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ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · JANUARY 2007

Impact Factor: 1.6 · DOI: 10.1016/j.molstruc.2006.04.021

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# An experimental and theoretical study of vibrational spectra of picolinamide, nicotinamide, and isonicotinamide

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Received 20 January 2006; received in revised form 13 April 2006; accepted 17 April 2006

Available online 5 June 2006

## Abstract

The molecular structures and vibrational spectra of the three isomers of pyridinecarboxamide (picolinamide, nicotinamide, isonicotinamide) were calculated with the Density Functional Theory (DFT) method using the B3LYP function and the 6-31++G(d,p), Z2PolX, Z3PolX basis sets. The calculations were performed by using the Gaussian98W packet program set. The total energy distributions (TED) of the vibrational modes of these molecules were calculated by using the Scale 2.0 program and the vibrational modes of the molecules were determined. The Scaled Quantum Mechanical (SQM) method was used in the scaling procedure. In the experimental part of the study, the solid phase FT-IR and Micro Raman spectra of the three isomers of pyridinecarboxamide have been recorded in the range of 4000–650 and 1200–100 cm<sup>-1</sup>, respectively. The calculated wavenumbers were compared to the corresponding experimental values. As a result, the observed bands of the three isomers of pyridinecarboxamide were assigned with good accuracy.

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**Keywords:** DFT calculations; Picolinamide; Nicotinamide; Isonicotinamide; Z3PolX basis set; SQM; Vibrational spectra

## 1. Introduction

The three isomers of pyridinecarboxamide; picolinamide (2-pyridinecarboxamide; 2-NH<sub>2</sub>COPY), nicotinamide (3-pyridinecarboxamide; 3-NH<sub>2</sub>COPY), and isonicotinamide (4-pyridinecarboxamide; 4-NH<sub>2</sub>COPY) are a class of medicinal agents with activity that includes the reduction of iron-induced renal damage [1]. The structure of picolinamide and nicotinamide has been determined by experimental methods and reported in previous papers [2–5]. In the present paper, we report a complete description of the molecular geometry and the molecular vibrations of the three isomers of pyridinecarboxamide. For that purpose, quantum chemical computations were performed on the three isomers of pyridinecarboxamide by using the Density Functional Theory (DFT). Experimental information on the molecular vibrations was obtained from the FT-IR and Micro Raman spectra measured. Our assignments

were made by using the advantages of theoretical computations.

## 2. Experimental details

The solid phase FT-IR spectra of the powdered three isomers of pyridinecarboxamide were recorded with the ATR unit by using the Perkin-Elmer FT-IR spectrometer in the range of 4000–650 cm<sup>-1</sup>. In these experiments a resolution of 4 cm<sup>-1</sup> was applied. The Raman spectra of the powdered samples were recorded on a Micro Raman Jobin YVON Horiba HR800 UV instrument using 632.8 nm excitation from a He–Ne laser in the range of 1200–100 cm<sup>-1</sup>, 1800 grating, 5 scans per 30 s pulse and with 10× zoom.

## 3. Computational details

The geometry optimizations and calculated wavenumbers have been carried out at the Density Functional Theory (DFT) method with the B3LYP exchange-correlation

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functional [6,7] by using the Gaussian 98W program [8]. The 6-31++G(d,p) basis set and the new highly compact Pol-type basis sets, Z2PolX and Z3PolX [9,10], for the three molecules and their conformers were used in the DFT calculations.

The vibrational modes of all these molecules were determined by using total energy distribution (TED) and the calculated wavenumbers were scaled by using the scaled quantum mechanical (SQM) analysis method, with the help of the Scale 2.0 program [11,12] for the results of B3LYP/6-31++G(d,p) basis set. The natural internal coordinates were used for SQM procedure and 10 scaling factors were classified according to different types of internal coordinates. The scaling factors were taken from previous studies for each group [13–15]. Only the scaling factors related to the out of plane bendings and NH<sub>2</sub> rocking were refined. The diagonal force constants were scaled by the factor associated with the internal coordinates and the off-diagonal force constants were scaled by the geometric mean of the associated scaling factors. As Oakes et al. have stated, [9,10] wavenumbers calculated with the Z2PolX and Z3PolX basis sets showed to be in conformity with the

experimental wavenumbers. For this reason, SQM method was not used on the results obtained from the Z2PolX and Z3PolX basis sets.

#### 4. Results and discussion

The optimized geometries for the *E*- and *Z*-forms of the three molecules were calculated and their total energies are given in Table 1. In addition to the calculated wavenumbers and the total energy distribution results for the *E*-forms of the three molecules were obtained by using the DFT/B3LYP method with the 6-31++G(d,p), Z2PolX and Z3PolX basis sets. The calculated data for the *E*- and *Z*-forms of the three molecules are very similar. However, it was found to be that the *E*-forms of these molecules are more stable than the *Z*-forms. Therefore, we gave a detailed explanation only for the *E*-form. The *E*-form structures of these molecules with the atomic numbering used in this study are shown in Fig. 1. The optimized geometry parameters were obtained by using the DFT/B3LYP method with the 6-31++G(d,p), Z2PolX, and Z3PolX basis sets according to these atom numberings are given

Table 1

The total energies (in hartree) of the optimized geometry for the *E*- and *Z*-forms of the three isomers of pyridinecarboxamide

	Picolinamide		Nicotinamide		Isonicotinamide	
	<i>E</i> -Form	<i>Z</i> -Form	<i>E</i> -Form	<i>Z</i> -Form	<i>E</i> -Form	<i>Z</i> -Form
B3LYP/6-31G++(d,p)	−417.0289	−417.0156	−417.0199	−417.0195	−417.0198	−417.01978
B3LYP/Z2POLX	−416.9806	−416.9648	−416.9712	−416.9694	−416.9699	−416.9698
B3LYP/Z3POLX	−417.0202	−417.0038	−417.0104	−417.0088	−417.0091	−417.0090

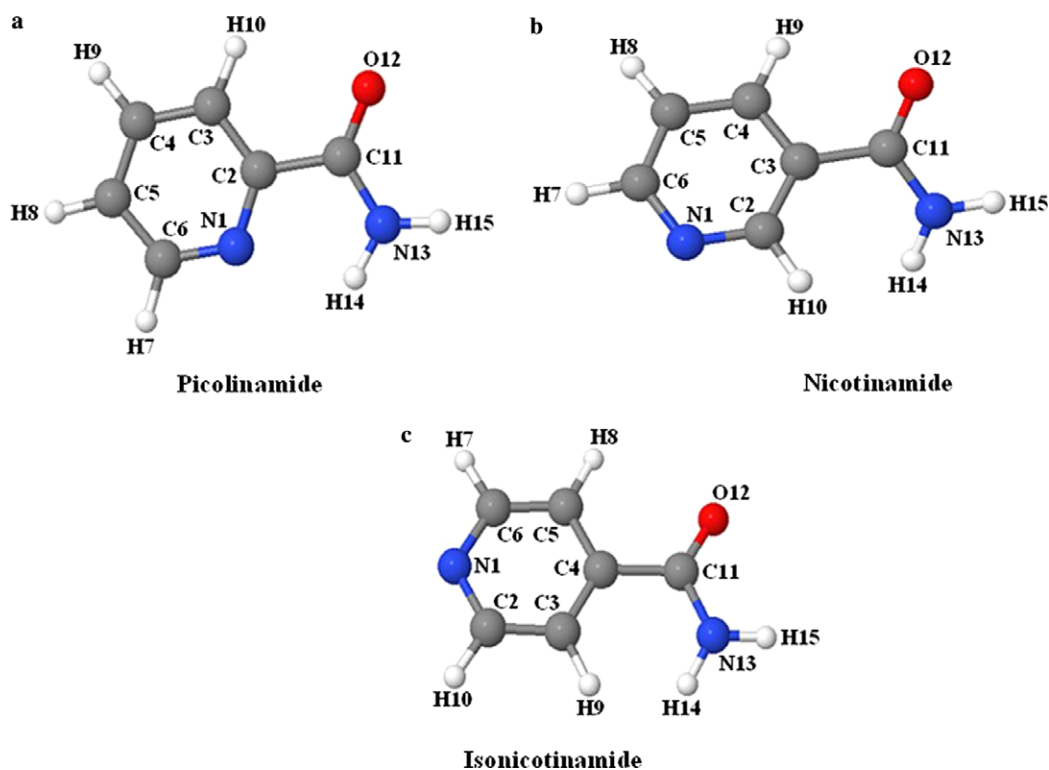


Fig. 1. The atom numbering of three isomers of pyridinecarboxamide.

