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Theoretical Investigation of Substituent Effect on the Carbonyl Stretcing Vibration in Carbonyl Oximes

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Abstract

In this study, changes in carbonyl vibrational frequency of isonitrosoacetophenone (inapH) molecules containing different substituents and affecting physicochemical parameters were investigated. In this context, the geometries and vibration frequencies of the selected molecules were calculated using the Density Functional Theory (B3LYP) with 6-311++G(d,p) basis set. The halogens (-F, -Cl and -Br), the hydroxyl (-OH) and the alkyl (-CH_3, -CH_2CH_3 and –$CH_2CH_2CH_3$) groups were used as a substituent. The carbonyl stretching vibrations, Mulliken charges on carbon and oxygen atoms, dipole moment and electronegativity of substitute groups of inapH molecules were calculated. The calculated values of the carbonyl stretching vibrations were used in the artificial neural networks (ANNs) to determine the contributions of the influencing physicochemical parameters. The developed ANNs has four input and one output neurons. It also has three hidden layers, five, seven and nine hidden layer neurons, and full connectivity between neurons. Input parameters are electronegativity, dipole moment, Mulliken charges of C and O atoms. The change of carbonyl stretching vibration was investigated as four variable.

***Keywords*:** Carbonyl stretching, Carbonyl oxime, DFT calculations, Artificial neural network

1. Introduction

2-Keto-2-phenyl-acetaldoxime (isonitrosoacetophenone, inapH) is a molecule containing in its structure carbonyl and oxime groups, which is seen Figure 1.

It is also named carbonyl oxime. These molecules are oxime derivatives with different crystal structures, interesting hydrogen bond systems have been analyzed and a correlation between hydrogen bond model and N–O bond lengths has been proposed [1,2]. The InapH molecule is used in drug discovery and biotransformation studies. In addition, inapH and their metal complexes are a lot of applications in different fields. For example, the biological activities of copper(II) complex with inapH were studied in 2014 [3]. Madala et al reported metabolomic analysis of the effect of isonitrosoacetophenone on the degradation of phenolic metabolism of Nicotiana tabacum cells [4]. The biotransformation of isonitrosoacetophenone in tobacco cell suspensions was studied in 2013 [5]. Moreover, it has been theoretically proposed that DFT and EPR studies on molecular geometry and ultrafine interactions in iminoxime radicals with C,O or CH_2 group have been in liquid and rigid media [6]. But, the theoretical vibrational spectroscopies of different substitute inapH molecules have not been studied in literature. In addition, the approach of using artificial neural networks (ANNs) to examine the correlations of molecular electronic and vibrational properties of molecules is not encountered in the literature.

In computer science and similar fields, ANNs are computational models with capabilities such as machine learning and pattern recognition, and are derived from an animal's central nervous system (especially the brain). Artificial neural networks are a system based on calculating the connection between inputs and outputs with interconnected "neurons" systems. [7]. In this study, the vibrational frequencies of inapH molecules to which different substituents such as -F, -Cl, -Br, -OH, -CH_3, -CH_2CH_3 and –$CH_2CH_2CH_3$ are added, density functional theory (DFT/B3LYP) and 6-311++G(d,p)) were calculated using the basis set. The values calculated as a result of this program are also used in the artificial neural network. The relationship between neural networks used in artificial intelligence and the biological architecture of the brain is still being discussed.

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While this discussion is ongoing, the relationship between them has not been fully explained, so in the ANN approach, they are defined as simplified models of neural processing in the brain. To embrace this understanding and advance work, neuroscientists seek to make a link between observed biological processes, neural processing and plausible mechanisms for learning (biological neural network models) and theory (statistical learning theory and information theory) [8].

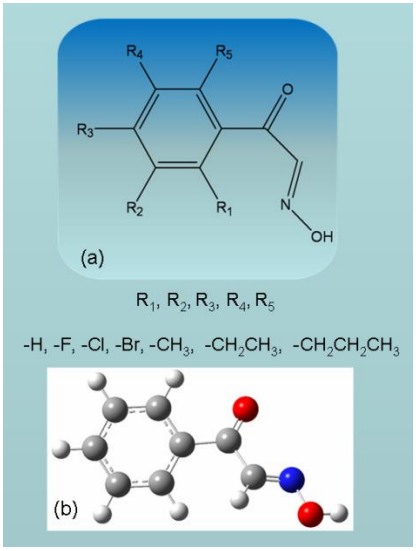

Figure 1. a) Molecular view of isonitrosoacetophenone and its substituted derivatives, b) optimized structure of isonitrosoacetophenone

2. Materials and Methods

Infrared spectroscopic measurements of inapH were measured using a Thermo Nicolet 6700 FT-IR spectrophotometer by creating KBr pellets. The measurements were performed with 1 cm^{-1} resolution, 32 backgrounds and 64 sample spectra.

