ over both the diagonal and off-diagonal elements of α using an SA-GPR model.

3.3. Computational Speed. It is now instructive to evaluate the computational performance of TNEP models in comparison with publicly available SA-GPR models.^{53,54} To this end, we consider liquid water systems with varying numbers of atoms. Starting from a cell containing 96 atoms, larger samples with up to 69984 atoms were created by replication.

The SA-GPR models can be run only serially on a central processing unit (CPU). In contrast, the TNEP model can be run on a CPU using NEP_CPU,⁶³ e.g., via the interface provided by the CALORINE package,⁶⁴ or on a graphics processing unit (GPU) by using the GPUMD package. The SA-GPR and TNEP (CPU) models were tested on a server containing two Intel XEON Platinum 8275CL processors with a system memory of 256 GB, while the TNEP (GPU) models were tested on a heterogeneous server containing two Intel XEON Gold 6148 processors and an Nvidia GeForce RTX 4090 card with a graphics memory of 24 GB.

The comparisons show that for system sizes ≥ 1000 atoms the TNEP CPU models are at least 1 order of magnitude faster than the SA-GPR models on CPUs for both dipole and polarizability (Figure 3). On CPUs, the TNEP models exhibit

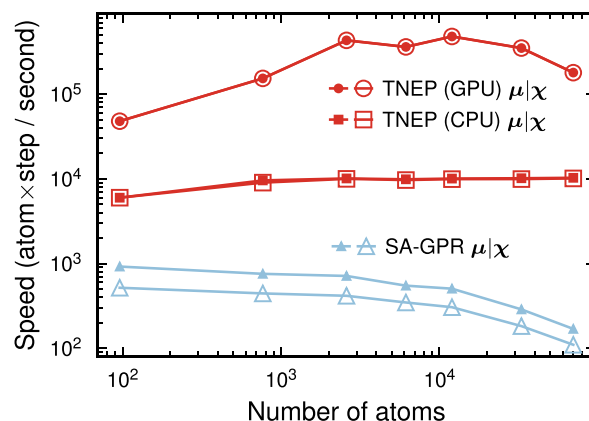


Figure 3. Comparison of computational speed of SA-GPR and TNEP models for the dipole (μ) and susceptibility (χ) of liquid water. Here, the SA-GPR results were obtained using the TENSOP-FAST implementation.⁵⁴

nearly perfect weak scaling over the system sizes considered here. In contrast, the SA-GPR models show a notable decrease in speed as the system size increases. Running the TNEP models on GPUs enables an additional speedup of an order of magnitude or more. For very small systems, the GPU implementation is limited by IO. In addition, we note that GPUMD allows one to evaluate TNEP models on-the-fly during MD simulations for prediction of tensorial properties with a small impact on simulation speed (Sect. S10).

4. APPLICATIONS

Having established the accuracy and computational performance of the TNEP approach by comparison with reference data sets, we now demonstrate the application of NEP and TNEP models in combination for predicting the IR and Raman spectra of molecules, liquids, and solids. To this end, we employ the correlation function approach outlined above (Sect. 2.8 and Figure 1).

4.1. IR Spectrum of Water. First, we developed a NEP PES model for liquid water using energy, atomic forces, and virial data from density functional theory (DFT) calculations (Sect. S2).

Next, a system of 216 water molecules was equilibrated in the NPT ensemble for 100 ps using the trained PES model at 298 K and 1 bar, followed by a further equilibration run in the NVT ensemble for another 100 ps. Three production runs were carried out in the NVE ensemble for a duration of 200 ps. A time step of 0.5 fs was used throughout. We note that quantum effects can be actually rather pronounced in water as has been shown by path integral MD simulations in, e.g., refs.^{65–67} Here, however, we decided to carry out classical MD simulations in order to enable a one-to-one comparison with the results of earlier studies.

The time dependence of the dipole ($\mu(t)$) was computed for the production trajectories with a spacing of 1 fs using the TNEP dipole model for liquid water described above (Sect. 3.1). The IR spectrum was then obtained by Fourier transform of the dipole moment ACF via eq 9. The final IR spectrum was obtained by averaging the IR spectra from the production runs.

For comparison, we also ran a 200 ps MD simulation with the TIP3P force field⁶⁸ via the CP2K software package,⁶⁹ where the TIP3P force field uses charges of $-0.834 e$ and $+0.417 e$ for oxygen and hydrogen, respectively.

The NEP-TNEP method yields an IR spectrum that is in very good agreement with experimental data^{70,71} over the entire frequency range from 0 to 4000 cm^{-1} (Figure 4a). This includes the hydrogen-bond stretching band¹⁰ between 160 and 250 cm^{-1} , the libration band¹⁰ from 400 to 800 cm^{-1} associated with hindered molecule rotations,³⁷ and the bending modes^{37,72} at about 1650 cm^{-1} as well as the OH stretching band^{37,72} from 2800 to 4000 cm^{-1} . The NEP and TNEP models for PES and μ in conjunction with the underlying exchange-correlation functional thus succeed in capturing the entire range stretching from soft intermolecular to stiff intramolecular modes. This performance is also observed for the DP model (Figure 4a).

By comparison, classical models produce rather large errors for the location of several features in the IR spectrum of water. MD simulations with classical force fields^{68,73} such as TIP3P (Figure 4a) and SPC/E tend to predict a blue-shifting of the bending modes by roughly 100 to 200 cm^{-1} . A similar tendency was also observed for the POLI2VS model.³⁶ The results from the MB-pol model on the other hand exhibit a blue-shift of the OH stretching band by about 50 cm^{-1} .³⁷

The width of the OH stretching band has been proven to be quite difficult to predict due to the anharmonicity of the OH stretch mode.³⁷ The NEP-TNEP approach yields a value of 380 cm^{-1} for the full width at half-maximum of this band, which is in good agreement with experimental estimates of about 350 cm^{-1} from Downing et al.⁷⁰ Both NEP-TNEP and DP predictions exhibit a slight high-frequency tail for this band, which is not visible in the experimental spectra. This small difference could originate from the strongly constrained and appropriately normed (SCAN) functional⁷⁴ that was used for generating the PES training data^{10,75} and/or the absence of quantum effects in the (classical) MD simulations.^{10,37}

4.2. Raman Spectra of Water. To obtain the Raman spectra of liquid water, we sampled the time dependence of $\chi(t)$ using the TNEP susceptibility model and subsequently computed the ACFs for the same trajectories used for the prediction of the IR spectra. The full spectrum given by eq 10

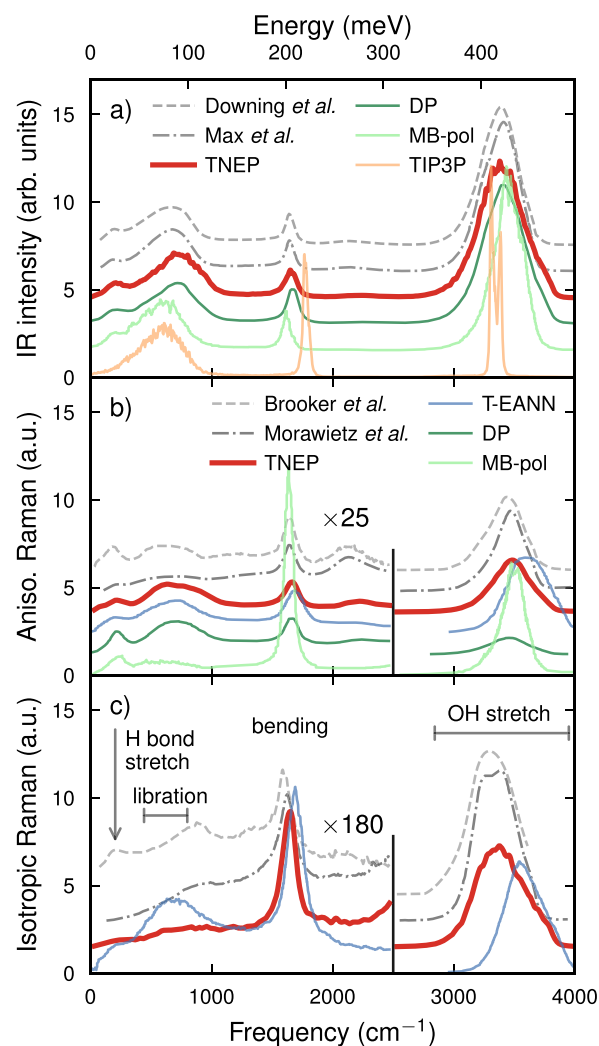


Figure 4. Comparison of (a) infrared as well as (b) anisotropic (depolarized) and (c) isotropic (polarized) Raman spectra of water at ambient conditions from simulations and experiment. Experimental data from Downing et al.,⁷⁰ Max et al.,⁷¹ Brooker et al.,⁷⁶ and Morawietz et al.⁷⁷ Simulated spectra from T-EANN,³⁹ MB-pol,³⁷ and DP^{10,44} models were adapted from the literature. In (a) and (b), the spectra were normalized by the integral between 80 and 2500 cm^{-1} , while in (c), they were normalized by the integral between 1000 and 2500 cm^{-1} .

and averaged over the available trajectories was then split into isotropic (polarized) and anisotropic (depolarized) contributions via eq 12.

The **anisotropic spectrum** predicted by the NEP-TNEP approach is overall in very good agreement with experimental data (Figure 4b).^{76,77} The locations of the peaks and relative intensities of the stretching, bending, and librational modes in the simulated anisotropic Raman spectra are all well produced. It is noteworthy that in the low frequency region below approximately 1000 cm^{-1} , the variation between the experimental spectra is larger than the variation between the ML models and the experimental data. This could be related to difficulties associated with processing the experimental raw data in this frequency region.

