Neural Network in determination of interatomic potential of diatomic molecule

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Molecular Spectroscopy and Quantum Information

Introduction

Nowadays, Neural Networks (NN) [1] – which principle of operation is based on principle of operation of biological brain – are considered as an effective tools for solving different computational problems from real time object recognition to stock market prediction. We present a method of obtaining potential energy curve (PEC) of diatomic molecule using a Neural Network. In the presented method, we use Matlab® [2] computing environment to create and train a Neural Network, which can find PEC of Z electronic energy state of diatomic molecule resulting in proper simulation of experimentally measured light induced fluorescence (LIF) excitation spectrum of the Z←X transition recorded with vibrational resolution.
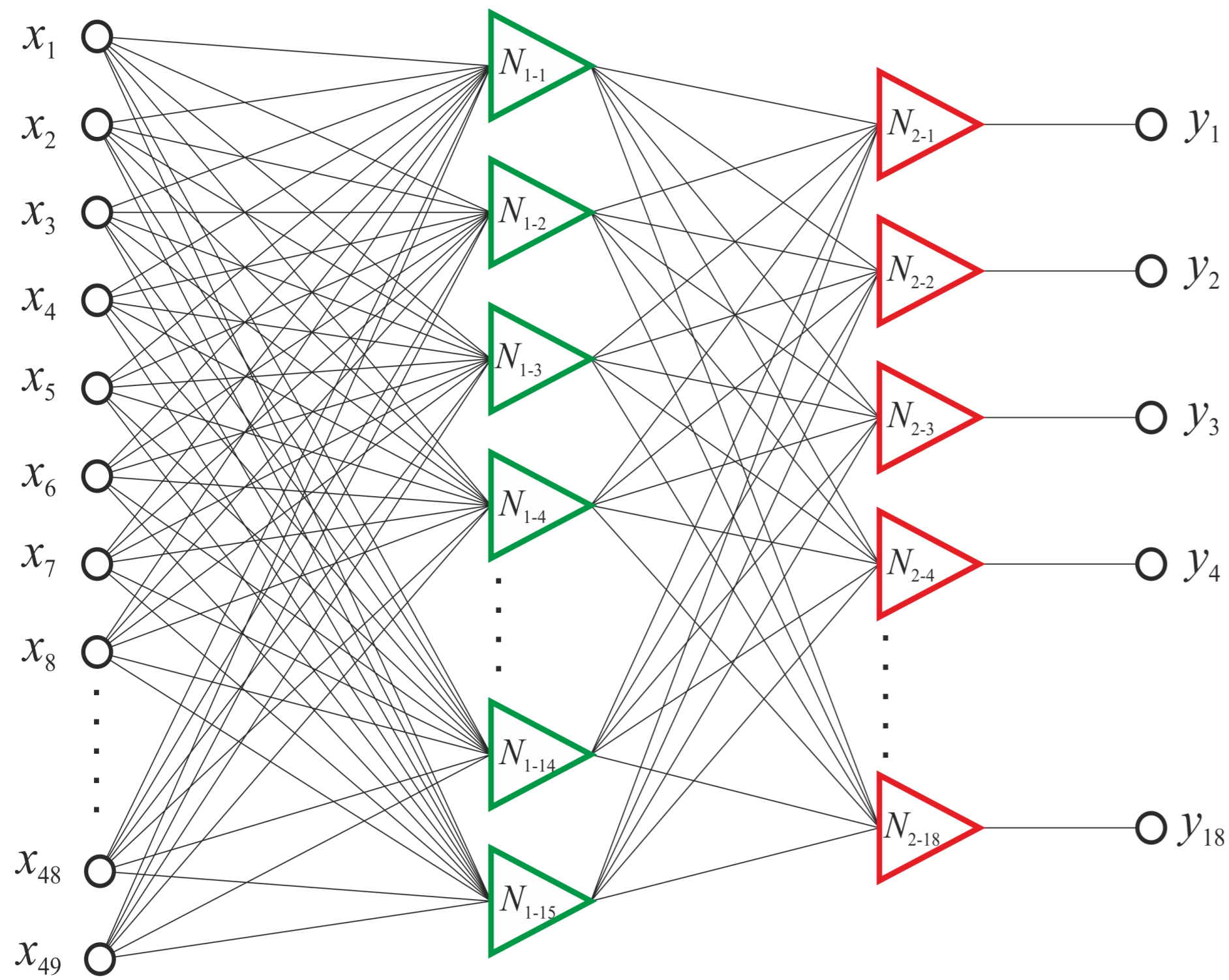

Fig.1. Schematic representation of two-layer NN used for determination of PEC. Empty circles represent inputs x_i and outputs y_i of the network. Green and red triangles (with symbols $N_{i,j}$) represent neurons in input and output layers, respectively, where indexes i and j denote layer's number and number of neurons in the layer, respectively.