Table 2

The optimized geometry parameters obtained by using the DFT/B3LYP method with the 6-31++G(d,p), Z2POLX, and Z3POLX basis sets of the three isomers of pyridinecarboxamide

Atoms	Picolinamide			Nicotinamide			Isonicotinamide		
	6-31++G(d,p) (Å/deg)	Z2POLX (Å/deg)	Z3POLX (Å/deg)	6-31++G(d,p) (Å/deg)	Z2POLX (Å/deg)	Z3POLX (Å/deg)	6-31++G(d,p) (Å/deg)	Z2POLX (Å/deg)	Z3POLX (Å/deg)
R(1,2)	1.3432	1.3542	1.3534	1.3383	1.3490	1.3480	1.3387	1.3496	1.3486
R(2,3)	1.3977	1.401	1.4014	1.4025	1.4058	1.4069	1.3973	1.4004	1.4033
R(3,4)	1.3941	1.3988	1.4013	1.4004	1.4057	1.4069	1.4001	1.4051	1.4060
R(4,5)	1.3959	1.4015	1.4032	1.3915	1.3959	1.3982	1.3985	1.404	1.4049
R(5,6)	1.3979	1.4022	1.4042	1.3984	1.4025	1.4043	1.3951	1.3982	1.4008
R(6,1)	1.3378	1.3471	1.3457	1.3398	1.3505	1.3499	1.3413	1.3524	1.3515
R(6,7)	1.0876	1.0902	1.0943	1.0877	1.0903	1.0945	1.0875	1.0897	1.0943
R(5,8)	1.0854	1.0889	1.0918	1.0854	1.089	1.0918	1.0844	1.0870	1.0904
R(4,9)	1.086	1.0893	1.0926	1.0851	1.0875	1.0913	–	–	–
R(3,10)	1.0839	1.0873	1.0903	–	–	–	–	–	–
R(2,11)	1.5133	1.5084	1.5095	–	–	–	–	–	–
R(2,10)	–	–	–	1.0883	1.0902	1.0955	1.0878	1.0899	1.0945
R(3,9)	–	–	–	–	–	–	1.0857	1.0885	1.0923
R(4,11)	–	–	–	–	–	–	1.5077	1.5069	1.5071
R(3,11)	–	–	–	1.5031	1.5023	1.5018	–	–	–
R(11,12)	1.2295	1.2532	1.2493	1.2277	1.2531	1.2490	1.2262	1.2518	1.2477
R(11,13)	1.3564	1.3595	1.3631	1.3696	1.3691	1.3728	1.3693	1.3685	1.3720
R(13,14)	1.0101	1.0112	1.0157	1.0077	1.007	1.0109	1.0079	1.0068	1.0106
R(13,15)	1.0081	1.0088	1.0105	1.0101	1.0101	1.0122	1.0102	1.0102	1.0122
A(11,13,14)	119.6839	119.0827	117.9942	122.2195	123.5099	123.296	121.8300	123.3605	123.1941
A(11,13,15)	118.978	119.531	120.0128	116.6389	117.6356	117.9044	116.695	117.7494	118.0125
A(14,13,15)	121.3381	121.3863	121.9930	117.8266	118.8545	118.799	117.767	118.8901	118.7934
A(13,11,12)	124.0067	124.0116	124.2953	121.7543	121.1288	121.1198	122.0911	121.2751	121.3221
A(13,11,2)	114.5465	114.5365	114.0045	–	–	–	–	–	–
A(13,11,3)	–	–	–	116.8525	117.8414	117.771	–	–	–
A(13,11,4)	–	–	–	–	–	–	116.4342	117.6682	117.5558
A(12,11,2)	121.4467	121.4519	121.7002	–	–	–	–	–	–
A(12,11,3)	–	–	–	121.3864	121.0298	121.1092	–	–	–
A(12,11,4)	–	–	–	–	–	–	121.4674	121.0566	121.1221
A(11,2,3)	119.0911	119.7337	119.6291	–	–	–	–	–	–
A(11,4,3)	–	–	–	–	–	–	123.8514	124.4989	124.6230
A(11,4,5)	–	–	–	–	–	–	118.213	117.5675	117.5815
A(11,2,1)	117.6005	117.4448	117.0388	–	–	–	–	–	–
A(10,2,1)	–	–	–	115.1379	114.6825	114.4778	116.1544	116.4706	116.1916
A(10,2,3)	–	–	–	120.9163	121.9127	121.6566	120.146	120.4776	120.3911
A(3,2,1)	123.3084	122.8215	123.3321	123.9241	123.4048	123.8656	123.6991	123.0519	123.4174
A(2,3,4)	118.3056	118.4752	118.3207	117.7444	117.7735	117.7515	118.7247	119.0682	119.0286
A(2,3,10)	119.0192	119.025	118.9831	–	–	–	–	–	–
A(4,3,10)	122.6751	122.4998	122.6961	–	–	–	–	–	–
A(4,3,11)	–	–	–	118.2621	117.7991	117.7965	–	–	–
A(2,3,11)	–	–	–	123.9788	124.4274	124.452	–	–	–
A(2,3,9)	–	–	–	–	–	–	119.3905	118.4175	118.5479
A(4,3,9)	–	–	–	–	–	–	121.8511	122.5143	122.4235
A(2,1,6)	117.8589	118.3733	117.8598	117.3681	118.0455	117.4645	117.1373	117.7617	117.2374
A(3,4,5)	118.8381	118.992	118.8357	118.9226	119.2708	119.0445	117.9268	117.9336	117.7954
A(5,4,9)	120.6538	120.5368	120.6132	122.1098	122.1284	122.2685	–	–	–
A(3,4,9)	120.5081	120.4712	120.5511	118.9674	118.6008	118.687	–	–	–
A(1,6,5)	123.1628	122.5937	122.9989	123.4783	122.7444	123.2168	123.7231	123.0342	123.5037
A(1,6,7)	116.2019	116.5838	116.3788	115.9815	116.3245	115.9926	116.0192	116.3148	115.9949
A(5,6,7)	120.6353	120.8226	120.6223	120.5394	120.9311	120.7905	120.2577	120.6510	120.5014
A(4,5,6)	118.5262	118.7444	118.6527	118.5477	118.761	118.6571	118.7802	119.1504	119.0175
A(4,5,8)	121.3385	121.1597	121.2474	121.1519	120.9935	121.0803	119.7488	119.1370	119.3303
A(6,5,8)	120.1353	120.0959	120.0999	120.3004	120.2455	120.2626	121.4708	121.7126	121.6521
D(14,13,11,12)	–179.9369	–180.0	180.0000	–164.4174	–180.0145	–179.8022	163.8062	179.9867	179.9592
D(14,13,11,2)	–0.0532	0.0139	–0.0079	–	–	–	–	–	–
D(14,13,11,3)	–	–	–	16.5246	–0.0258	0.2138	–	–	–
D(14,13,11,4)	–	–	–	–	–	–	–17.1629	–0.0148	–0.0439
D(15,13,11,12)	0.0577	0.0036	0.0075	–5.4448	–0.0332	–0.1041	6.0024	0.0045	0.0131
D(15,13,11,2)	179.9415	180.0175	–180.0000	–	–	–	–	–	–
D(15,13,11,3)	–	–	–	175.4972	–180.0445	179.912	–	–	–
D(15,13,11,4)	–	–	–	–	–	–	–174.9666	–179.9970	–179.9900

Table 2 (continued)