The T-EANN and DP models yield results similar to those of the NEP-TNEP approach in the region up to about 1900

cm^{-1} . On the other hand, all ML models underestimate the intensity of the association band between 1900 and 2500 cm^{-1} , which is arising from the combination of librational and bending modes.^{37,77} Here, the NEP-TNEP prediction is actually still the one that comes closest to the experimental spectra.

The broad high-frequency peak above 3000 cm^{-1} , which is associated with the OH stretch mode, is notably blue-shifted and broadened for the T-EANN model, while the DP model strongly underestimates the intensity of this peak. In contrast, the NEP-TNEP combination predicts this feature in good agreement with the experimental data.

Finally, the parametric MB-pol model yields the worst agreement with experiment, for example, strongly overestimating the intensity of the bending band while underestimating the libration band.

With regard to the **isotropic Raman spectrum** (Figure 4c), one should first note the variation among the experimental data. In particular, in the region below 1000 cm^{-1} , the resulting uncertainty is comparable or even larger than the deviation between the NEP-TNEP prediction and the experimental data, while the position of the libration band predicted by T-EANN appears red-shifted. With regard to the higher frequency region, both NEP-TNEP and T-EANN reproduce the bending band well. In the case of NEP-TNEP, this also applies for the OH stretch band, whereas in the case of T-EANN, a blue-shift can be observed similar to that of the anisotropic spectrum (Figure 4b).

4.3. IR Spectrum of PTAF⁻. The NEP-TNEP method for predicting IR spectra can be easily adopted for other molecular systems as long as the underlying observables to be learned are available. Naturally, this includes the molecular configurations along a chemical reaction such that experimentally observable spectral changes can be connected to metastable complexes. One such complex is PTAF⁻ (see inset in Figure 5), the intermediate reaction minimum in the deprotection reaction 1-phenyl-2-trimethylsilylacetylene (PTA) with tetra-*n*-butylammonium fluoride.^{78–81}

To train NEP and TNEP models, we obtained PES and μ data for a set of 20170 structures via DFT calculations using the ORCA code,⁸² the PBE functional,⁸³ and a def2-TZVP basis set⁸⁴ while enforcing tight convergence of the self-consistent field cycles. Subsequently, MD simulations at various temperatures were performed in the NVE ensemble using a time step of 0.1 fs for 1 ns, during which $\mu(t)$ was recorded with a time resolution of 0.5 fs.

The IR spectra obtained via the analysis of the ACF of μ show a pronounced temperature dependence in particular of the line widths (Figure 5). The molecule supports several soft modes with frequencies in the region below 250 cm^{-1} , which are associated with the bending of and rotation about the ethynyl linker. These modes in particular lead to strong mode coupling (i.e., anharmonicity), which underlies the changes in line width and the redistribution of the dipole strength across the spectrum. Here, the computational efficiency of the NEP-TNEP implementation in GPUMD was crucial to resolve these features, as it enabled sampling on the nanosecond time scale, which would be prohibitive for DFT-MD simulations and computationally very expensive for a CPU implementation.

4.4. Raman Spectra of BaZrO₃. BaZrO₃ is a perovskite that is being investigated, e.g., as a proton conductor for applications in fuel cells. It has also been the subject of various fundamental studies, as it is a prototypical antiferroelectric

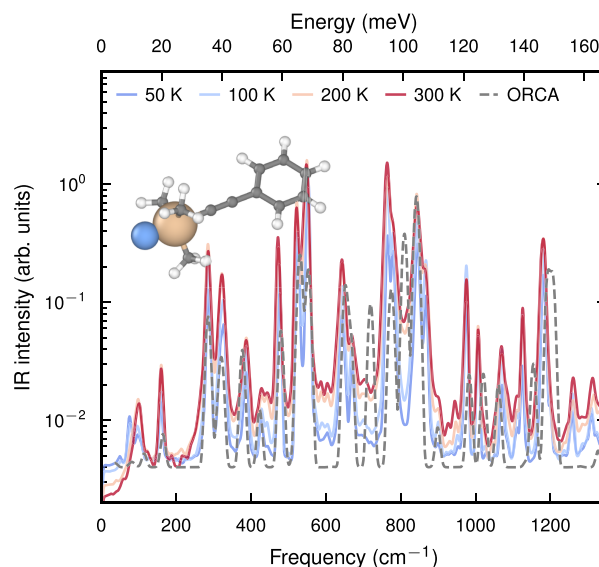


Figure 5. IR spectra for the metastable PTAF⁻ complex (see the inset) at various temperatures. The gray dashed line represents the broadened integrated absorption coefficients of the harmonic spectrum obtained directly from DFT calculations. The overall agreement is good considering the lack of anharmonic corrections (intensity and vibrational frequencies) and temperature sensitivity of the spectrum obtained from DFT calculations.

perovskite.^{85–87} It features soft and strongly temperature-dependent phonon modes,^{88,89} which have been carefully analyzed with Raman spectroscopy,⁹⁰ rendering BaZrO₃ an ideal application for the present approach.

For benchmarking, we constructed models for χ using both the TNEP and SA-GPR approaches. The reference data set comprised cubic and tetragonal supercells with up to 40 atoms. The training structures were taken from MD simulations at different temperatures and pressures, generated using a NEP PES model constructed in an earlier study.⁸⁹ In total, the reference data set contained 940 structures. 140 structures were randomly placed in a holdout set for validation, while training sets were compiled by the shuffle-split method (random selection with replacement) with 200 to 800 structures and five data sets per training set size.

A comparison of models generated using different choices for the size of the neural network as well as the descriptor demonstrates that viable models can be obtained for a wide range of parameters and that even small models with as few as 1500 or so parameters can yield very good results (Figure S12). Yet fine-tuning of these parameters as well as the regularization parameters (Figure S13) allows one to maximize model performance.

The convergence of RMSEs and R^2 scores with training set size is similar for TNEP and SA-GPR with slightly better performance for TNEP (Figure 6). In both cases, training sets of about 400 structures already yield very good models, demonstrating the data efficiency of these approaches. This behavior has also been observed in the construction of models for amino acids.⁹¹

Next MD simulations were carried out using $12 \times 12 \times 12$ supercells (8640 atoms) and a time step of 1 fs using the NEP model for the PES. Following equilibration at 300 K and 0 GPa in the NPT ensemble, the time-dependent susceptibility $\chi(t)$

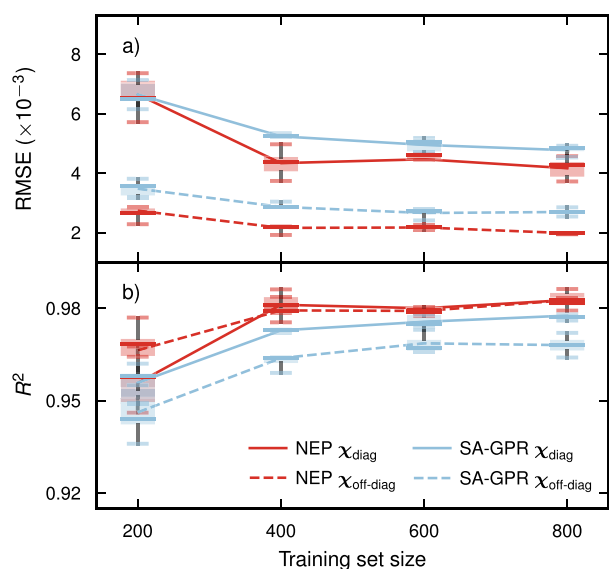


Figure 6. Variation of (a) RMSEs and (b) R^2 scores with training set size for TNEP and SA-GPR models based on five training sets per size generated by shuffle-split. In the case of TNEP, we used $N_{\text{neu}} = 20$, $n_{\text{max}}^R = n_{\text{max}}^A = 4$, and $\lambda_1 = \lambda_2 = 2 \times 10^{-3}$ (compare Figures S12 and S13).

was recorded for 500 ps using a time resolution of 5 fs. For production, we used a TNEP model for χ trained against the full data set, but we found that models based on at least approximately 400 structures yield results that are practically indistinguishable within the statistical uncertainty. The Raman line shape was subsequently obtained via the ACF of χ according to eq 11. We then computed the Raman spectra for parallel (Figure 7a,b) and crossed polarization (Figure 7c,d), which in Porto notation correspond to $Z(XX)\bar{Z}$ and $Z(XY)\bar{Z}$, respectively, where X and Y are arbitrary crystal axes. The final spectra were obtained by averaging over 20 independent MD trajectories.

The results are overall in very good agreement with experiment, especially considering the very strong anharmonicity of this material and the strong temperature dependence of the vibrational spectrum.⁸⁸ The main difference with respect to the position of the peaks is a slight red-shift in the predicted spectra in the region above 600 cm^{-1} . This overly soft response can be attributed to the underlying exchange-correlation functional (vdW-DF-cx, refs.^{92,93}), which the NEP model truthfully reproduces. One can also observe an inversion in the intensity of the low- and high energy features. This effect is almost certainly due to the classical sampling used here. It is rather common to correct for quantum effects in IR and *first order* Raman spectra by including a factor similar to the prefactor in eq 8. In the case of BaZrO_3 the room-temperature Raman spectrum arises, however, due to *second-order* scattering, i.e., due to combinations of modes. In that case, the application of the commonly used correction factor is no longer valid. Here, we omit such corrections entirely.