Type of the *reference* spectrum	artificial test spectrum	artificial test spectrum	experimental spectrum
Type of the Neural Network "initial" potential	Morse with random noise	modified Morse with different parameters	IPA result
Agreement coefficient for "initial" PEC	3.2	2.1	6.7
Agreement coefficient for PEC resulting from Neural Network method	0.016	0.0027	0.43
Neural Network description	*25-15s-12l*	*25-15s-13l*	*49-15s-18l*

Table 1. Parameters of potentials and type of NN used in this work in order to obtain pointwise PEC representing interatomic potentials of Cd₂. The most important is comparison of the agreement coefficients of initial PEC (row 3) with the agreement coefficients for PEC resulting from NN (row 4). This comparison shows, that potentials obtained by the NN method lead to more accurate simulations than those based on initial PECs.

References

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What is Neural Network

Neural Network (NN) is a collection of large number of simple computational units called neurons. A single neuron (perceptron) is a unit with several inputs x_i and one output y. The output signal from the neuron is computed as a weighted sum of signals from neuron inputs supplemented by a weighted bias (weights are denoted by w and bias by b):

$$y = f(\sum_{i=1}^{N} w_i x_i + w_0 b)$$

The most commonly used activation functions are linear function $f(x)=x$ and sigmoid function $f(x)=1/(1+e^{-x})$.

Neurons in the network are interconnected. In one of the most popular neuron grouping metod, called *layer architecture*, neurons are grouped in layers where the output of *j*-th layer is an input for the *(j+1)*-th layer. In presented study we use multilayer perceptron network (MLP) [1] which example is presented in Fig.1. The structure of multilayer NN can be described by designating the size of input vector x and number of neurons in consecutive layers. Additionally, next to the number of neurons in the layer, one can denote a letter symbol of transfer function used in neurons in a given layer. For example, 49-15*s*-18*l*, where *s* and *l* denote sigmoid and linear activation functions, respectively, designates a network with 49 inputs, 15 neurons with sigmoidal transfer function in the first layer and 18 neurons with linear transfer function in the output layer. NN can be used to solve different computational problems, which can be described by pairs of input and output vectors. A properly configured NN can compute correct output vector y based on the input vector x for a given problem. The configuration of NN, so called *training* of the network, consist of finding correct weights w for each neuron in the structure. In this process (which is an example of a so-called *supervised learning* [3]), one has to give to the network a set of pairs containing input and output vectors. It is important that in each pair, the output vector presents a proper solution of the considered problem for the input vector from this pair. Based on the training data, using the back-propagation algorithm [2], the correct weights for each neuron can be found.

Quantitative assessment of quality of PEC

To quantitatively assess the agreement between simulation (prepared for a particular PEC) and the experimental spectrum, we used the agreement coefficient defined as:

$$C = \frac{1}{N} \sum_{v,iso} \left(E_{v,iso}^{exp} - E_{v,iso}^{sim} \right)^2$$

Where $E_{v,iso}^{exp}$ and $E_{v,iso}^{sim}$ denotes experimental and simulated energies, respectively, of given component in the examined spectrum (we assume, that we can identify only vibrational and isotopic structure).