Atoms	Picolinamide			Nicotinamide			Isonicotinamide		
	6-31++G(d,p) (Å/deg)	Z2POLX (Å/deg)	Z3POLX (Å/deg)	6-31++G(d,p) (Å/deg)	Z2POLX (Å/deg)	Z3POLX (Å/deg)	6-31++G(d,p) (Å/deg)	Z2POLX (Å/deg)	Z3POLX (Å/deg)
D(13,11,2,3)	−179.946	180.0492	−179.9891	—	—	—	—	—	—
D(13,11,3,4)	—	—	—	−163.1349	−179.9988	−179.853	—	—	—
D(13,11,4,5)	—	—	—	—	—	—	159.1972	179.996	179.9777
D(13,11,2,1)	<b>0.0593</b>	<b>−0.0063</b>	<b>−0.0028</b>	—	—	—	—	—	—
D(13,11,3,2)	—	—	—	<b>18.2965</b>	<b>0.0001</b>	<b>0.1509</b>	—	—	—
D(13,11,4,3)	—	—	—	—	—	—	<b>−21.9052</b>	<b>−0.0040</b>	<b>−0.0259</b>
D(12,11,2,3)	−0.0589	0.0627	0.0055	—	—	—	—	—	—
D(12,11,3,4)	—	—	—	17.8034	−0.0101	0.163	—	—	—
D(12,11,4,5)	—	—	—	—	—	—	−21.7653	−0.0055	−0.0254
D(12,11,2,1)	179.9464	−179.9928	179.9917	—	—	—	—	—	—
D(12,11,3,2)	—	—	—	−160.7652	−180.0112	−179.833	—	—	—
D(12,11,4,3)	—	—	—	—	—	—	157.1323	179.9944	179.971
D(11,2,3,4)	−179.9936	180.0094	179.9866	—	—	—	—	—	—
D(11,3,4,5)	—	—	—	−179.8916	180.0033	−179.9894	—	—	—
D(11,4,5,6)	—	—	—	—	—	—	179.9795	−179.9998	−179.9994
D(11,2,3,10)	0.0042	−0.067	0.0000	—	—	—	—	—	—
D(11,3,2,10)	—	—	—	1.5115	−0.0376	0.0514	—	—	—
D(11,3,4,9)	—	—	—	−0.0397	−0.0089	0.0073	—	—	—
D(11,4,5,8)	—	—	—	—	—	—	0.1554	0.0004	0.001
D(1,2,3,11)	—	—	—	179.7362	180.0068	179.9638	—	—	—
D(1,2,3,4)	0.0008	0.068	0.0000	1.1607	0.0056	−0.0322	−0.3005	−0.0006	−0.0028
D(1,2,3,10)	179.9986	179.998	−179.9872	—	—	—	—	—	—
D(1,2,3,9)	—	—	—	—	—	—	−178.2303	−179.9995	−179.9953
D(11,2,1,6)	179.9924	180.0155	−179.9879	—	—	—	—	—	—
D(11,4,3,2)	—	—	—	—	—	—	−179.4685	−179.9996	−179.9968
D(11,4,3,9)	—	—	—	—	—	—	−1.5920	−0.0007	−0.0046
D(3,2,1,6)	−0.0021	−0.0419	0.0000	−0.1679	−0.0163	0.0268	0.6776	0.0002	0.0021
D(2,3,4,5)	−0.0001	−0.0547	0.0000	−1.2326	0.0044	0.0069	−0.5679	0.0004	−0.0004
D(2,3,4,9)	179.9996	−180.0244	180.0000	178.6192	−180.0079	−179.9963	—	—	—
D(4,3,2,10)	—	—	—	−177.0640	−180.0387	−179.9446	179.4103	179.9999	179.9978
D(9,3,2,10)	—	—	—	—	—	—	1.4805	0.0009	0.0053
D(10,3,4,5)	−179.9978	−179.9821	179.9871	—	—	—	—	—	—
D(9,3,4,5)	—	—	—	—	—	—	177.3085	179.9993	179.9918
D(10,3,4,9)	0.0018	0.0482	−0.0120	—	—	—	—	—	—
D(9,4,5,8)	0.0008	−0.0029	0.0046	0.5246	0.028	0.0094	—	—	—
D(10,2,1,6)	—	—	—	178.1497	180.0252	179.9448	−179.0438	179.9997	−179.9985
D(8,5,6,7)	0.0005	−0.0174	0.0062	0.3439	−0.0285	0.0309	−0.7547	0.0004	−0.001
D(2,1,6,5)	0.0027	0.0035	0.0028	−0.7561	0.0172	0.0039	−0.1834	0.0005	0.0019
D(2,1,6,7)	−179.9995	180.0195	179.9907	179.55683	−179.98065	179.96215	179.7273	179.9993	179.9978
D(3,4,5,6)	0.0007	0.0194	0.0000	0.4083	−0.0035	0.0207	1.0157	0.0002	0.004
D(3,4,5,8)	−179.9995	180.0274	−179.9946	−179.6285	180.0152	−179.994	−178.8084	−179.9996	−179.9957
D(9,4,5,6)	−179.999	−180.0108	−180.0000	−179.4387	−179.9907	−179.9759	—	—	—
D(1,6,5,4)	−0.0021	0.0071	0.0000	0.6341	−0.0076	−0.0274	−0.6685	−0.0007	−0.005
D(1,6,5,8)	179.9981	179.9992	179.9935	−179.3295	179.9738	179.9872	179.1524	179.9992	179.9947
D(7,6,5,4)	−179.9997	−180.0096	0.00622	−179.6925	179.990	−179.9837	179.4244	−179.9994	179.9993

R, A, and D stand for bond, angle and dihedral angle, respectively.

in Table 2. The dihedral angles between the ring plane and CONH<sub>2</sub> group for picolinamide, nicotinamide, and isonicotinamide are marked in bold. These angles show that nicotinamide and isonicotinamide have a non-planar environment, and picolinamide has a planar environment. It was reported that the substitution of the amide group into the pyridine ring does not affect the dimensions of the ring very much [2]. The results of optimized geometry parameters were found to support this. The optimized geometry parameters obtained by using the DFT/B3LYP method with the 6-31++G(d,p) basis set were found to

be in better agreement with the experimental ones than the Z2PolX and Z3PolX basis sets.

The assignments of experimental wavenumbers, the calculated wavenumbers by using the DFT/B3LYP method with the 6-31++G(d,p), Z2PolX, and Z3PolX basis sets compared with experimental wavenumbers and total energy distribution results for each molecule are given in Tables 3–5. When compared with experimental spectra the results showed that the Z2PolX and Z3PolX basis sets gave accurate relative band intensities and band positions better than 6-31++G(d,p) basis set

without scaling. The simulated IR and Raman spectra and the experimental spectra are shown in Figs. 2–4 for picolinamide, nicotinamide, and isonicotinamide, respectively. IR and Raman intensities, scaled wavenumbers obtained from the SQM procedure, were found to

be in good agreement with the Z2PolX and Z3PolX basis sets. We found that the Z3PolX basis set gives the best results for predicting experimental IR and Raman spectra. Scaled wavenumbers at the 6-31++G(d,p) basis set were calculated by using the scaling factors which were

Table 3

The assignments of experimental wavenumbers, the calculated wavenumbers by using the DFT/B3LYP method with the 6-31++G(d,p), Z2PolX, and Z3PolX basis sets compared with the experimental wavenumbers and the total energy distribution results for picolinamide