The Raman spectra depend on the crystal orientation with respect to the excitation laser. The present approach allows one to readily map out this dependence via eqs 10 and 11 (Figure 7b,d). While we are unaware of experimental measurements of the polarization dependence for BaZrO_3 , we note that such experiments have been carried out for, e.g.,

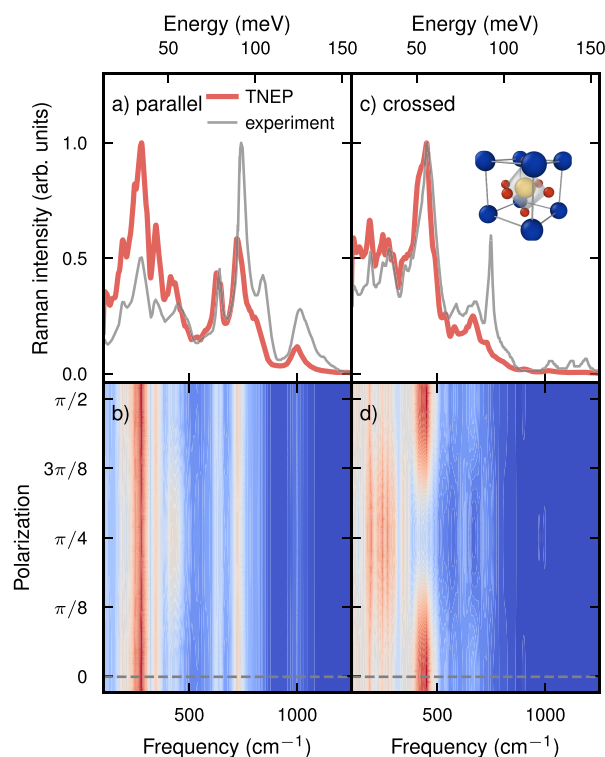


Figure 7. Raman spectra of BaZrO_3 for (a,b) parallel and (c,d) crossed polarization from simulations using a combination of NEP and TNEP models (red lines) as well as experiment (gray lines).⁹⁰ The spectra shown in (a,c) have been predicted for the nominal alignments used in the experimental measurements. The corresponding polarizations are indicated by the dashed horizontal lines in (b,d).

NaCl .⁹⁴ As demonstrated in the previous study, such measurements can provide valuable additional information.

5. CONCLUSIONS

In this contribution, we introduced an extension of the NEP approach to tensors, resulting in the TNEP scheme. This was achieved by constructing expressions for rank-1 and rank-2 tensors based on the expression for the virial, which is a rank-2 tensor that arises naturally from derivatives of the energy (a rank-0 tensor) with respect to the atomic distances. This approach, which can be extended to tensors of higher rank, thus allows one to easily construct models that are equivariant.

We demonstrated the accuracy of this approach and its computational efficiency by constructing models for the dipole moment μ , the molecular polarizability α , and the electric susceptibility χ for several molecules, a liquid, and two crystalline materials. In particular, the computational speed of the current method and its implementation in the `GPUMD` package provide a significant advantage in terms of both the time scales and system sizes that can be sampled.

Finally, we applied the approach to predict IR and Raman spectra of liquid water, the molecule PTAF^- , and the perovskite BaZrO_3 in very good agreement with available experimental data, illustrating the range of systems that can be readily addressed by using the TNEP methodology introduced here.

■ ASSOCIATED CONTENT

Data Availability Statement

The source code and documentation for GPUMD are available at <https://github.com/brucefan1983/GPUMD> and <https://gpumd.org>, respectively. The source code and documentation for CALORINE are available at <https://gitlab.com/materials-modeling/calorine> and <https://calorine.materialsmodeling.org>, respectively. NEP models and data are available via Zenodo via 10.5281/zenodo.10257363 (water and BaZrO₃), 10.5281/zenodo.10255268 (PTAF⁻), and 10.5281/zenodo.8337182 (BaZrO₃).

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.3c01343>.

Training process of SA-GPR models for water systems; calculations of dipole moment for liquid water and α -Fe₂O₃; notes on the Clausius-Mossotti relation and the units of polarizability and electric susceptibility; parity plots of the TNEP predicted dipole moment, diagonal and off-diagonal elements of the polarizability tensor versus the *ab initio* references for water systems; demonstration of rotational invariance; parameters used in the training of NEP and TNEP models; dependence of TNEP model performance for BaZrO₃ on model and training hyperparameters; timing of on-the-fly model evaluation during MD simulations (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Yi He – Institute of Zhejiang University-Quzhou, Quzhou 324000, P. R. China; College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310058, P. R. China; Department of Chemical Engineering, University of Washington, Seattle, Washington 98195, United States; orcid.org/0000-0002-8807-0892; Email: yihezj@zju.edu.cn

Zheyong Fan – College of Physical Science and Technology, Bohai University, Jinzhou 121013, P. R. China; orcid.org/0000-0002-2253-8210; Email: brucenju@gmail.com

Paul Erhart – Department of Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden; orcid.org/0000-0002-2516-6061; Email: erhart@chalmers.se

Authors

Nan Xu – Institute of Zhejiang University-Quzhou, Quzhou 324000, P. R. China; College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310058, P. R. China; orcid.org/0000-0003-3986-6883

Petter Rosander – Department of Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden

Christian Schäfer – Department of Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden; orcid.org/0000-0002-8557-733X

Eric Lindgren – Department of Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden; orcid.org/0000-0002-8549-6839

Nicklas Österbacka – Department of Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden; orcid.org/0000-0002-6043-4607

Mandi Fang – Institute of Zhejiang University-Quzhou, Quzhou 324000, P. R. China; College of Chemical and

Biological Engineering, Zhejiang University, Hangzhou 310058, P. R. China; orcid.org/0009-0006-8273-3508

Wei Chen – State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China; orcid.org/0000-0002-0165-4896

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.jctc.3c01343>

Notes

The authors declare no competing financial interest.

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Supporting Information:

Tensorial properties via the neuroevolution potential framework: Fast simulation of infrared and Raman spectra

Nan Xu^{1,2}, Petter Rosander³, Christian Schäfer³, Eric Lindgren³, Nicklas Österbacka³, Mandi Fang^{1,2}, Wei Chen⁴, Yi He^{1,2,5,*}, Zheyong Fan^{6,†}, and Paul Erhart^{3,‡}

¹*Institute of Zhejiang University-Quzhou, Quzhou 324000, P. R. China*

²*College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310058, P. R. China*

³*Department of Physics, Chalmers University of Technology, SE-41296, Gothenburg, Sweden*

⁴*State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, P. R. China*

⁵*Department of Chemical Engineering, University of Washington, Seattle, WA 98195, USA*

⁶*College of Physical Science and Technology, Bohai University, Jinzhou 121013, P. R. China*

**yihezj@zju.edu.cn*

†*brucenju@gmail.com*

‡*erhart@chalmers.se*

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S1 Dipole, polarizability, and susceptibility data for water systems

Data for the dipole moment ($\boldsymbol{\mu}$), the polarizability ($\boldsymbol{\alpha}$), and the electronic part of the electric susceptibility ($\boldsymbol{\chi}_e$) for molecular water species as well as liquid water were retrieved from a public repository.^{1,2} The $\boldsymbol{\mu}$ and $\boldsymbol{\alpha}$ data for the molecules H_2O , $(\text{H}_2\text{O})_2$, and H_5O_2^+ provided in the repository were calculated at the coupled cluster singles and doubles (CCSD) level of theory^{3,4} with the d-aug-cc-pVTZ^{5,6} basis set. The data for liquid water in the repository were generated using the Perdew–Burke–Ernzerhof (PBE)⁷ functional and ultra-soft pseudo-potentials (USPPs).⁸ The repository contains data for the relative dielectric permittivity ϵ_r . Here, the latter was converted to the electric susceptibility $\boldsymbol{\chi}_e = \epsilon_r - 1$ for training.

We demonstrate here two approaches to calculate dipole moment for periodic systems (liquid water) via the modern theory of polarization^{2,9,10}. A total of 50 structures was randomly selected from the liquid water data set. In the first approach, the total $\boldsymbol{\mu}$ of each structure was calculated using the Berry phase formulation⁹. The calculations were performed using the CP2K software package¹¹ with density functional theory (DFT) implemented using the gaussians and plane waves (GPW) method. The TZV2PX-MOLOPT-GTH basis set and GTH-PBE pseudopotentials were used.^{7,12} In addition, the DFT-D3 correction¹³ was employed to capture dispersive van-der-Waals interactions. As shown in Fig. S4a, most of the calculated $\boldsymbol{\mu}$ are consistent with the reference $\boldsymbol{\mu}$, while some of them have significant offsets. These $\boldsymbol{\mu}$ data points were shifted by $N \cdot L$, where N is an integer and L is the lattice parameter, thereby account for the phase shift that arises in the modern theory of polarization⁹. As shown in Fig. S4b, the shifted $\boldsymbol{\mu}$ data points are consistent with the reference $\boldsymbol{\mu}$ data. In the second approach, the total $\boldsymbol{\mu}$ of each structure was calculated using maximally localized Wannier functions (MLWFs)¹⁴

$$\boldsymbol{\mu} = 6e \sum_i r_i^{\text{O}} + e \sum_j r_j^{\text{H}} - 2e \sum_k r_k^{\text{MLWF}},$$

where r_i^{O} and r_j^{H} are the coordinates of oxygen and hydrogen atoms and r_k^{MLWF} is the coordinate of the Wannier centers belonging to a water molecule.¹⁵ In this case, a proper coordinate transformation of the oxygen and hydrogen atoms as well as the Wannier centers is required before calculating the total dipole moment.(Fig. S5) As shown in Fig. S4c, the $\boldsymbol{\mu}$ data points calculated from MLWFs are consistent with the reference $\boldsymbol{\mu}$ data.