All theoretical calculations were performed using GAUSSIAN 03 program [9]. The molecular geometries and vibrational frequencies of the all molecules have been calculated using the DFT/B3LYP [10] with the 6-311++G(d,p) basis set. These basis set calculations involve systematic errors of known origin and therefore a scale factor of 0.978 is used for carbonyl strengthing frequency of all molecules. [11]. The carbonyl stretching vibrations, Mulliken charges on carbon and oxygen atoms, dipole moment are calculated and listed in Table 1. In addition, the mulliken electronegativities of substitute groups were given in Table 1.

Table 1. The carbonyl stretching vibrations, Mulliken charges on carbon and oxygen atoms, dipole moment and electronegativity of substitute groups of isonitrosoacetophenone molecules[1].

	Molecules					χ	μ (D)	Mulliken charges		ν (cm^{-1})		k (N/m) ($*10^{-3}$)
	R_1	R_2	R_3	R_4	R_5			C	O	Exp.	Theor.	
1	H	H	H	H	H	2.10	3.4140	-0.360	-0.217	1678	1729	1.17
2	H	H	H	H	F	4.00	3.4027	-0.228	-0.217		1685	1.11
3	H	H	H	H	Cl	3.00	3.5279	-0.717	-0.212		1695	1.12
4	H	H	H	H	Br	2.80	3.5721	-0.480	-0.210		1698	1.13
5	H	H	H	H	Me	2.52	2.9799	-0.514	-0.190		1673	1.09
6	H	H	H	H	Et	2.46	2.8640	-0.328	-0.192		1674	1.10
7	H	H	H	H	Pr	2.41	2.8835	-0.302	-0.185		1674	1.10
8	H	H	H	H	OH	3.50	4.5658	-0.215	-0.246		1683	1.11
9	H	F	H	H	H	4.00	4.2687	-0.301	-0.212		1674	1.09
10	H	Cl	H	H	H	3.00	4.2708	-0.445	-0.212	1679	1674	1.10
11	H	Br	H	H	H	2.80	4.2358	-0.334	-0.208	1679	1674	1.10
12	H	Me	H	H	H	2.52	3.3700	-0.376	-0.214		1669	1.09
13	H	Et	H	H	H	2.46	3.2836	-0.370	-0.213		1669	1.09