Results

To generate the data to train the NN we used pointwise *initial potential* of the upper state involved in the network. This potential leads to simulation with energies of components close to those observed in the experimental spectrum. Next, we randomly modified several points of the initial potential and use LEVEL [4] program to obtain values of simulated energies of components from experimental spectrum. The pair which contain simulated energies of components and corresponding PEC constitutes one point in the training dataset. We run the procedure few thousend times to generate a large dataset to train the NN. After training the Network, we use as an input vector the experimental energies of observed components. In this case the Network should return potential, which leads to proper simulation of those experimental energies. We test our method on two artificially generated spectra - called *reference spectra* – of the b³0$_u^+$(5³P₁) ←X¹0$_g^+$ transition in Cd₂ (where the exact representation of the upper state potential was precisely known) and one real experimental spectrum of the B¹1$_u$ (5¹P₁) ←X¹0$_g^+$ trainstion in Cd₂. The results of our tests are presented in Table 1 and in Figs.2 and 3.
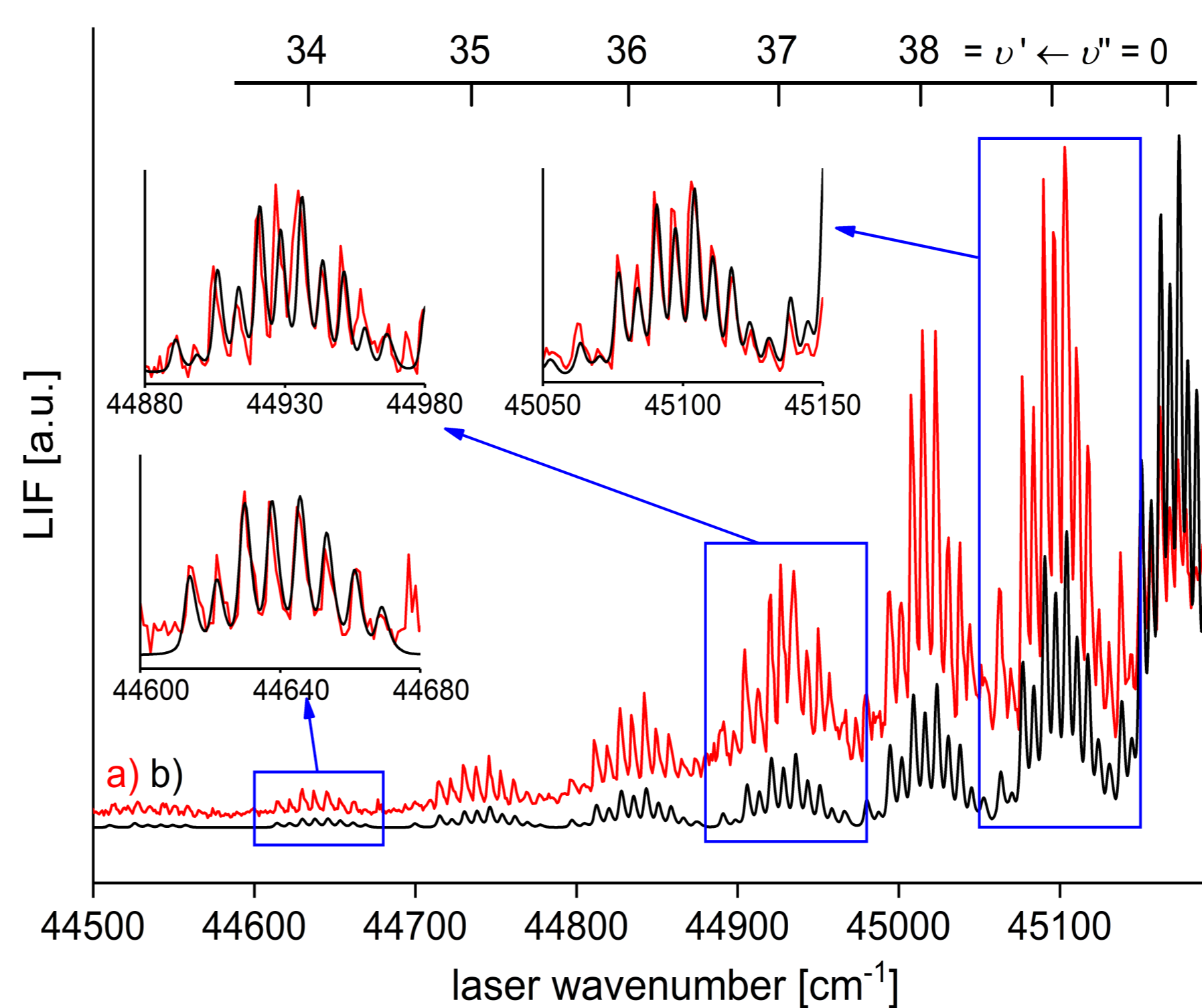
