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Anharmonic Vibrational Spectroscopy of Nitriles and Their Complexes with Water

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Three nitrile molecules, cyanamide ($H_2N-C\equiv N$), acetonitrile ($CH_3-C\equiv N$), and aminoacetonitrile ($H_2N-CH_2-C\equiv N$), and their complexes with one water molecule are studied at the ab initio level of theory (second-order Møller−Plesset perturbation theory with triple-ζ basis sets). Anharmonic vibrational spectra are estimated with the Correlation Corrected Vibrational Self-Consistent Field (CC-VSCF) method that accounts for anharmonicities and couplings between different vibrational normal modes. Effects of complexation with water on geometries and vibrational spectra of nitriles are investigated. The effects are very different from those found earlier for acids (in particular, the amino acid glycine). While the intermolecular hydrogen bonding interactions lead to significant red shifts of carboxyl group (O−H and C=O) vibrational stretching frequencies of acids, C≡N stretches of nitriles shift to a much lesser extent and in the opposite direction (to the blue) upon complexation with water.

I. Introduction

Nitriles are among the most common organic molecules identified in the gas phase in interstellar clouds. A number of nitriles, isonitriles, and other related compounds have been studied in laboratory experiments to assist in the interpretation of astronomical observations. Infrared spectra have been measured of nitriles as pure solids,[1] isolated in Ar matrix,[2] and in H_2O ices.[2] Recently, the infrared spectrum of matrix-isolated aminoacetonitrile, a precursor to the amino acid glycine, has been obtained as well.[3] Since amino nitriles are precursors of amino acids, knowledge of their spectra and interactions with water may be very important from the point of view of the search for signatures of life on other worlds, one of NASA's astrobiology goals.[4] One of the objectives of the present study is to obtain accurate theoretical spectra of several nitrile molecules, as well as their complexes with water. Theoretical spectra can assist in the interpretation and analysis of observational data and the data obtained in laboratory experiments. In our study we will consider effects of complexation with water on the structural and spectroscopic properties of both nitrile and water molecules. Complexes with water describe important intermediate states between the isolated gas-phase molecules and the conditions of molecules adhered to small ice particles in space, or on the surface of icy moons. In addition, we will compare interactions of nitrile molecules with water to interactions of acids (in particular, amino acids) with water.

In this study, we investigate anharmonic vibrational spectroscopy of three nitrile molecules, cyanamide ($H_2N-C\equiv N$), acetonitrile ($CH_3-C\equiv N$), and aminoacetonitrile ($H_2N-CH_2-C\equiv N$), and their complexes with one water molecule. We compare the calculated spectra with those obtained experimentally in cold matrix environments.[2−3] We also compare the results obtained for aminoacetonitrile−water complex with similar results for the amino acid glycine−water complex obtained previously.[5] The direct ab initio anharmonic vibrational spectroscopy method is used which enables us to account for anharmonicities and couplings between vibrational normal modes.[6] The predicted ab initio anharmonic spectra can be used to guide and interpret future observational and laboratory experimental studies of nitriles and their complexes with water.

II. Methodology

The level of ab initio theory used in this work for studying the potential energy surfaces of the nitrile molecules and their complexes with water is second-order Møller−Plesset perturbation theory (MP2)[7] with the Dunning's triple ζ + polarization (TZP) basis set.[8] This level of theory was used previously to calculate potential energy surfaces of a number of hydrogen-bonded complexes[9−11] and found to be sufficiently accurate for predictions of their geometries and anharmonic vibrational spectra. Equilibrium geometries of all systems are optimized by using analytic gradients of the MP2/TZP energies. The second derivative (Hessian) matrices are calculated numerically by using double differencing of analytical gradients. Anharmonic vibrational frequencies are obtained by using the Vibrational Self-Consistent Field (VSCF) method[12,13] and its Correlation Corrected (CC-VSCF) extension via second-order perturbation theory.[14] The CC-VSCF approach combined with the MP2/TZP ab initio level of theory was shown to provide good accuracy for vibrational frequencies of many hydrogen-bonded systems studied previously (with average errors of the order of 30−50 cm^{-1} compared to available experimental data).[9−11]