14	H	Pr	H	H	H	2.41	3.2417	-0.385	-0.211		1669	1.09
15	H	OH	H	H	H	3.50	4.6710	-0.276	-0.215	1605	1673	1.09
16	H	H	F	H	H	4.00	2.6959	-0.321	-0.218		1669	1.09
17	H	H	Cl	H	H	3.00	2.7091	-0.362	-0.214	1675	1670	1.09
18	H	H	Br	H	H	2.80	2.7153	-0.350	-0.214	1679	1670	1.09
19	H	H	Me	H	H	2.52	3.8465	-0.356	-0.220	1679	1666	1.09
20	H	H	Et	H	H	2.46	3.8442	-0.394	-0.217		1666	1.09
21	H	H	Pr	H	H	2.41	3.8512	-0.360	-0.217		1666	1.08
22	H	H	OH	H	H	3.50	2.8916	-0.371	-0.227		1662	1.08
23	F	H	H	H	F	4.00	4.2222	-0.018	-0.209		1709	1.14
24	Cl	H	H	H	Cl	3.00	4.0640	-1,314	-0.201		1716	1.15
25	Br	H	H	H	Br	2.80	3.9738	-0.565	-0.195		1715	1.15
26	Me	H	H	H	Me	2.52	3.0170	-0.646	-0.199		1692	1.12
27	Et	H	H	H	Et	2.46	2.7079	-0.252	-0.205		1694	1.12
28	Pr	H	H	H	Pr	2.41	2.6446	-0.780	-0.153		1692	1.12
29	OH	H	H	H	OH	3.50	4.8474	-0.074	-0.186		1709	1.14
30	F	F	H	H	H	4.00	5.2804	-0.213	-0.209		1697	1.13
31	Cl	Cl	H	H	H	3.00	4.6440	-0,768	-0.182		1706	1.14
32	Br	Br	H	H	H	2.80	3.3315	-0.469	-0.204		1704	1.13
33	Me	Me	H	H	H	2.52	3.0398	-0.589	-0.200		1675	1.10
34	Et	Et	H	H	H	2.46	3.0432	-0.514	-0.192		1675	1.10
35	Pr	Pr	H	H	H	2.41	3.1643	-0.552	-0.187		1676	1.10
36	OH	OH	H	H	H	3.50	2.5279	-0.256	-0.214		1670	1.09
37	H	F	H	F	H	4.00	2.8106	-0.217	-0.207		1678	1.10
38	H	Cl	H	Cl	H	3.00	2.7958	-0.392	-0.206		1678	1.10
39	H	Br	H	Br	H	2.80	2.7843	-0.279	-0.202		1677	1.10
40	H	Me	H	Me	H	2.52	3.7735	-0.417	-0.214		1668	1.09
41	H	Et	H	Et	H	2.46	3.6747	-0.439	-0.210		1667	1.09
42	H	Pr	H	Pr	H	2.41	3.7091	-0.565	-0.206		1667	1.09
43	H	OH	H	OH	H	3.50	2.5279	-0.256	-0.214		1670	1.09
44	H	F	F	H	H	4.00	4.1383	-0.311	-0.212		1672	1.09
45	H	Cl	Cl	H	H	3.00	3.9257	-0.437	-0.209		1673	1.09
46	H	Br	Br	H	H	2.80	3.8101	-0.345	-0.205		1673	1.09
47	H	Me	Me	H	H	2.52	3.8076	-0.384	-0.213		1665	1.08
48	H	Et	Et	H	H	2.46	3.9340	-0.581	-0.214		1664	1.08
49	H	Pr	Pr	H	H	2.41	3.8909	-0.464	-0.213		1664	1.08
50	H	OH	OH	H	H	3.50	3.5921	-0.378	-0.226		1658	1.07
51	F	H	F	H	H	4.00	3.9172	-0.197	-0.213		1692	1.12
52	Cl	H	Cl	H	H	3.00	3.7502	-0.968	-0.174		1699	1.13
53	Br	H	Br	H	H	2.80	3.6754	-0.467	-0.179		1700	1.13
54	Me	H	Me	H	H	2.52	3.4135	-0.523	-0.202		1668	1.09
55	Et	H	Et	H	H	2.46	3.5423	-0.392	-0.192		1668	1.09
56	Pr	H	Pr	H	H	2.41	3.3623	-0.527	-0.184		1668	1.09
57	OH	H	OH	H	H	3.50	4.6670	-0.256	-0.216		1663	1.08
58	F	H	F	H	F	4.00	3.2661	-0.036	-0.208		1708	1.14
59	Cl	H	Cl	H	Cl	3.00	3.1828	-1.408	-0.200		1717	1.15
60	Br	H	Br	H	Br	2.80	3.1316	-0.587	-0.193		1716	1.15
61	Me	H	Me	H	Me	2.52	3.2050	-0.534	-0.198		1688	1.11
62	Et	H	Et	H	Et	2.46	3.1261	-0.340	-0.176		1691	1.12
63	Pr	H	Pr	H	Pr	2.41	3.1311	-0.302	-0.168		1691	1.12
64	OH	H	OH	H	OH	3.50	4.8323	-0.099	-0.194		1701	1.13
65	H	F	F	F	H	4.00	3.1963	-0.243	-0.207		1676	1.10
66	H	Cl	Cl	Cl	H	3.00	2.9165	-0.441	-0.204		1675	1.10
67	H	Br	Br	Br	H	2.80	2.8293	-0.293	-0.201		1676	1.10
68	H	Me	Me	Me	H	2.52	4.1821	-0.365	-0.211		1664	1.08