Experimental				Calculation									
Assign.	IR	Ra	Gas <sup>a</sup>	6-31++G(d,p)			Z2POLX		Z3POLX				
				U	S	TED (%)	U	TED(%)	U	TED (%)			
$\gamma(\text{CO})$	$\tau_{\text{ring}}$	754	747	77	75	100 $\tau_{\text{CCCO}}$	77	100 $\tau_{\text{CCCO}}$	93	100 $\tau_{\text{CCCO}}$			
				157	147	52 $\gamma(\text{CC})$ , 40 $\tau_{\text{ring}}$	157	47 $\gamma(\text{CC})$ , 46 $\tau_{\text{ring}}$	170	51 $\tau_{\text{ring}}$ , 41 $\gamma(\text{CC})$			
				219	219	62 $\delta(\text{CC})$ , 25 $\delta(\text{CN})$	219	62 $\delta(\text{CC})$ , 25 $\delta(\text{CN})$	216	62 $\delta(\text{CC})$ , 26 $\delta(\text{CN})$			
				335	301	99 $\text{NH}_{2\text{wag}}$	335	96 $\text{NH}_{2\text{wag}}$	373	24 $\nu(\text{CC})$ , 24 $\delta_{\text{ring}}$ , 22 $\delta(\text{CO})$ , 19 $\delta(\text{CN})$			
				379	373	32 $\nu(\text{CC})$ , 25 $\delta_{\text{ring}}$ , 18 $\delta(\text{CO})$ , 15 $\delta(\text{CN})$	379	29 $\nu(\text{CC})$ , 26 $\delta_{\text{ring}}$ , 19 $\delta(\text{CO})$ , 16 $\delta(\text{CN})$	425	100 $\tau_{\text{ring}}$			
				414	399	100 $\tau_{\text{ring}}$	414	100 $\tau_{\text{ring}}$	438	45 $\text{NH}_{2\text{wag}}$ , 40 $\tau_{\text{ring}}$			
				451	428	76 $\tau_{\text{ring}}$ , 16 $\gamma(\text{CC})$	451	69 $\tau_{\text{ring}}$ , 21 $\gamma(\text{CC})$	486	39 $\delta(\text{CN})$ , 24 $\delta(\text{CC})$ , 11 $\nu_{\text{ring}}$			
				495	490	43 $\delta(\text{CN})$ , 22 $\delta(\text{CC})$ , 12 $\nu_{\text{ring}}$	495	42 $\delta(\text{CN})$ , 23 $\delta(\text{CC})$ , 11 $\nu_{\text{ring}}$	498	55 $\text{NH}_{2\text{wag}}$ , 31 $\tau_{\text{ring}}$ , 12 $\gamma(\text{CC})$			
				602	612	604 69 $\text{NH}_{2\text{twist}}$ , 15 $\gamma(\text{CO})$ , 11 $\tau_{\text{ring}}$	612	42 $\delta(\text{CO})$ , 41 $\delta_{\text{ring}}$	597	45 $\delta(\text{CO})$ , 36 $\delta_{\text{ring}}$			
				629	608	44 $\delta(\text{CO})$ , 38 $\delta_{\text{ring}}$	629	78 $\text{NH}_{2\text{twist}}$	632	83 $\delta_{\text{ring}}$			
				640	636	76 $\delta_{\text{ring}}$	640	76 $\delta_{\text{ring}}$	671	81 $\text{NH}_{2\text{twist}}$			
				680	717	679 41 $\gamma(\text{CO})$ , 29 $\text{NH}_{2\text{twist}}$ , 29 $\tau_{\text{ring}}$	717	51 $\tau_{\text{ring}}$ , 33 $\gamma(\text{CO})$ , 19 $\text{NH}_{2\text{twist}}$	724	54 $\tau_{\text{ring}}$ , 36 $\gamma(\text{CO})$ , 16 $\text{NH}_{2\text{twist}}$			
				$\tau_{\text{ring}}$	754	747	763	735	60 $\tau_{\text{ring}}$ , 34 $\gamma(\text{CH})$	763	57 $\gamma(\text{CH})$ , 37 $\tau_{\text{ring}}$	776	42 $\delta_{\text{ring}}$ , 23 $\nu(\text{CC})$ , 21 $\nu_{\text{ring}}$
				$\delta_{\text{ring}}$	794		781	765	43 $\delta_{\text{ring}}$ , 21 $\nu(\text{CC})$ , 21 $\nu_{\text{ring}}$	780	42 $\delta_{\text{ring}}$ , 23 $\nu(\text{CC})$ , 19 $\nu_{\text{ring}}$	795	47 $\gamma(\text{CH})$ , 36 $\tau_{\text{ring}}$ , 12 $\gamma(\text{CO})$
				$\gamma(\text{CH})$	825	817	832	781	46 $\gamma(\text{CH})$ , 20 $\gamma(\text{CC})$ , 20 $\gamma(\text{CO})$ , 14 $\tau_{\text{ring}}$	832	34 $\gamma(\text{CO})$ , 28 $\gamma(\text{CH})$ , 25 $\gamma(\text{CC})$ , 13 $\tau_{\text{ring}}$	870	44 $\gamma(\text{CH})$ , 24 $\gamma(\text{CC})$ , 22 $\gamma(\text{CO})$
$\gamma(\text{CH})$	909		928	896	100 $\gamma(\text{CH})$	928	100 $\gamma(\text{CH})$	978	100 $\gamma(\text{CH})$				
$\gamma(\text{CH})$			988	954	100 $\gamma(\text{CH})$	988	100 $\gamma(\text{CH})$	1000	57 $\delta_{\text{ring}}$ , 41 $\nu_{\text{ring}}$				
$\gamma(\text{CH})$			1016	988	100 $\gamma(\text{CH})$	1016	54 $\delta_{\text{ring}}$ , 45 $\nu_{\text{ring}}$	1057	59 $\nu_{\text{ring}}$ , 19 $\delta(\text{CH})$				
$\nu_{\text{ring}}$	996	998	996	1022	996	59 $\nu_{\text{ring}}$ , 39 $\delta_{\text{ring}}$	1022	100 $\gamma(\text{CH})$	1061	100 $\gamma(\text{CH})$			
$\nu_{\text{ring}}$	1043	1043	1030	1064	1032	60 $\nu_{\text{ring}}$ , 23 $\delta(\text{CH})$ , 14 $\delta_{\text{ring}}$	1064	68 $\nu_{\text{ring}}$ , 22 $\delta(\text{CH})$	1065	48 $\text{NH}_{2\text{rock}}$ , 15 $\nu_{\text{ring}}$			
$\text{NH}_{2\text{rock}}$		1083		1091	1065	43 $\text{NH}_{2\text{rock}}$ , 21 $\nu(\text{CN})$ , 12 $\nu_{\text{ring}}$	1091	51 $\text{NH}_{2\text{rock}}$ , 18 $\nu(\text{CN})$	1110	45 $\delta(\text{CH})$ , 40 $\nu_{\text{ring}}$			
$\delta(\text{CH})$	1095	1100	1086	1115	1085	39 $\delta(\text{CH})$ , 35 $\nu_{\text{ring}}$	1115	43 $\delta(\text{CH})$ , 36 $\nu_{\text{ring}}$	1134	100 $\gamma(\text{CH})$			
$\delta(\text{CH})$	1143	1142		1172	1140	74 $\delta(\text{CH})$ , 21 $\nu_{\text{ring}}$	1171	67 $\delta(\text{CH})$ , 21 $\nu_{\text{ring}}$	1170	48 $\delta(\text{CH})$ , 24 $\nu_{\text{ring}}$			
$\nu_{\text{ring}}$	1164	1168	1156	1178	1148	29 $\nu_{\text{ring}}$ , 22 $\delta_{\text{ring}}$ , 16 $\delta(\text{CH})$	1178	32 $\nu_{\text{ring}}$ , 28 $\delta(\text{CH})$ , 13 $\delta_{\text{ring}}$	1178	49 $\delta(\text{CH})$ , 27 $\nu_{\text{ring}}$			
$\nu_{\text{ring}}$	1254		1244	1310	1267	76 $\nu_{\text{ring}}$ , 18 $\delta(\text{CH})$	1310	65 $\nu_{\text{ring}}$ , 29 $\delta(\text{CH})$	1305	54 $\delta(\text{CH})$ , 40 $\nu_{\text{ring}}$			
$\delta(\text{CH})$	1284		1291	1324	1287	54 $\delta(\text{CH})$ , 36 $\nu_{\text{ring}}$	1324	47 $\nu_{\text{ring}}$ , 44 $\delta(\text{CH})$	1326	70 $\nu_{\text{ring}}$ , 18 $\delta(\text{CH})$			
$\nu(\text{CN})$	1387		1362	1386	1346	25 $\nu(\text{CN})$ , 16 $\nu(\text{CC})$ , 13 $\delta(\text{CO})$ , 12 $\delta(\text{CH})$ , 12 $\text{NH}_{2\text{scis}}$	1386	28 $\nu(\text{CN})$ , 16 $\nu(\text{CC})$ , 12 $\delta(\text{CH})$ , 12 $\delta(\text{CO})$ , 11 $\nu_{\text{ring}}$	1378	23 $\nu(\text{CN})$ , 17 $\nu(\text{CC})$ , 15 $\nu_{\text{ring}}$ , 14 $\delta(\text{CH})$			
$\delta(\text{CH})$	1442		1433	1471	1429	57 $\delta(\text{CH})$ , 33 $\nu_{\text{ring}}$	1471	55 $\delta(\text{CH})$ , 35 $\nu_{\text{ring}}$	1461	59 $\delta(\text{CH})$ , 33 $\nu_{\text{ring}}$			
$\delta(\text{CH})$	1468		1472	1505	1461	56 $\delta(\text{CH})$ , 36 $\nu_{\text{ring}}$	1505	54 $\delta(\text{CH})$ , 38 $\nu_{\text{ring}}$	1490	51 $\delta(\text{CH})$ , 37 $\nu_{\text{ring}}$			
$\text{NH}_{2\text{scis}}$	1603		1567	1594	1528	78 $\text{NH}_{2\text{scis}}$	1594	81 $\text{NH}_{2\text{scis}}$	1551	74 $\text{NH}_{2\text{scis}}$			
$\nu_{\text{ring}}$	1568			1620	1570	71 $\nu_{\text{ring}}$ , 16 $\delta(\text{CH})$	1620	73 $\nu_{\text{ring}}$ , 15 $\delta(\text{CH})$	1611	74 $\nu_{\text{ring}}$ , 15 $\delta(\text{CH})$			
$\nu_{\text{ring}}$	1587		1645	1637	1588	65 $\nu_{\text{ring}}$ , 21 $\delta(\text{CH})$	1637	67 $\nu_{\text{ring}}$ , 20 $\delta(\text{CH})$	1629	70 $\nu_{\text{ring}}$ , 18 $\delta(\text{CH})$			
$\nu(\text{CO})$	1658		1722	1760	1702	74 $\nu(\text{CO})$	1760	75 $\nu(\text{CO})$	1707	71 $\nu(\text{CO})$			
$\nu(\text{CH})$			3020	3176	3037	100 $\nu(\text{CH})$	3176	100 $\nu(\text{CH})$	3153	100 $\nu(\text{CH})$			
$\nu(\text{CH})$	3061			3194	3054	100 $\nu(\text{CH})$	3194	100 $\nu(\text{CH})$	3178	100 $\nu(\text{CH})$			
$\nu(\text{CH})$			3075	3213	3072	99 $\nu(\text{CH})$	3213	99 $\nu(\text{CH})$	3202	99 $\nu(\text{CH})$			
$\nu(\text{CH})$				3233	3091	99 $\nu(\text{CH})$	3233	100 $\nu(\text{CH})$	3220	99 $\nu(\text{CH})$			
$\nu(\text{NH}_2)$	3164		3415	3589	3431	100 $\nu(\text{NH}_2)$	3589	100 $\nu(\text{NH}_2)$	3519	100 $\nu(\text{NH}_2)$			
$\nu(\text{NH}_2)$	3414		3552	3738	3574	100 $\nu(\text{NH}_2)$	3738	100 $\nu(\text{NH}_2)$	3691	100 $\nu(\text{NH}_2)$			