S2 Training of NEP PES model for water

We used the potential energy surface (PES) data set for liquid water from Ref. 16,17 to train a neuroevolution potential (NEP) PES model to be used for MD simulations. The data set contains 1888 structures in total, for which energy, forces, and virials have been computed using DFT calculations. The strongly constrained and appropriately normed (SCAN)¹⁸ functional and the projector augmented wave (PAW) method¹⁹ (with hard setups) were used. All data were randomly divided into training and validation data sets with a ratio of 4:1. The hyperparameters used in the training of the NEP model are tabulated in Table S3. The root-mean-square errors (RMSEs) for energy, forces, and virials converged after 3×10^5 generations of training, and the predicted energies, forces, and virials closely match the DFT reference data, as shown in Fig. S9. We also performed an NPT (isothermal-isobaric) MD simulation of liquid water (64 molecules) using the NEP PES model at 330 K and 1 bar. The radial distribution functions (RDFs) for O–O and O–H pairs extracted from these simulations agree well with *ab initio* molecular dynamics (AIMD) simulation in the literature²⁰ (Fig. S10).

S3 Training of SA-GPR models for water molecules

Since we did not find publicly accessible models for H_2O , $(\text{H}_2\text{O})_2$ and H_5O_2^+ , we trained new symmetry-adapted Gaussian process regression (SA-GPR) models for $\boldsymbol{\mu}$ and $\boldsymbol{\alpha}$ using the same data sets as those used for training the tensorial neuroevolution potential (TNEP) models (Sect. S1). The default hyperparameters were used in the training.

S4 Training of TNEP models for QM7b data set

We also consider the QM7b data set²¹ that comprises 7211 small organic molecules with up to six elements (H, C, N, O, S, Cl). The reference μ and α data²² were calculated at the CCSD level of theory using the d-aug-cc-pVDZ basis set^{5,6}. 70% of the data were used for training, while the remaining data were used for validation. The parameters in the training of the TNEP dipole and polarizability models are shown in Table S1 and Table S2. Both the dipole and polarizability models achieve very high precision for the QM7B data set (Fig. S3).

S5 Training of TNEP dipole model for α -Fe₂O₃

We also consider yet another crystalline system in α -Fe₂O₃. The primitive structure of α -Fe₂O₃ reported by Mendili *et al.*²³ was used here, which is defined by three vectors: $\mathbf{a} = (5.03, 0.00, 0.00)$, $\mathbf{b} = (-2.515, 4.356, 0.00)$, and $\mathbf{c} = (0.00, 0.00, 13.75)$, measured in units of Å. A $2 \times 2 \times 1$ supercell was created and used as the initial structure for AIMD simulations. The simulation system contained 120 atoms. The AIMD simulations were performed using a time step of 0.5 fs and the CP2K software package¹¹. The forces on the atoms were evaluated using the DZVP-GTH-PADE basis set and GTH-PADE pseudopotentials^{24,25}. To maintain the temperature at 300 K, a Nosé-Hoover thermostat was employed²⁶. During the simulation, a magnetic moment of $5 \mu_B$ was assigned to each iron atom, where μ_B represents the Bohr magneton. The simulation was run for a total of 2000 time steps, and snapshots were saved with an interval of 1 fs. In total, 1000 structures were sampled and used for post-processing. The μ data of the 1000 structures were calculated using the Berry phase formulation,⁹ where the origin of the coordinate system was used as the reference point. The calculated values vary continuously with the simulation time, indicating that all configurations are on the same branches of the Berry phase and no shifts are required for calculating μ (Fig. S6a). The 1000 data points were randomly divided into a training data set and a validation data set with a ratio of 7:3. The hyperparameters used for training the TNEP dipole model are tabulated in Table S1. The μ values predicted by the TNEP model are consistent with the DFT reference values (Fig. S6b). The coefficient of determination (R^2) is close to one.

S6 Training of TNEP susceptibility model for BaZrO₃

The training data points were taken from MD snapshots at various temperatures and pressures obtained using a previously published NEP model for the BaZrO₃ PES.²⁷ Both the cubic and tetragonal phases were included, with supercell sizes varying from the primitive cell to $4 \times 2 \times 1$ repetitions. The final dataset consisted of 940 structures, for which the relative permittivity ϵ_r was obtained from DFT calculations using the PAW formalism^{19,28} as implemented in the Vienna Ab-initio Simulation Package^{29,30}. The van-der-Waals density functional with consistent exchange (vdW-DF-cx) was used to describe the exchange-correlation energy contribution^{31,32}. A plane-wave energy cutoff of 510 eV was used along with Gaussian smearing with a width of 0.01 eV. Projection operators were evaluated in reciprocal space and an additional support grid was used for evaluation of augmentation charges for increased accuracy.

The hyperparameters used for training the TNEP models for BaZrO₃ are tabulated in Table S2. The relative permittivity was converted to electric susceptibility via the relation $\chi_e = \epsilon_r - 1$ for training. Five-fold leave-one-out cross validation was carried out, where the dataset was split into five equal parts. Five separate models were then trained, each using one of these splits as a validation set. These models were trained until their validation set RMSE stopped improving, which occurred after 6×10^5 generations. Their mean coefficient of determination (R^2) was 0.950(2) for the diagonal and 0.984(2) for the off-diagonal elements. These quantities serve as accuracy estimates for the final model, which was trained on the entire dataset. Training of this model was considered converged after 6×10^5 generations based on the cross validation result, after which the TNEP model predicted values for the susceptibility consistent with DFT reference values (Fig. S11).

S7 Note on units of polarizability and susceptibility

For a single molecule, the *molecular polarizability* α connects the induced dipole moment μ_{ind} (charge times distance per molecule) to the electric field \mathbf{E} (potential per distance),

$$\mu_{\text{ind}} = \alpha \mathbf{E}. \tag{S1}$$

For a bulk material, the *electric susceptibility* χ connects the polarization (or dipole density) \mathbf{P} (charge times distance per volume) to the electric field \mathbf{E} (potential per distance),

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E}. \tag{S2}$$

It is now instructive to consider the different units involved in the expressions above. Here, we explicitly included the unit mol, which is strictly part of the SI system but often left out. This is done in order to emphasize the transition from molecular quantities (α) to bulk quantities ($\epsilon_0 \chi$). This occurs, for example, in the Clausius-Mossotti relation, where α is related to $\epsilon_0 \chi$ by scaling with the number volume density ρ . Here, we see that α has units of F m²/mol whereas $\epsilon_0 \chi$ has units of F/m and thus units of α per volume. The following table summarizes the SI units of the quantities as defined above.

Quantity	SI unit
μ_{ind}	C m/mol
\mathbf{E}	V/m
α	C m ² /(V mol) = F m ² /mol
\mathbf{P}	C/m ²
ϵ_0	F/m
χ	1
ρ	mol/m ³

We note that there are various ways in which the relations Eqs. (S1) and (S2) are written in the literature. One can for example subsume ϵ_0 into χ , which emphasizes the symmetry with α . One can also choose to express α in units of ϵ_0 , i.e., $\alpha = \epsilon_0 \alpha'$, in which case α' has units of volume.

S8 Note on the Clausius-Mossotti relation

For non-polar liquids or gases, the Clausius-Mossotti relation³³ can be used to approximate the relation between the average molecular polarizability $\alpha = \text{Tr}(\alpha)/3$ and the average electric susceptibility $\chi = \text{Tr}(\chi)/3$. It is based on a mean-field approximation to account for local field effect and is given by

$$\frac{\chi_e}{\chi_e + 3} = \frac{\rho \alpha}{3 \epsilon_0},$$

where ρ is the number volume density. The quantities are expressed in SI units. The Clausius-Mossotti can also be written in terms of the relative permittivity ϵ_r , which is related to the electric susceptibility via $\epsilon_r = 1 + \chi$.

Note that all quantities here are isotropic and therefore represented by scalars. Here, α is the molecular polarizability, ρ is the number volume density, ϵ_0 is the permittivity of vacuum, and ϵ_r is the relative permittivity.

S9 Rotational equivariance of TNEP models

Here, we explicitly demonstrate that the TNEP dipole and polarizability model are invariant to rotations by taking the water monomer (H₂O) as an example. Dipole moments (μ) and polarizabilities (α) were predicted for the validation set using the TNEP models described in the manuscript. Then, structures were subjected to rotations (\mathbf{R}) at random angles. Dipole moments (μ') and polarizabilities

(α') of the rotated structures were also predicted using the TNEP models. According to the rotational symmetries of rank-1 and rank-2 tensors, the rotational transformed dipole moments (μ'') and polarizabilities (α'') should be $(\mathbf{R}\mu^T)^T$ and $\mathbf{R}\alpha\mathbf{R}^{-1}$, respectively. The parity plots of μ'' and α'' versus μ' and α' for the validation set of H₂O clearly demonstrate the expected rotational invariance (Fig. S14).

S10 On-the-fly prediction of dipoles and polarizability during MD simulations

Predicting dipoles or polarizabilities can be efficiently performed on-the-fly during MD runs in GPUMD. Fig. S15 shows how the performance of MD simulations scales with system size when tensorial properties are predicted at every tenth timestep, compared to a baseline without any tensorial predictions. Note that the overhead of evaluating tensorial properties on-the-fly during MD of course depends on how often they are to be evaluated, i.e., the number of timesteps between predictions.