69	H	Et	Et	Et	H	2.46	4.2588	-0.337	-0.216	1662	1.08
70	H	Pr	Pr	Pr	H	2.41	4.0932	-0.549	-0.204	1662	1.08
71	H	OH	OH	OH	H	3.50	2.5186	-0.262	-0.222	1660	1.08
72	F	F	H	H	F	4.00	3.4401	-0.011	-0.203	1722	1.16
73	Cl	Cl	H	H	Cl	3.00	3.6364	-0.131	-0.191	1718	1.15
74	Br	Br	H	H	Br	2.80	3.5172	-0.521	-0.189	1717	1.15
75	Me	Me	H	H	Me	2.52	3.2355	-0.395	-0.195	1693	1.12
76	Et	Et	H	H	Et	2.46	3.0162	-0.335	-0.171	1692	1.12
77	Pr	Pr	H	H	Pr	2.41	2.8702	-0.601	-0.142	1691	1.12
78	OH	OH	H	H	OH	3.50	5.7615	-0.077	-0.188	1709	1.14

[1]Me: Metyl (-CH_3); Et: Ethyl (-CH_2CH_3); Pr: Propyl (-$CH_2CH_2CH_3$), χ is mulliken electronegativity of substituent and k is bond constant of carbonyl.

Artificial Neural Network software was used for determine of the degree of dependence of these four variables of the carbonyl stretching vibration. The neural network developed in such a way that the entire connection between neurons is established is shown in Figure 2. In this neural network, there are four input and output neurons, three hidden layers, and five, seven and nine hidden layer neurons. Electronegativity, dipole moment, C and O Mulliken charges were determined as input parameters. There are a total of 312 input vectors in the training data, and they were obtained from various samples. The optimum value of the number of hidden layers and neurons in each layer and the hyperbolic tangent, sigmoid and hybrid functions were determined by trial and error. The obtained results are improved by training the network. The number of epochs for the training was 105.