The VSCF method,[12,13] used here to estimate the anharmonic vibrational spectra, is based on a separability approximation, where the total vibrational state of the system is represented by a product of one-dimensional wave functions:

$$\Psi = \prod_{j}^{N} \psi_j(Q_j) \qquad (1)$$

where N is the number of vibrational degrees of freedom and Q_j are mass-weighted normal coordinates. This reduces the problem of solving the N-dimensional vibrational Schrödinger equation to solving N single-mode VSCF equations. The

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resulting VSCF solutions are further corrected for correlation effects between the vibrational modes by using second-order perturbation theory (CC-VSCF).[14] A combined ab initio/CC-VSCF approach is used, which has been described in detail previously.[6,9] A pairwise approximation for the potential[14] is used in the same way as in previous papers,[9−11] namely, the potential of the system is represented by the sum of separable (single mode) terms and pair coupling terms, neglecting interactions of triples of normal modes and higher order interactions:

$$V(Q_1,...,Q_N) = \sum_{j}^{N} V_j^{\mathrm{diag}}(Q_j) + \sum_{i}^{N-1} \sum_{j>i}^{N} V_{ij}^{\mathrm{coup}}(Q_i,Q_j) \quad (2)$$

Experience from previous studies on several related systems, such as glycine,[15] *N*-methylacetamide,[16] and water clusters and hydrogen-bonded complexes[9−11] shows that the errors due to this approximation are small, no more than 10 cm^{-1} for the stretching modes. “Diagonal” (single-mode) terms $V_j^{\mathrm{diag}}(Q_j) = V(0,...,Q_j,...,0)$ and the pairwise mode−mode coupling terms $V_{ij}^{\mathrm{coup}}(Q_i,Q_j) = V(0,...,Q_i,...,Q_j,...,0) - V^{\mathrm{diag}}(Q_i) - V^{\mathrm{diag}}(Q_j)$ are calculated directly from the ab initio program on 8 point grids along each normal coordinate, and on 8 × 8 square grids for each pair of normal coordinates. Obtaining the potential points along each single normal mode allows us to account for one-dimensional anharmonicities, while the square grids of points for each pair of normal modes is required to account for coupling effects between the modes. The calculated ab initio potentials are then interpolated into 16 and 16 × 16 point grids and used for numerical solution of the one-dimensional VSCF equations. This technique (including the grid size and interpolation scheme) was shown to work reasonably well in our previous studies and to predict anharmonic frequencies for the highest frequency stretching vibrations with the accuracy of 30−50 cm^{-1} compared with experiment.[9−11,15,16] It should be noted that the accuracy of the above VSCF approximation was previously tested primarily for higher frequency modes. Its accuracy may be lower for low-frequency torsional modes where not only the pairwise approximation but more fundamental approximations (e.g. the separability (VSCF) approximation and the use of normal mode coordinates) may sometimes fail in the case of very floppy systems. Therefore, we expect the VSCF approach to work more reliably for high-frequency stretching vibrations than for low-frequency torsional modes. All ab initio calculations in this study were performed with the electronic structure package GAMESS.[17] Infrared intensities were calculated using VSCF wave functions and dipole moments estimated along normal mode coordinates (see ref 9 for more details on intensity calculations).

III. Results and Discussion

(a) Cyanamide ($H_2N-C\equiv N$) and Its Complexes with Water. Equilibrium geometries of cyanamide and its complexes with water are shown in Figure 1. Binding energies for the two complexes with water are given in Table 1. In the first complex ($H_2N-C\equiv N\cdots H_2O$), the C≡N group of the cyanamide is hydrogen bonded to one of the hydrogen atoms of water, and the C≡N bond is shortened by 0.001 Å compared with the isolated cyanamide. One of the O−H bonds of the water molecule is elongated due to the hydrogen bonding by 0.006 Å. In the second conformer $H_2O\cdots H_2N-C\equiv N$ (more stable at the MP2/TZP level of theory), the oxygen atom of the water molecule forms a hydrogen bond with one of the H atoms of the cyanamide. This leads to the opposite effect on the C≡N bond, namely its elongation by 0.001 Å. Additionally, the N−H bond participating in the hydrogen bonding elongates significantly, by 0.009 Å. The binding energies (D_e) of the two conformers ($H_2N-C\equiv N\cdots H_2O$ and $H_2O\cdots H_2N-C\equiv N$) are 5.50 and 7.75 kcal/mol at the MP2/TZP level, respectively. When harmonic zero-point energy corrections are added, the estimated D_0 values are 4.1 and 5.9 kcal/mol, respectively.