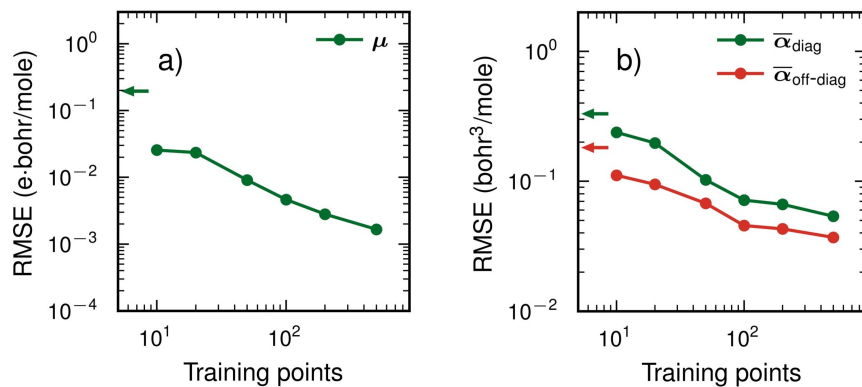


Figure S1: The learning curves for (a) dipole moment and (b) effective polarizability of liquid water. The effective polarizability is given by $\bar{\alpha} = \chi/\rho$, where ρ is the number volume density. For all cases, the validation data set consists of 500 independent configurations. Arrows indicate the intrinsic standard deviation of the validation data set.

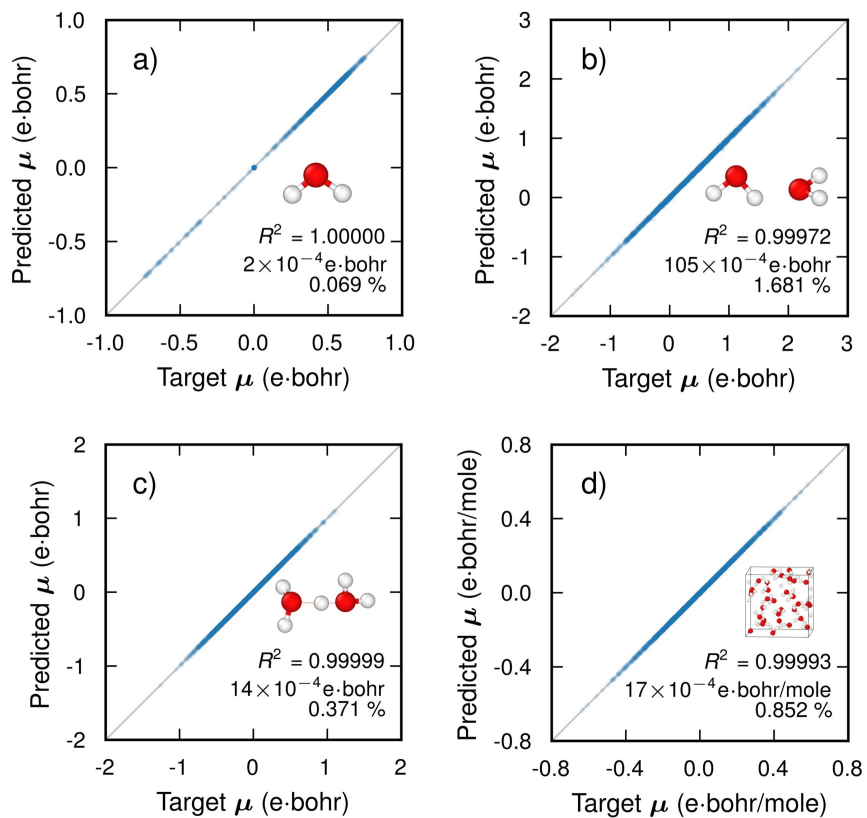


Figure S2: TNEP predicted dipole moment compared to *ab initio* data for the validation sets of (a) H₂O, (b) (H₂O)₂, (c) H₅O₂⁺, and (d) liquid water. The coefficients of determination (R^2), RMSEs and RRMSEs are indicated in each subpanel. For liquid water, the dipole moment is given per water molecule.

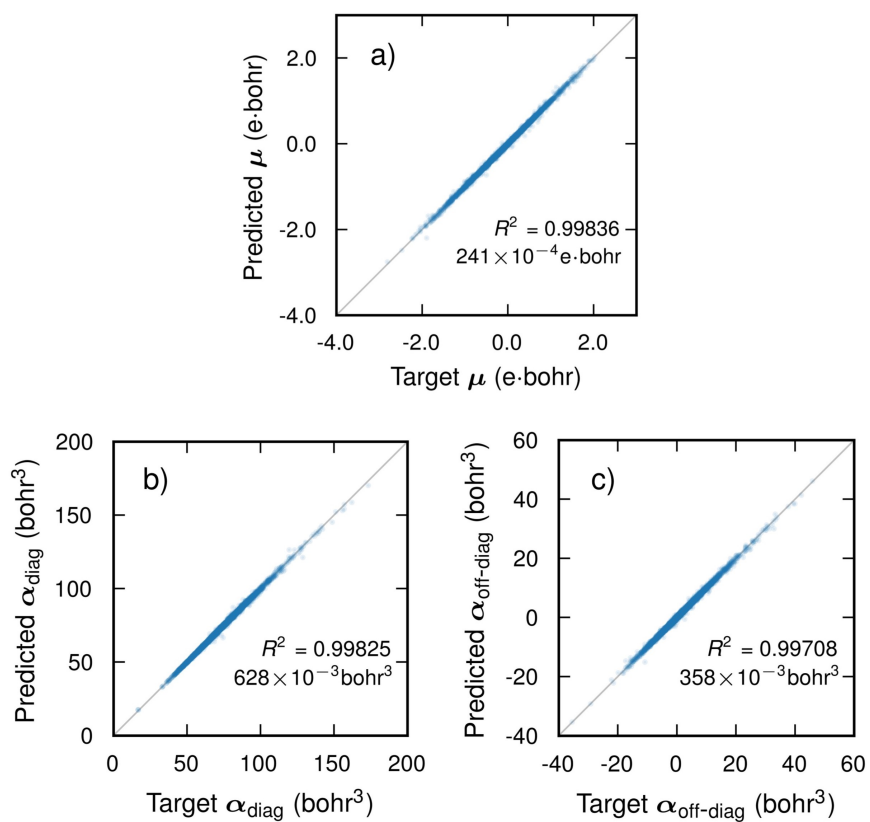


Figure S3: TNEP predictions as compared to CCSD reference data of (a) dipole moment, (b) diagonal elements of the polarizability, and (c) off-diagonal elements of the polarizability for the validation set of the QM7b set.

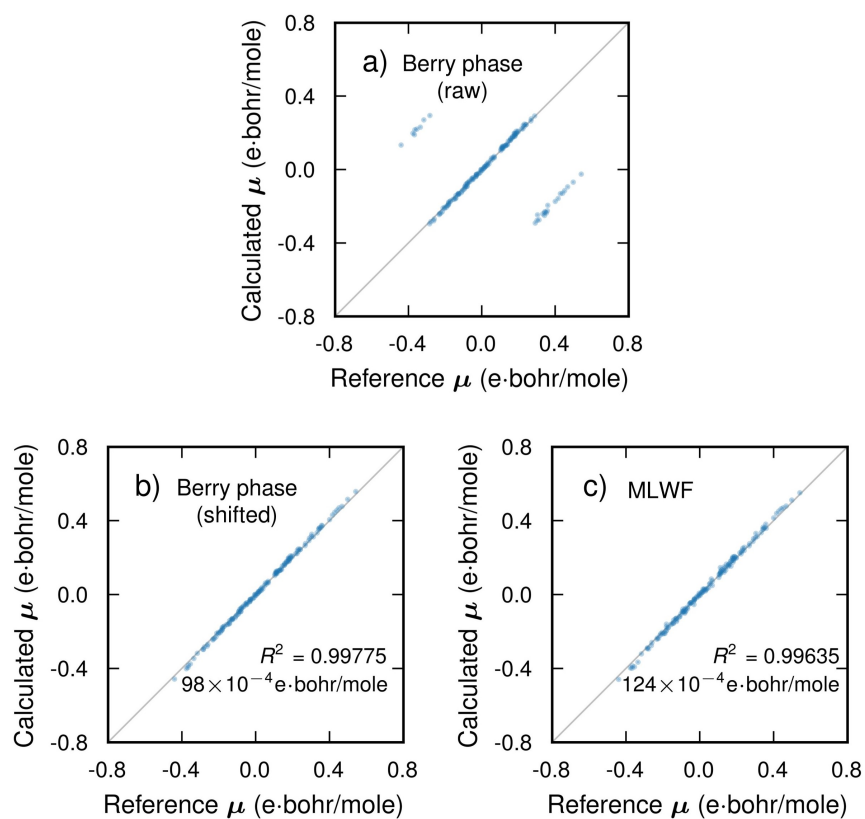


Figure S4: Dipole moments per molecule calculated in this work compared to reference data^{1,2} for 50 liquid water structures that were evaluated in this work.