IR, experimental IR solid phase wavenumbers; Ra, the experimental Raman wavenumbers; Gas, experimental IR gas phase wavenumbers; U, unscaled wavenumbers; S, scaled wavenumbers; TED, total energy distribution of picolinamide obtained by using the Scale 2.0 program;  $\tau$ , torsion;  $\delta$ , in plane bending;  $\nu$ , stretching;  $\gamma$ , out of plane bending vibrations.

<sup>a</sup> Taken from Ref. [19].

The assignments of experimental wavenumbers, the calculated wavenumbers by using the DFT/B3LYP method with the 6-31++G(d,p), Z2PolX and Z3PolX basis sets compared with the experimental wavenumbers and the total energy distribution results for nicotinamide

IR, experimental IR solid phase wavenumbers; Ra, experimental Raman wavenumbers; Gas, experimental IR gas phase wavenumbers; U, unscaled wavenumbers; S, scaled wavenumbers; TED, total energy distribution of nicotinamide obtained by using the Scale 2.0 program;  $\tau$ , torsion;  $\delta$ , in plane bending;  $\nu$ , stretching;  $\gamma$ , out of plane bending vibrations.

determined by Pulay and Pongor [13–15]. Only the scaling factors related to the out of plane bendings and NH<sub>2</sub> rocking were refined. The final scaling factors are given

in Table 6. They were used without making any changes for the three isomers. In this way we showed that these scaling factors are transferable.

Table 5

The assignments of experimental wavenumbers, the calculated wavenumbers by using the DFT/B3LYP method with the 6-31++G(d,p), Z2PolX and Z3PolX basis sets compared with the experimental wavenumbers and the total energy distribution results for isonicotinamide