Fig.2. Red trace (a) previously recorded [5] spectrum of the B¹1$_u$(5¹P₁)←X¹0$_g^+$(5¹S₀) transition in Cd₂ and (b) its simulation (black trace), which was obtained assuming a Morse representation for the X¹0$_g^+$-state potential and B¹1-state potential represented with the result of NN method (see Table 1 and Fig. 3). Simulation obtained using LEVEL [4] and PGOPHER [6] programs included all Cd₂ isotopologues with abundances larger than 1%, for Δ$_L$=1.5cm⁻¹ and Δ$_G$=2cm⁻¹ convolutions (corresponding to the bandwidth of the laser beam and a residual Doppler broadening in the molecular beam, respectively), and rotational temperature T$_{rot}$=3K. In the simulation, an influence of a transition dipole moment (TDM) function was omitted due to a lack of reliable data. For the sake of comparison, the experimental and simulated spectra in insets were plotted using separate, arbitrary chosen vertical scales.
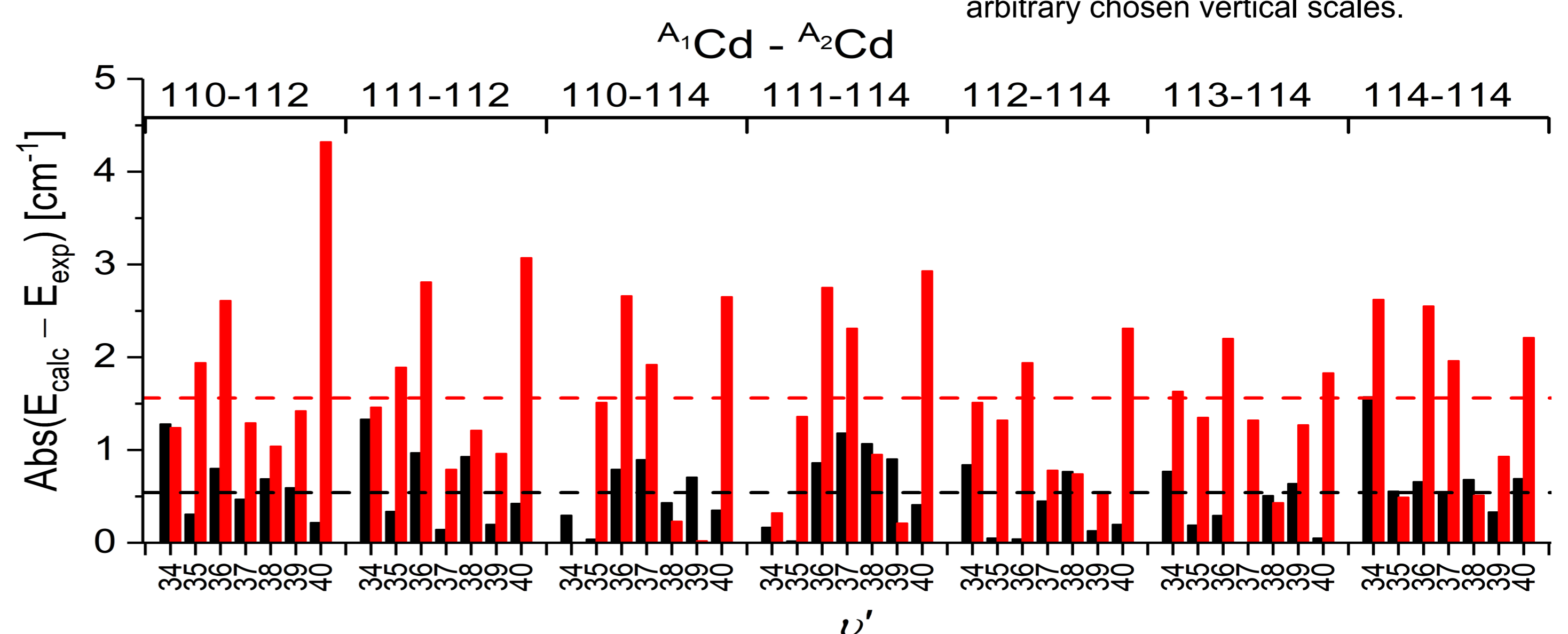

Fig. 3. Comparison of agreements between result of IPA methodology (red bars) and result of Neural Network method (black bars), and the experimental excitation spectrum of the B¹1$_u$(5¹P₁)←X¹0$_g^+$(5¹S₀) transition in Cd₂. Each bar depicts one vibrational component in one ^A1Cd-^A2Cd isotopologue observed in the experimental spectrum. The height of each bar corresponds to the difference between simulated and experimental energies of particular vibrational transitions (lower bar means better agreement). Red and black dashed horizontal lines show averaged height of corresponding bars, respectively.