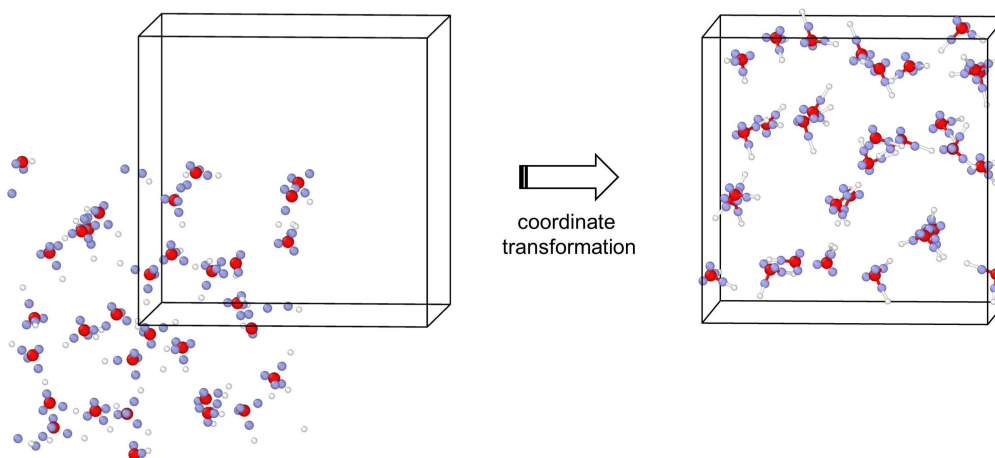


Figure S5: Schematic plot of coordinate transformation of water molecules and their Wannier centers before calculating the total dipole moment. Red, white, and slate-blue balls represent oxygen atoms, hydrogen atoms, and Wannier centers, respectively.

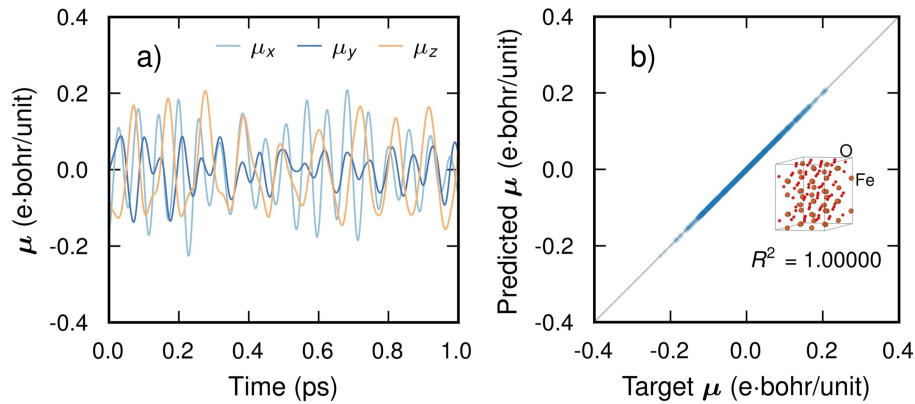


Figure S6: (a) Dipole moment per formula unit of α -Fe₂O₃ calculated by DFT as a function of simulation time. (b) The comparison between the TNEP predictions and DFT values of dipole moment for the validation data set of α -Fe₂O₃.

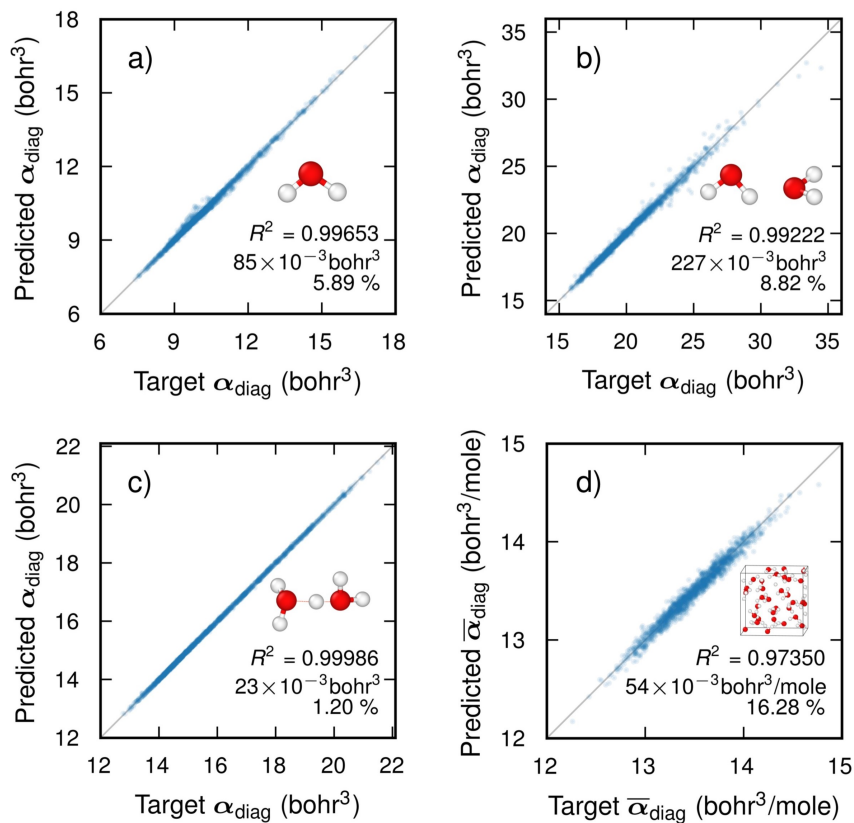


Figure S7: TNEP predicted diagonal polarizability as compared to *ab initio* data for the validation sets of (a) H₂O, (b) (H₂O)₂, (c) H₅O₂⁺, and (d) liquid water. For liquid water we show the effective polarizability given by $\bar{\alpha} = \chi/\rho$, where ρ is the number volume density. R^2 scores, RMSEs, and RRMSEs are given in each subpanel. For liquid water the polarizability is divided given per water molecule.

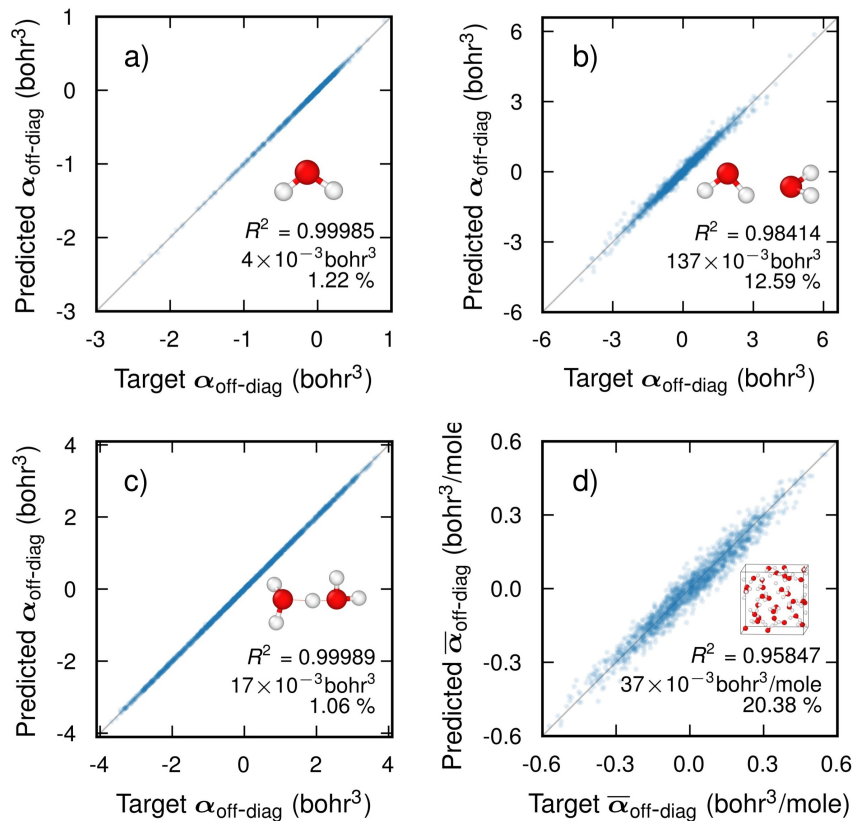


Figure S8: TNEP predicted off-diagonal polarizability compared to the *ab initio* values for the validation sets of (a) H₂O, (b) (H₂O)₂, (c) H₅O₂⁺, and (d) liquid water. For liquid water we show the effective polarizability given by $\bar{\alpha} = \chi/\rho$, where ρ is the number volume density. R^2 scores, RMSEs, and RRMSEs are given in each subpanel. For liquid water the polarizability is given per water molecule.