Experimental			Calculation						
			6-31++G(d,p)			Z2POLX		Z3POLX	
Assign.	IR	Ra	U	S	TED(%)	U	TED(%)	U	TED (%)
NH <sub>2</sub> twist $\delta_{\text{ring}}$ $\delta_{\text{ring}}$ $\gamma(\text{CO})$ $\delta_{\text{ring}}$ $\tau_{\text{ring}}$ $\gamma(\text{CH})$ $\gamma(\text{CH})$ $\gamma(\text{CH})$ $\nu_{\text{ring}}$ NH <sub>2</sub> rock $\nu_{\text{ring}}$ $\delta(\text{CH})$ $\nu_{\text{ring}}$ $\delta(\text{CH})$ $\nu_{\text{ring}}$ $\delta(\text{CH})$ $\nu_{\text{ring}}$ $\nu(\text{CO})$ $\nu(\text{CH})$ $\nu(\text{CH})$ $\nu(\text{CH})$ $\nu(\text{NH}_2)$ $\nu(\text{NH}_2)$	668 708 754 776 795 852 984 1007 994 1065 1086 1122 1148 1219 1263 1322 1390 1408 1496 1622 1551 1596 1655 3042 3066 3178 3362	664 783 867 783 867 995 1063 1084 1128 1152 1246 1297 1352 1371 1444 1527 1606 1623 1642 1759 3173 3180 3200 3226 3596 3731	56	54	98 $\tau\text{CCCO}$	32	98 $\tau\text{CCCO}$	35	98 $\tau\text{CCCO}$
			151	141	57 $\gamma(\text{CC})$ , 33 $\tau_{\text{ring}}$	166	48 $\gamma(\text{CC})$ , 44 $\tau_{\text{ring}}$	168	48 $\tau_{\text{ring}}$ , 45 $\gamma(\text{CC})$
			211	209	64 $\delta(\text{CC})$ , 18 $\delta(\text{CN})$	229	65 $\delta(\text{CC})$ , 23 $\delta(\text{CN})$	228	66 $\delta(\text{CC})$ , 23 $\delta(\text{CN})$
			341	309	91 NH <sub>2</sub> wag	383	33 $\delta_{\text{ring}}$ , 29 $\nu(\text{CC})$ , 15 $\delta(\text{CO})$	350	83 NH <sub>2</sub> wag, 13 NH <sub>2</sub> twist
			368	365	30 $\delta_{\text{ring}}$ , 28 $\nu(\text{CC})$ , 14 $\delta(\text{CO})$ , 12 $\delta(\text{CN})$	391	100 $\tau_{\text{ring}}$	374	31 $\delta_{\text{ring}}$ , 26 $\nu(\text{CC})$ , 16 $\delta(\text{CO})$ , 15 $\delta(\text{CN})$
			387	375	100 $\tau_{\text{ring}}$	445	34 $\tau_{\text{ring}}$ , 26 NH <sub>2</sub> twist, 23 NH <sub>2</sub> wag	393	100 $\tau_{\text{ring}}$
			415	400	61 $\tau_{\text{ring}}$ , 11 $\delta(\text{CN})$	472	52 NH <sub>2</sub> wag, 31 $\tau_{\text{ring}}$	461	58 $\tau_{\text{ring}}$ , 19 $\gamma(\text{CC})$ , 15 $\gamma(\text{CO})$
			510	501	38 $\delta(\text{CN})$ , 14 $\delta(\text{CC})$ , 10 $\tau_{\text{ring}}$	476	49 $\delta(\text{CN})$ , 17 $\delta(\text{CC})$	468	47 $\delta(\text{CN})$ , 18 $\delta(\text{CC})$
			565	542	71 NH <sub>2</sub> twist	606	53 $\delta(\text{CO})$ , 24 $\delta_{\text{ring}}$	582	74 NH <sub>2</sub> twist, 10 NH <sub>2</sub> wag
			614	610	49 $\delta(\text{CO})$ , 28 $\delta_{\text{ring}}$	610	60 NH <sub>2</sub> twist, 21 NH <sub>2</sub> wag	595	53 $\delta(\text{CO})$ , 28 $\delta_{\text{ring}}$
			681	675	52 $\delta_{\text{ring}}$ , 25 $\gamma(\text{CO})$ , 10 $\tau_{\text{ring}}$	686	88 $\delta_{\text{ring}}$	670	89 $\delta_{\text{ring}}$
			720	683	36 $\delta_{\text{ring}}$ , 27 $\gamma(\text{CO})$ , 22 $\tau_{\text{ring}}$	735	49 $\tau_{\text{ring}}$ , 40 $\gamma(\text{CO})$	724	57 $\tau_{\text{ring}}$ , 41 $\gamma(\text{CO})$
			766	731	82 $\tau_{\text{ring}}$ , 15 $\gamma(\text{CO})$	760	40 $\delta_{\text{ring}}$ , 24 $\nu(\text{CC})$ , 18 $\nu_{\text{ring}}$	760	38 $\delta_{\text{ring}}$ , 25 $\nu(\text{CC})$ , 17 $\nu_{\text{ring}}$
			769	761	35 $\delta_{\text{ring}}$ , 25 $\nu(\text{CC})$ , 17 $\nu_{\text{ring}}$	780	59 $\tau_{\text{ring}}$ , 22 $\gamma(\text{CH})$ , 15 $\gamma(\text{CO})$	778	49 $\tau_{\text{ring}}$ , 24 $\gamma(\text{CH})$ , 20 $\gamma(\text{CO})$
			855	812	85 $\gamma(\text{CH})$ , 14 $\gamma(\text{CC})$	883	66 $\gamma(\text{CH})$ , 19 $\gamma(\text{CC})$ , 18 $\gamma(\text{CO})$	892	70 $\gamma(\text{CH})$ , 18 $\gamma(\text{CC})$ , 15 $\gamma(\text{CO})$
			896	865	100 $\gamma(\text{CH})$	928	97 $\gamma(\text{CH})$	936	99 $\gamma(\text{CH})$
			984	950	100 $\gamma(\text{CH})$	996	64 $\nu_{\text{ring}}$ , 34 $\delta_{\text{ring}}$	994	51 $\nu_{\text{ring}}$ , 48 $\delta_{\text{ring}}$
			1007	973	100 $\gamma(\text{CH})$	1053	100 $\gamma(\text{CH})$	1045	58 NH <sub>2</sub> rock, 17 $\nu(\text{CN})$ , 11 $\nu(\text{CO})$
			1011	1004	56 $\nu_{\text{ring}}$ , 43 $\delta_{\text{ring}}$	1084	31NH <sub>2</sub> rock, 16 $\nu(\text{CN})$ , 16 $\nu_{\text{ring}}$ , 12 $\nu(\text{CO})$	1052	100 $\gamma(\text{CH})$
			1083	1067	46 NH <sub>2</sub> rock, 20 $\nu(\text{CN})$ , 11 $\nu_{\text{ring}}$	1085	100 $\gamma(\text{CH})$	1081	46 $\nu_{\text{ring}}$ , 33 $\delta(\text{CH})$ , 21 $\delta_{\text{ring}}$
			1091	1076	41 $\nu_{\text{ring}}$ , 34 $\delta(\text{CH})$ , 20 $\delta_{\text{ring}}$	1091	38 $\nu_{\text{ring}}$ , 27 $\delta_{\text{ring}}$ , 21 $\delta(\text{CH})$	1085	100 $\gamma(\text{CH})$
			1116	1097	43 $\delta(\text{CH})$ , 38 $\nu_{\text{ring}}$	1121	40 $\nu_{\text{ring}}$ , 35 $\delta(\text{CH})$	1116	47 $\nu_{\text{ring}}$ , 40 $\delta(\text{CH})$
			1151	1138	32 $\nu_{\text{ring}}$ , 20 $\delta_{\text{ring}}$ , 12 $\nu(\text{CN})$ , 12 $\nu(\text{CC})$ , 11 $\delta(\text{CH})$	1161	32 $\nu_{\text{ring}}$ , 18 $\delta_{\text{ring}}$ , 18 NH <sub>2</sub> rock, 13 $\nu(\text{CC})$	1146	37 $\nu_{\text{ring}}$ , 15 $\delta(\text{CH})$ , 15 $\nu(\text{CN})$ , 12 $\delta_{\text{ring}}$ , 10 $\nu(\text{CC})$
			1246	1221	64 $\delta(\text{CH})$ , 34 $\nu_{\text{ring}}$	1243	64 $\delta(\text{CH})$ , 32 $\nu_{\text{ring}}$	1241	65 $\delta(\text{CH})$ , 33 $\nu_{\text{ring}}$
			1297	1284	94 $\nu_{\text{ring}}$	1292	97 $\nu_{\text{ring}}$	1302	95 $\nu_{\text{ring}}$
			1352	1322	79 $\delta(\text{CH})$ , 15 $\nu_{\text{ring}}$	1356	72 $\delta(\text{CH})$ , 13 $\nu_{\text{ring}}$	1341	78 $\delta(\text{CH})$ , 17 $\nu_{\text{ring}}$
			1371	1352	32 $\nu(\text{CN})$ , 19 $\nu(\text{CC})$ , 14 $\delta(\text{CO})$	1387	36 $\nu(\text{CN})$ , 19 $\nu(\text{CC})$ , 14 $\delta(\text{CH})$ , 12 $\delta(\text{CO})$ , 10 NH <sub>2</sub> rock	1372	35 $\nu(\text{CN})$ , 21 $\nu(\text{CC})$ , 12 $\delta(\text{CO})$ , 10 $\delta(\text{CH})$
			1444	1417	55 $\delta(\text{CH})$ , 40 $\nu_{\text{ring}}$	1429	57 $\delta(\text{CH})$ , 37 $\nu_{\text{ring}}$	1428	59 $\delta(\text{CH})$ , 36 $\nu_{\text{ring}}$
			1527	1497	59 $\delta(\text{CH})$ , 35 $\nu_{\text{ring}}$	1507	65 $\delta(\text{CH})$ , 30 $\nu_{\text{ring}}$	1508	62 $\delta(\text{CH})$ , 32 $\nu_{\text{ring}}$
			1606	1559	85 NH <sub>2</sub> scis	1588	66 $\nu_{\text{ring}}$ , 15 $\delta(\text{CO})$	1584	70 NH <sub>2</sub> scis, 12 $\nu(\text{CO})$
			1623	1589	77 $\nu_{\text{ring}}$	1628	65 $\nu_{\text{ring}}$ , 21 $\delta(\text{CH})$	1599	70 $\nu_{\text{ring}}$
			1642	1621	67 $\nu_{\text{ring}}$ , 20 $\delta(\text{CH})$	1646	38 NH <sub>2</sub> scis, 37 $\nu(\text{CO})$	1630	66 $\nu_{\text{ring}}$ , 20 $\delta(\text{CH})$
			1759	1740	80 $\nu(\text{CO})$	1684	54 NH <sub>2</sub> scis, 26 $\nu(\text{CO})$	1696	69 $\nu(\text{CO})$
			3173	3044	100 $\nu(\text{CH})$	3174	99 $\nu(\text{CH})$	3150	100 $\nu(\text{CH})$
			3180	3050	100 $\nu(\text{CH})$	3179	99 $\nu(\text{CH})$	3158	100 $\nu(\text{CH})$
			3200	3070	99 $\nu(\text{CH})$	3194	99 $\nu(\text{CH})$	3181	99 $\nu(\text{CH})$
			3226	3095	99 $\nu(\text{CH})$	3221	99 $\nu(\text{CH})$	3218	99 $\nu(\text{CH})$
			3596	3450	100 $\nu(\text{NH}_2)$	3568	99 $\nu(\text{NH}_2)$	3552	100 $\nu(\text{NH}_2)$
			3731	3578	100 $\nu(\text{NH}_2)$	3714	99 $\nu(\text{NH}_2)$	3701	100 $\nu(\text{NH}_2)$