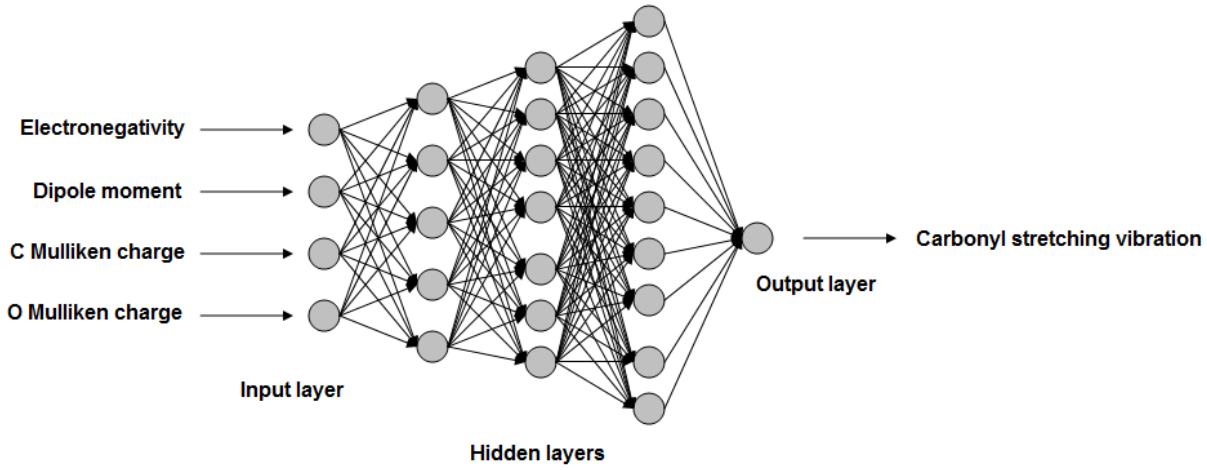

Figure 2. Architecture of artificial neural network

3. Result and Discussion

Vibrational assignments of 79 different molecules of inapH were calculated from optimized geometry. As a result of the all frequencies were calculated positives, all molecules were optimized global minumum. The calculated frequency values were scaled as described in the theoretical methods to compensate for the errors. The IR spectra of the inapH molecule are depicted in Figure 3, and the corresponding frequencies are listed in Table 1. In general, the test frequency values are in good agreement with the calculated values. The carbonyl strength vibration of inapH was observed at 1678 cm^{-1}, while calculated at 1728 cm^{-1}. A deviation of approximately 50 cm^{-1} can be observed between the experimental and theoretical values. These deviations may be due to the hydrogen bond interactions of the group causing the vibrational mode and can cause large deviations between the crystalline state and the calculated values. Also, in the high wavenumber region of the spectrum, discrepancies between the experimental and calculated values can explain the significant differences [12]. In addition, 3-chloroinapH, 3-bromoinapH, 3-hydroxyinapH, 4-chloroinapH, 4-bromoinapH and 4-methylinapH were synthsized and recorded experimental IR spectra, so the carbonyl stretching vibrations of these molecules were observed between 1679 and 1606 cm^{-1}, while calculeted at ca. 1670 cm^{-1}.

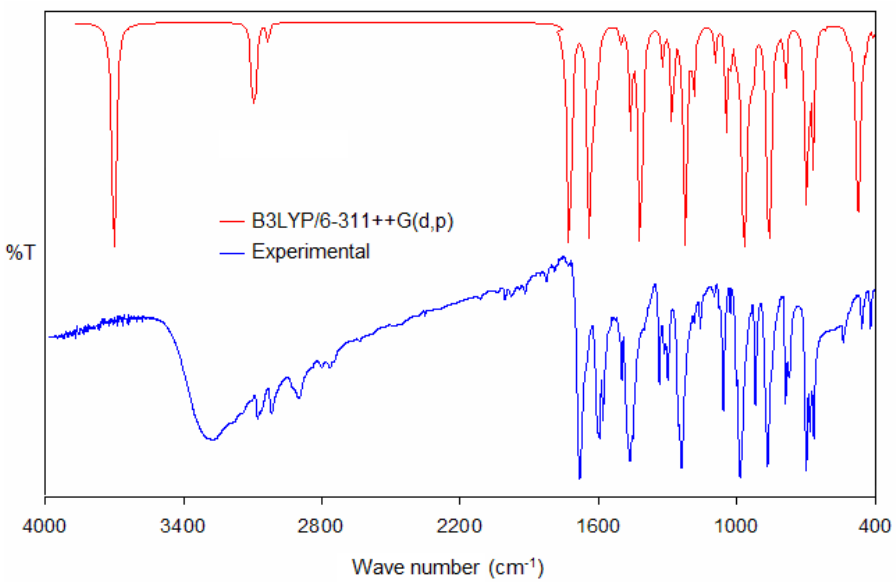

Figure 3. Experimental and calculated infrared spectra of isonitrosoacetophenone

In addition, in this study, the carbonyl strength vibrations were investigated depending on the Mulliken charges on carbon and oxygen atoms, dipole moment and electronegativity of substituents. The carbonyl stretching vibrations show alteration by to these four variables. But changes of vibrations were not observed regularly by a variable. These results are shown in Table 1.

In the ANN calculations, the theoretical frequency values obtained with the Gaussian 03 program were used and thus experimental validation of the proposed model was provided. The relationship between the experimental and the ANN output (estimations) is given in Figure 4. The values obtained by training the ANN model are very close to the experimental values. According to this result, it can be said that there is a high correlation between the input and output parameters. The statistical value of R2 is determined as 1,000 from the ANN training. The average percentage effect of electronegativity, dipole moment, C and O Mulliken charges are 24.81, 18.01, 20.48 and 21.36 respectively, shown as Figure 5. The highest ratio was found in electronegativity. Figure 6 shows the correlation of calculated by Gaussian 03 program and predicted values obtained from the ANN models. The average correlation was found to be 99.9% for tested samples.

Figure 4. Artificial neural network outputs plotted against the calculated with density functional theory