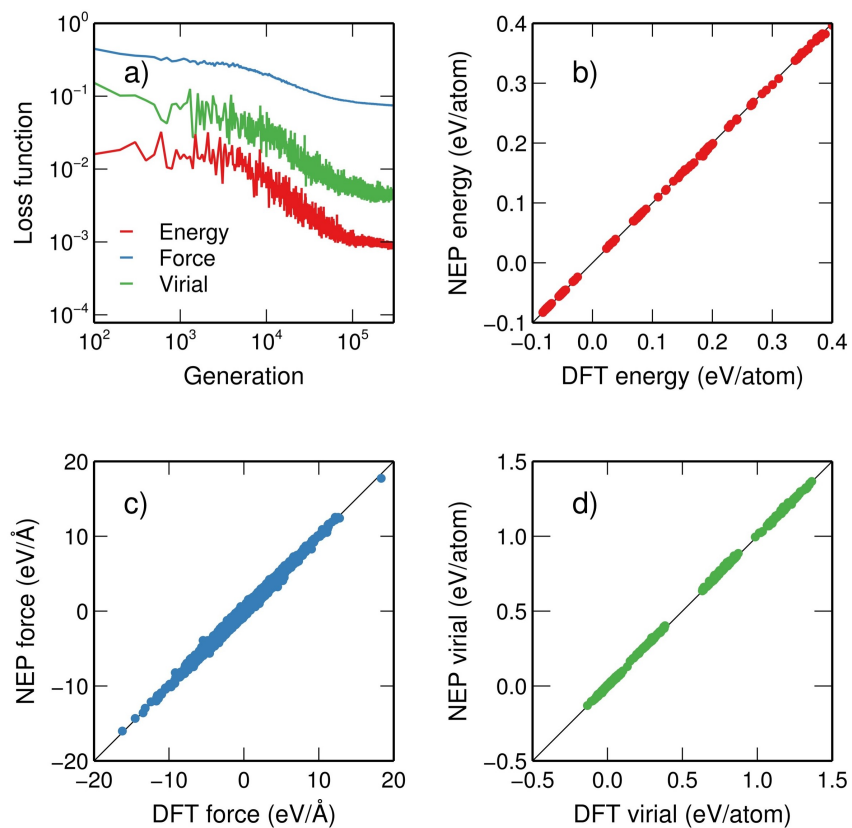


Figure S9: NEP model for the PES of liquid water. (a) RMSEs of energy, force, and virial for the validation set as a function of the number of generations. (b–d) Comparison between NEP predictions and DFT reference values of energies, forces, and virials for the validation set of liquid water.

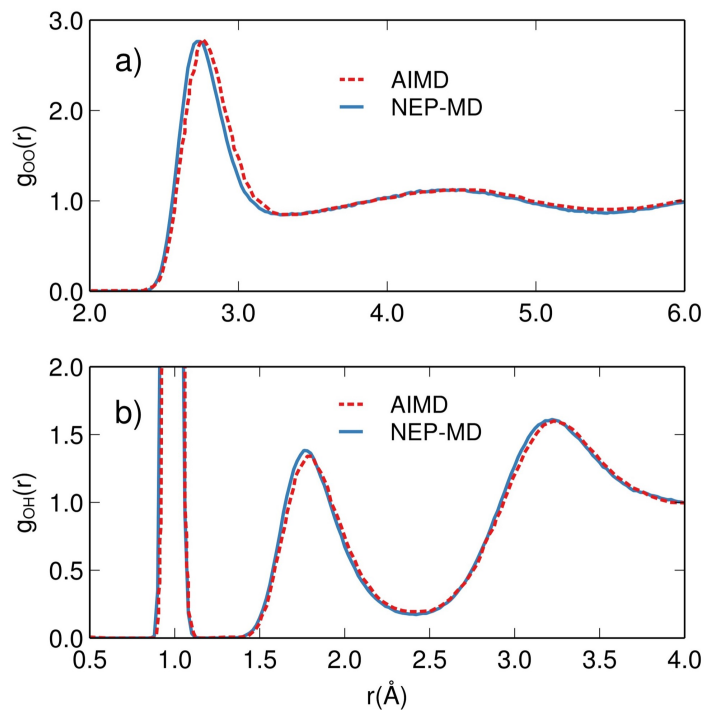


Figure S10: Validation of NEP model for the PES of liquid water. RDFs for (a) O–O and (b) O–H pairs extracted from MD simulations based on the NEP PES model constructed in this work and AIMD simulations²⁰ at 330 K and 1 bar.

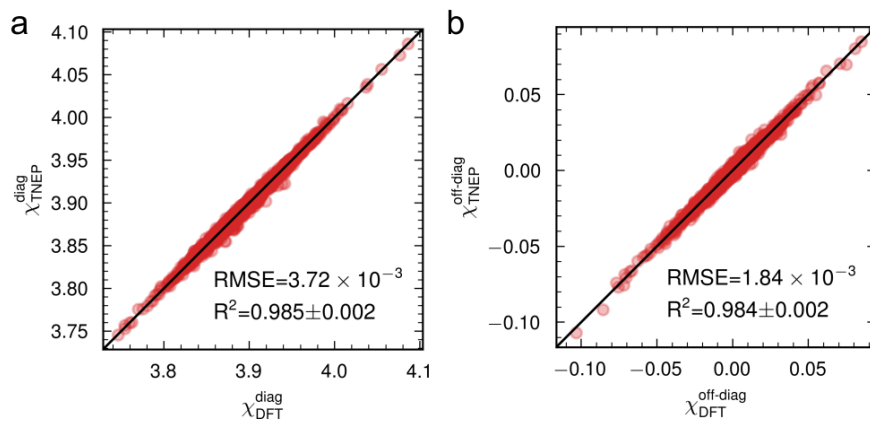


Figure S11: Comparison between TNEP predictions and DFT reference values for the (a) diagonal and (b) off-diagonal elements of the susceptibility χ of BaZrO₃. The R^2 scores and RMSEs represent the means from five-fold hold-one-out cross-validation.

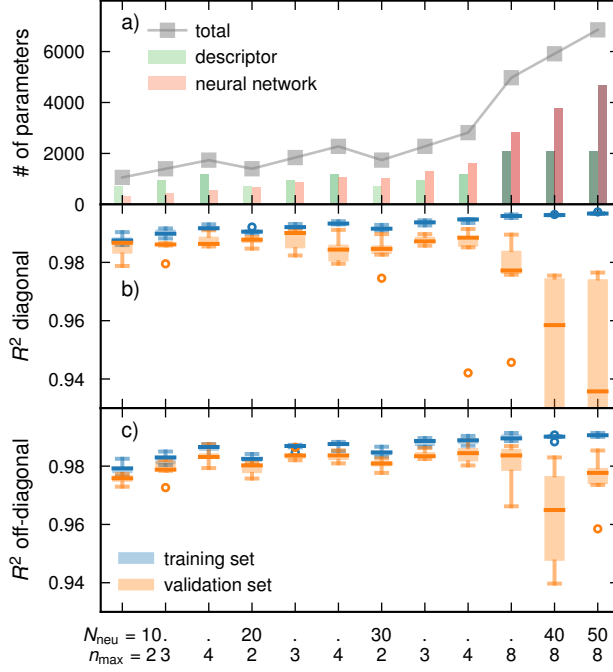


Figure S12: Impact of neural network architecture on model performance for TNEP models for the susceptibility of χ of BaZrO_3 . (a) The number of model parameters split by descriptor and neural network. (b, c) Box plots of R^2 for the (b) diagonal and (c) off-diagonal components of χ ; outliers are shown by small open circles. N_{neu} indicates the number of neurons in the hidden layer of the neural network. n_{max} specifies the number of basis functions used to construct the radial ($n_{\text{max}}^{\text{R}}$) and angular ($n_{\text{max}}^{\text{A}}$) descriptors; see Ref. 34 for the full expressions for the network and the descriptors. Here, we use $n_{\text{max}} = n_{\text{max}}^{\text{R}} = n_{\text{max}}^{\text{A}}$. Training was carried out using training sets generated by k -fold splitting of the 940 structures available. The comparison demonstrates that viable models can be obtained for a wide range of parameters, and that even small models with as few as 1500 or so parameters can yield very good results. Yet fine-tuning of the architecture (and the regularization parameters, see Fig. S13) allows one to optimize model performance.

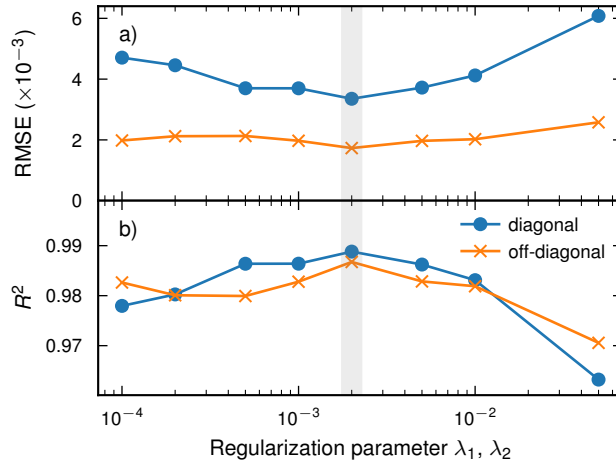


Figure S13: Hyperparameter tuning for TNEP models for the susceptibility of χ of BaZrO_3 . Variation of (a) RMSE and (b) R^2 for a validation set comprising 140 structures with the hyperparameters $\lambda_1 = \lambda_2$ that set the strength of the L_1 and L_2 -norm regularization terms in the loss function. The value of $\lambda_1 = \lambda_2 = 2 \times 10^{-3}$ used for building the models in Fig. 6 is indicated by gray bars. Training was carried out using a set comprising 800 structures. The neural network contained $N_{\text{neu}} = 20$ neurons and the radial and angular descriptors were constructed using $n_{\text{max}} = 4$ (see Fig. S12).