IR, experimental IR solid phase wavenumbers; Ra, experimental Raman wavenumbers; U, unscaled wavenumbers; S, scaled wavenumbers; TED, total energy distribution of isonicotinamide obtained by using the Scale 2.0 program;  $\tau$ , torsion;  $\delta$ , in plane bending;  $\nu$ , stretching;  $\gamma$ , out of plane bending vibrations.



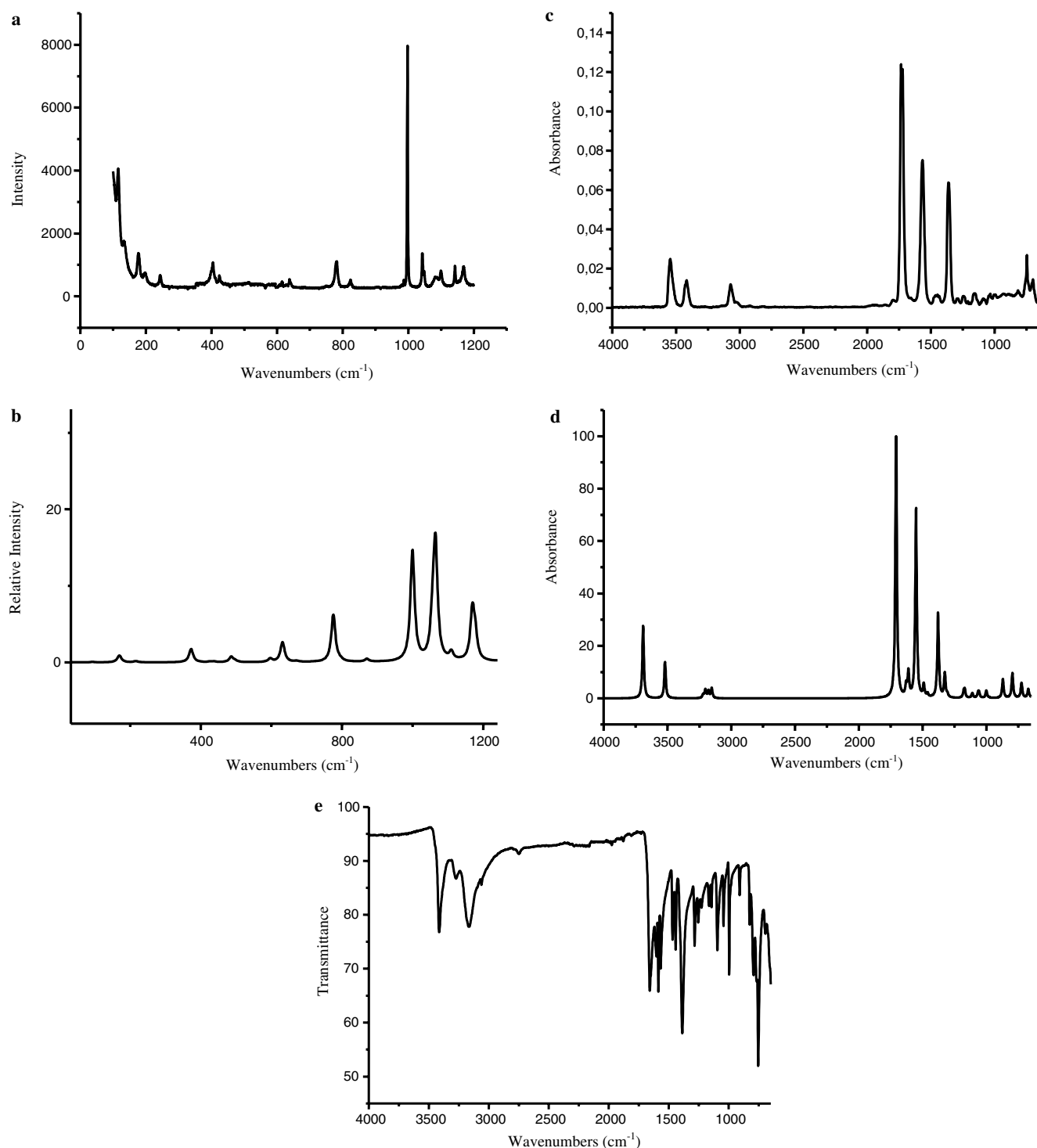


Fig. 2. (a) The experimental Raman spectrum, (b) the simulated Raman spectrum, (c) the experimental IR gas phase spectrum, (d) the simulated IR gas phase spectrum, (e) the IR solid phase spectrum of picolinamide.

In the present work, TED calculations indicate a very significant mixing of all ring and bending vibrations. Such mixing was indicated in previous studies [16,17] and it should increase with respect to the pyridine case due to the lowering of molecular symmetry and presence of an amide group which is a heavy group. For example, the ring breathing mode includes ring vibrations and ring bond

stretching in different proportions. Therefore, it does not resemble the ring breathing mode of the pyridine. In this study, the ring breathing modes of picolinamide, nicotinamide, and isonicotinamide were assigned in Raman spectra 998, 1042, 995  $\text{cm}^{-1}$ , respectively. Also, it was reported that the ring breathing mode of coordinated nicotinamide was found to be at 1033  $\text{cm}^{-1}$  in Raman spectra [18].