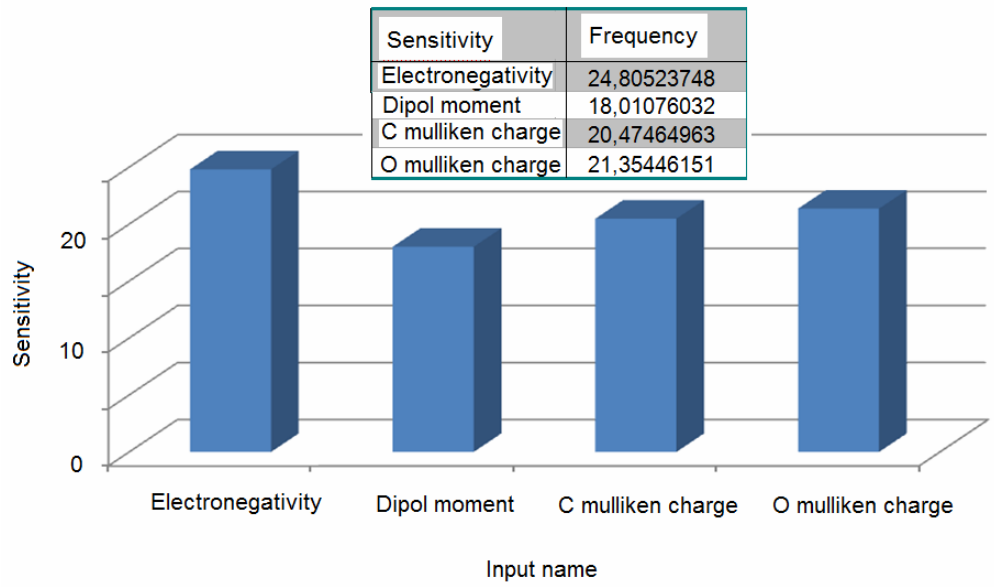

Figure 5. Effect of electronegativity (e), dipole moment (d), carbon (c) and oxygen (o) Mulliken charges on the change of carbonyl stretching vibration

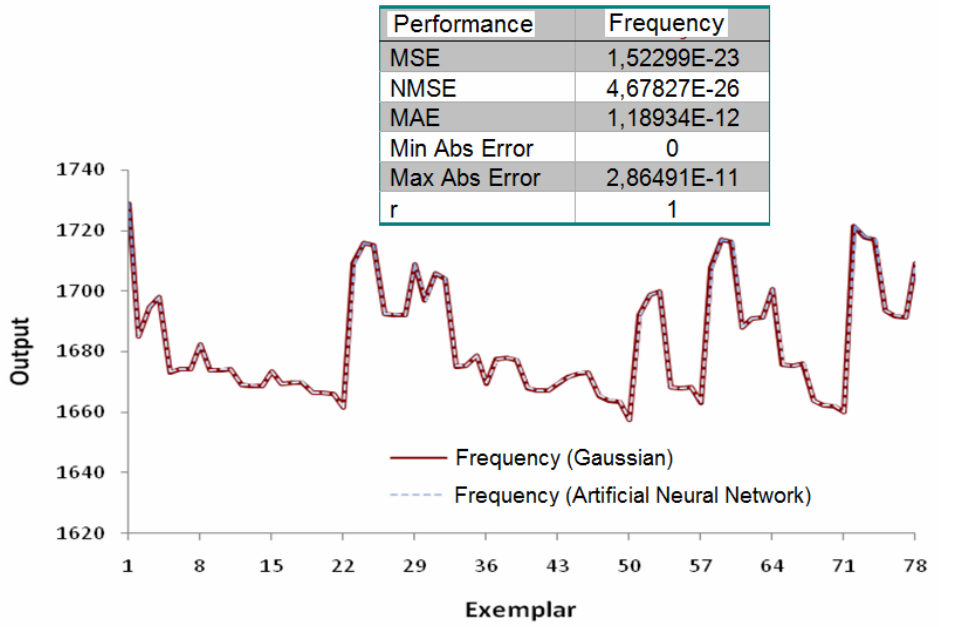

Figure 6. Correlation of calculated with density functional theory and predicted by artificial neural network values

4. Conclusions

In this study, the theoretical and experimental infrared vibrational analysis of inapH and its substituted derivatives (77 molecules) have bee performed. In order to study optimization and vibrational spectra of the inapH and its substituted derivatives, all calculations were successfully performed by using DFT/6-311++G(d,p) level. The calculated frequency values and the experimental spectrum are in agreement with the values of some inaph molecules measured. The suggested model improved from calculated values by the Gaussian 03 program can be used to predict more easily change of carbonyl stretching vibration. It has been determined that the results obtained from the experimental and theoretical data have a 99.9% correlation with the study in the ANN model. All statistical calculations with this result prove that the proposed ANN model is suitable for estimating vibration frequency values.

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