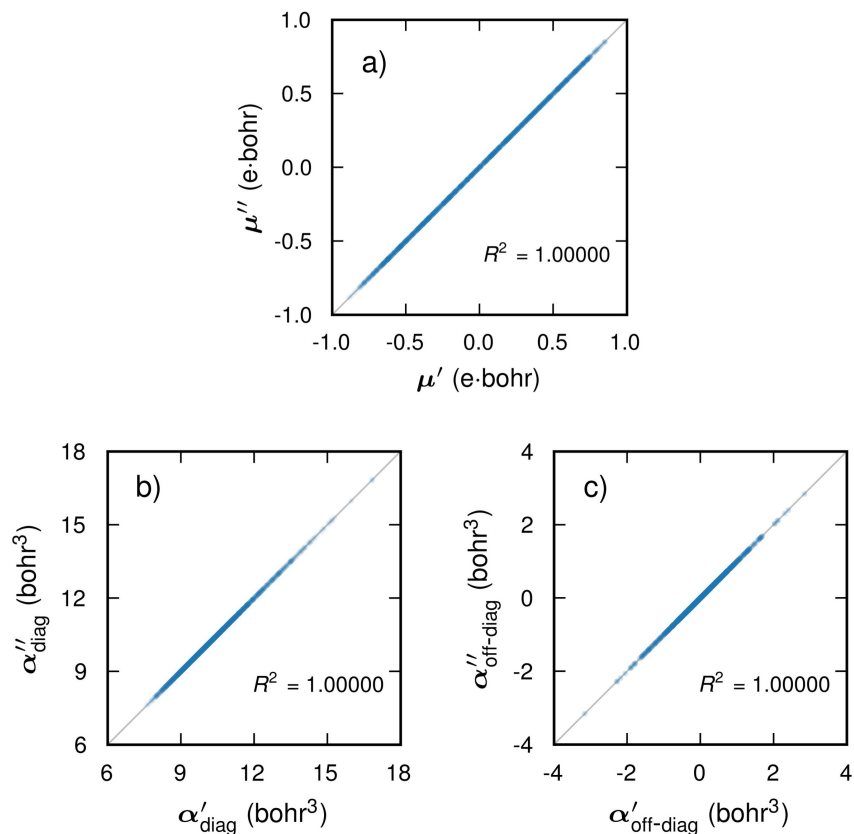


Figure S14: Demonstration of rotational invariance of TNEP predictions. The comparison shows the prediction for unrotated structures (with superscript $''$) vs predictions for rotated structures (with superscript $'$) of (a) dipole moment, (b) diagonal elements of the polarizability, and (c) off-diagonal elements of the polarizability for the validation set of monomeric H_2O .

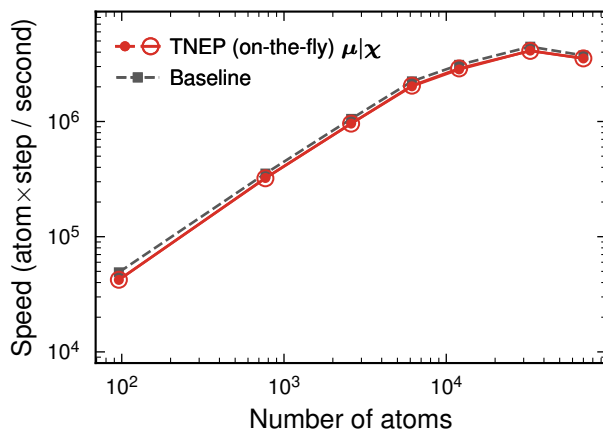


Figure S15: Scaling benchmark demonstrating cost of evaluating dipoles or polarizabilities/susceptibilities on-the-fly during MD simulations. The speed is compared to baseline MD simulations without predictions of tensorial properties, i.e., only sampling the PES. The system under study is bulk water at 300 K in the NVT ensemble, simulated with a timestep of 0.5 fs. The benchmark was run on a heterogeneous server with a Intel Core i7-4770K CPU and a RTX 3080Ti GPU with 12 GB VRAM.

Table S1: Hyperparameters used in training of TNEP models for the dipole moment (μ) for H_2O , $(\text{H}_2\text{O})_2$, H_5O_2^+ , liquid water, organic molecules (QM7B set), and $\alpha\text{-Fe}_2\text{O}_3$. Here, r_c^{R} (r_c^{A}) is the cutoff radius for the radial (angular) components of the descriptor, $n_{\text{max}}^{\text{R}}$ ($n_{\text{max}}^{\text{A}}$) is the Chebyshev polynomial expansion order for the radial (angular) components, l_{max}^{3b} (l_{max}^{4b} , l_{max}^{5b}) is the Legendre polynomial expansion order for the three-body (four-body, five-body) terms angular components, $N_{\text{bas}}^{\text{R}}$ ($N_{\text{bas}}^{\text{A}}$) is the number of basis functions that are used to build the radial (angular) descriptor functions, N_{neu} is the number of neurons in the hidden layer of the neural network, λ_1 (λ_2) is the \mathcal{L}_1 (\mathcal{L}_2) regularization parameter, N_{pop} is the population size in the natural evolution strategy algorithm, N_{bat} is the size of each batch used during training, and N_{gen} is the maximum number of generations to be evolved.

Parameter	H_2O	$(\text{H}_2\text{O})_2$	H_5O_2^+	liquid water	QM7B set	$\alpha\text{-Fe}_2\text{O}_3$
r_c^{R} (\AA)	6	6	6	6	6	6
r_c^{A} (\AA)	4	4	4	4	4	4
$n_{\text{max}}^{\text{R}}$	6	6	6	6	6	6
$n_{\text{max}}^{\text{A}}$	6	6	6	6	6	6
l_{max}^{3b}	4	4	4	4	4	4
l_{max}^{4b}	2	2	2	2	2	2
l_{max}^{5b}	1	1	1	1	1	1
$N_{\text{bas}}^{\text{R}}$	10	10	10	10	10	10
$N_{\text{bas}}^{\text{A}}$	10	10	10	10	10	10
N_{neu}	10	10	10	10	30	10
λ_1	0.00005	0.0008	0.0012	0.0005	0.001	0.0001
λ_2	0.00005	0.0008	0.0012	0.0005	0.001	0.0001
N_{batch}	full-batch	full-batch	full-batch	full-batch	full-batch	full-batch
N_{pop}	80	80	80	80	80	80
N_{gen}	2×10^5	2×10^5	2×10^5	2×10^5	4×10^5	2×10^5

Table S2: Hyperparameters used in training of TNEP polarizability and susceptibility models for H_2O , $(\text{H}_2\text{O})_2$, H_5O_2^+ , liquid water, and BaZrO_3 . Compared to the TNEP dipole model, an additional parameter λ_s should be set, which stands for the relative weight between the off-diagonal elements and diagonal elements of rank-2 tensors in the construction of loss functions.

Parameter	H_2O	$(\text{H}_2\text{O})_2$	H_5O_2^+	liquid water	QM7B set	BaZrO_3
r_c^{R} (\AA)	6	6	6	6	6	6
r_c^{A} (\AA)	4	4	4	4	4	4
$n_{\text{max}}^{\text{R}}$	6	6	6	6	6	4
$n_{\text{max}}^{\text{A}}$	6	6	6	6	6	4
l_{max}^{3b}	4	4	4	4	4	4
l_{max}^{4b}	2	2	2	2	2	0
l_{max}^{5b}	1	1	1	1	1	0
$N_{\text{bas}}^{\text{R}}$	10	10	10	10	10	12
$N_{\text{bas}}^{\text{A}}$	10	10	10	10	10	12
N_{neu}	10	10	10	10	30	20
λ_1	0.008	0.02	0.002	0.001	0.03	-1 (adaptive adjustment)
λ_2	0.008	0.02	0.002	0.001	0.03	-1 (adaptive adjustment)
N_{batch}	full-batch	full-batch	full-batch	full-batch	full-batch	full-batch
N_{pop}	80	80	80	80	80	50
N_{gen}	2×10^5	2×10^5	2×10^5	2×10^5	4×10^5	6×10^5
λ_s	10	1	1	1	1	1

Table S3: Hyperparameters used in training a NEP PES model for MD simulations of water.

Parameter	Liquid water
r_c^{R} (\AA)	6
r_c^{A} (\AA)	4
$n_{\text{max}}^{\text{R}}$	9
$n_{\text{max}}^{\text{A}}$	7
l_{max}^{3b}	4
l_{max}^{4b}	2
l_{max}^{5b}	0
$N_{\text{bas}}^{\text{R}}$	9
$N_{\text{bas}}^{\text{A}}$	7
N_{neu}	100
λ_1	-1 (adaptive adjustment)
λ_2	-1 (adaptive adjustment)
N_{batch}	750
N_{pop}	50
N_{gen}	3×10^5

Table S4: Hyperparameters used in training a NEP models for the prediction of infrared spectra for PTAF⁻.

Parameter	PTAF ⁻ PES	PTAF ⁻ μ
r_c^R (Å)	8	8
r_c^A (Å)	4	6
n_{\max}^R	8	15
n_{\max}^A	6	8
l_{\max}^{3b}	4	4
l_{\max}^{4b}	0	2
l_{\max}^{5b}	0	0
N_{bas}^R	8	12
N_{bas}^A	8	12
N_{neu}	40	80
λ_1	0.1	-1 (adaptive adjustment)
λ_2	0.1	-1 (adaptive adjustment)
λ_e	1	1
λ_f	3	1
λ_v	0	0.1
N_{batch}	1×10^5	5×10^5
N_{pop}	50	50
N_{gen}	2×10^5	5×10^5

Table S5: Validation data for dipole and polarizability of water. RRMSEs (unitless) for μ and α for the validation sets using NEP, T-EANN and SA-GPR rank-1 tensor models.

System	μ			α		
	TNEP	T-EANN	SA-GPR	TNEP	T-EANN	SA-GPR
H ₂ O	0.069%	0.020%	0.023%	0.991%	0.020%	0.024%
(H ₂ O) ₂	1.681%	6.600%	3.866%	1.762%	4.200%	1.258%
H ₅ O ₂ ⁺	0.371%	1.300%	0.130%	0.246%	0.300%	0.080%
liquid water	0.852%	16.000%	0.544%	0.680%	2.200%	0.329%

Supplemental References

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