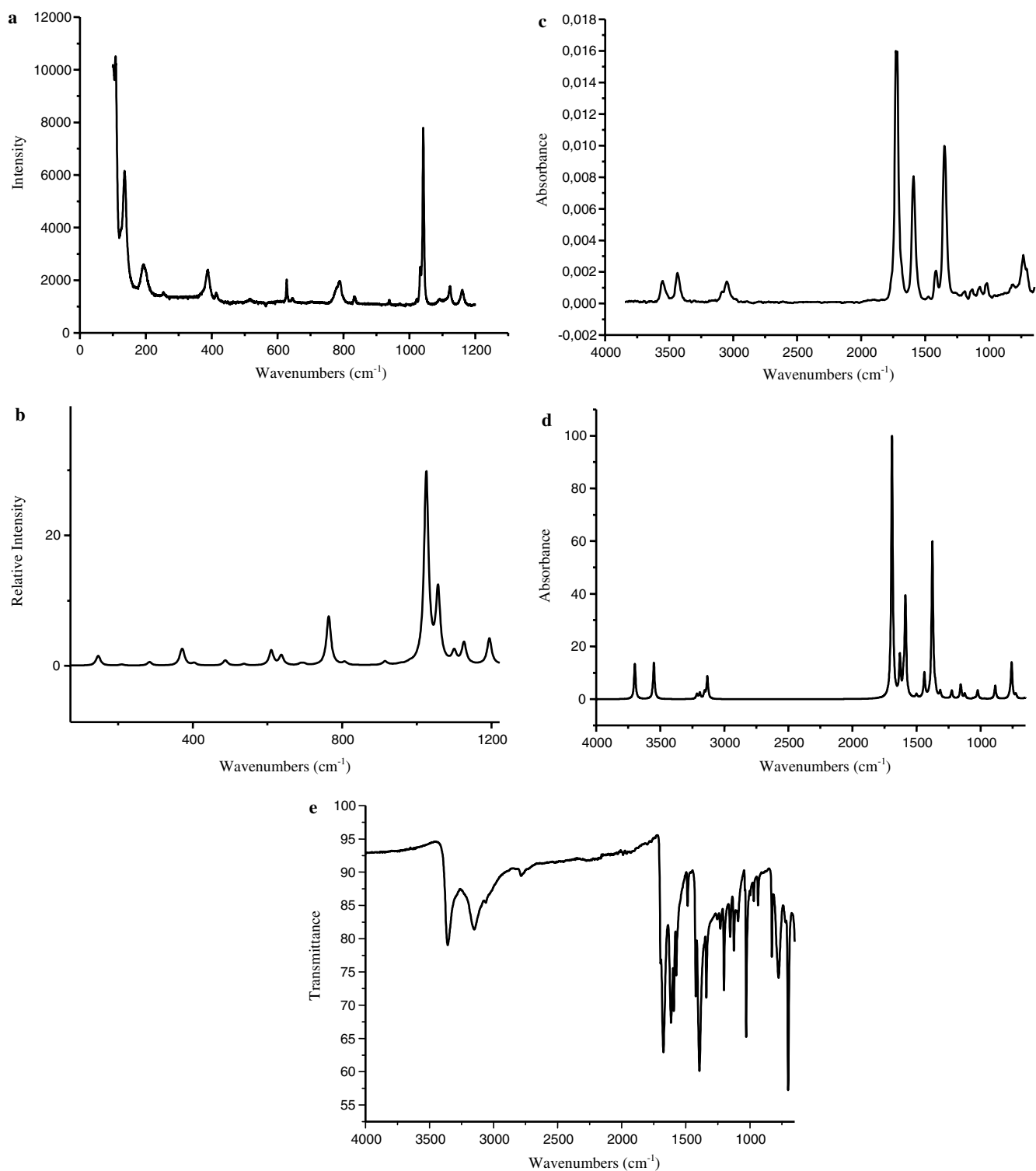


Fig. 3. (a) The experimental Raman spectrum, (b) the simulated Raman spectrum, (c) the experimental IR gas phase spectrum, (d) the simulated IR gas phase spectrum, (e) the IR solid phase spectrum of nicotinamide.

## 5. Conclusion

The combination of good intensity and wavenumber data made it possible for the isomers of pyridinecarboxamide to have a close correspondence between the simulated IR and Raman spectra and experimental data. The

results of 6-31++G(d,p) basis set, which were obtained by applying the SQM procedure and the results of Z3PolX basis set, showed us that the observed bands could easily be assigned. We found that the Z3PolX basis set gave the best results for predicting experimental IR and Raman spectra.

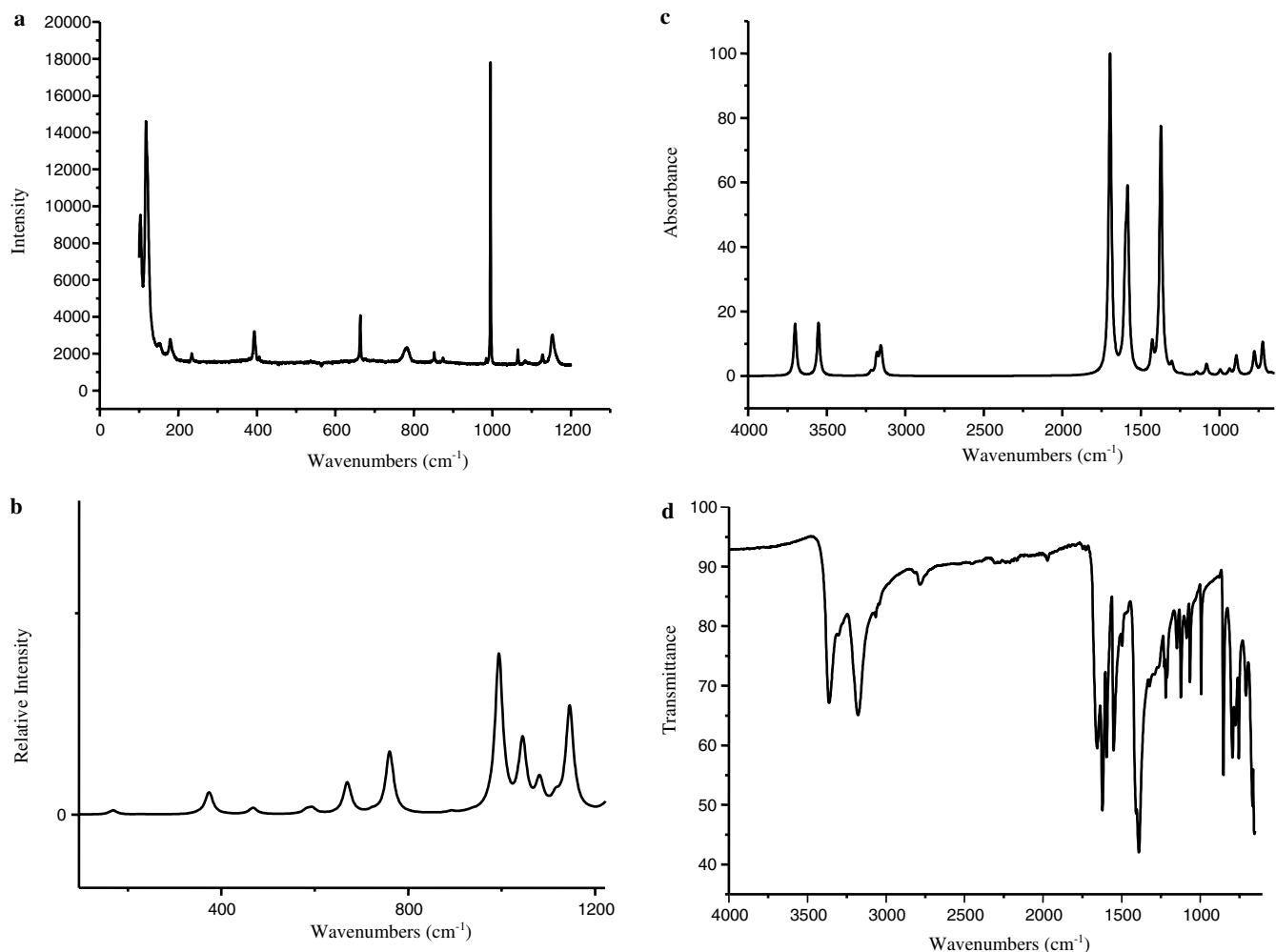


Fig. 4. (a) The experimental Raman spectrum, (b) the simulated Raman spectrum, (c) the simulated IR gas phase spectrum, (d) the IR solid phase spectrum of isonicotinamide.

Table 6  
The scaling factors for the isomers of pyridinecarboxamide

Internal coordinates	Scaling factors
X–Y stretching	0.9300
X–H stretching	0.9140
X–Y–Z in plane bending	0.9950
X–Y–H in plane bending	0.9500
CO/CC out of plane bending	0.8300
CH out of plane bending	0.9340
All torsion	0.9350
NH <sub>2</sub> scissoring	0.9130
NH <sub>2</sub> rocking	0.9672
NH <sub>2</sub> wagging	0.8000

H means hydrogen; X, Y, and Z mean first-row heavy atoms C, N, O.

### Acknowledgement

The authors thank Prof. Dr. Mustafa Urgan and Assoc. Prof. Dr. Gultekin Goller for Raman and FT-IR measurements at the Istanbul Technical University, Istanbul, Turkey.

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