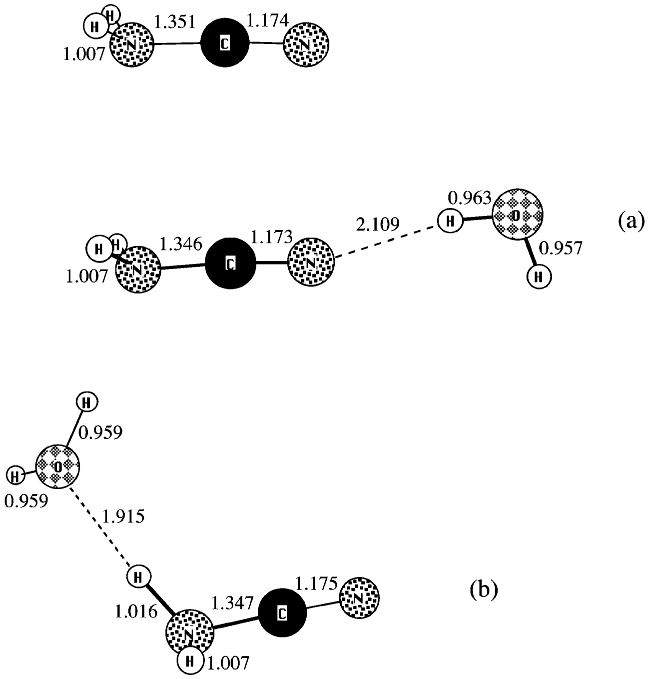

Figure 1. MP2/TZP geometrical structures of cyanamide and its complexes with water (bond lengths are in Å).

TABLE 1: Binding Energies (kcal/mol) of Nitrile−Water Complexes

complex	D_e	D_0
cyanamide−water		
complex (a)	5.50	4.11
complex (b)	7.75	5.91
acetonitrile−water		
complex (a)	5.05	3.76
complex (b)	4.88	3.62
aminoacetonitrile−water		
complex (a)	4.94	3.68
complex (b)	7.23	5.26
complex (c)	7.23	5.50

The results of vibrational spectroscopy calculations are presented in Table 2. Both harmonic and anharmonic (CC-VSCF) vibrational frequencies are shown, as well as the infrared intensities. It is seen from the table that the most characteristic vibration of the cyanamide spectrum, the C≡N stretch, is quite intense and is located at 2263 cm^{-1} at the harmonic level. This frequency is reduced to 2223 cm^{-1} when anharmonic corrections are taken into account. The position of the C≡N stretch is shifted to the blue (by 16 and 19 cm^{-1} at the harmonic and CC-VSCF levels, respectively) in the $H_2N-C\equiv N\cdots H_2O$ complex (a), and slightly to the red (by about 6 cm^{-1}) in the $H_2O\cdots H_2N-C\equiv N$ complex (b). The intensity of this vibration increases in both complexes as compared to the isolated cyanamide. Comparison with experimental values[2] shows that our CC-VSCF corrected cyanamide C≡N stretching frequency is somewhat lower than the experimental value (2264 cm^{-1}), but the difference (~40 cm^{-1}) is within the accuracy of our method.

The calculated spectra of the hydrogen-bonded complexes with one H_2O molecule do not show significant red shifts of the C≡N stretching frequency observed experimentally.[2] Instead,

TABLE 2: Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of Cyanamide and Its Complexes with Water

	$H_2N{-}C{\equiv}N$			$H_2N{-}C{\equiv}N{\cdots}H_2O$ (a)			$H_2O{\cdots}H_2N{-}C{\equiv}N$ (b)			
mode	harm	cc-vscf	intens	harm	cc-vscf	intens	harm	cc-vscf	intens	description
1	3727	3461	70	3729	3459	82	3695	3473	110	N−H asym stretch
2	3617	3413	55	3618	3417	74	3508	3298	433	N−H sym stretch
3	2263	2223	152	2279	2242	206	2256	2217	191	C≡N stretch
4	1666	1611	56	1664	1619	57	1681	1630	46	NH_2 bend
5	1216	1194	0	1211	1196	0	1259	1227	3	CNH bend/ NH_2 rock
6	1075	1057	4	1091	1069	2	1086	1066	4	C−N/N−N stretch
7	681	528	226	656	735	257	817	829	267	out-of-plane
8	466	466	15	476	509	17	501	506	6	out-of-plane
9	396	404	0	398	431	3	416	441	1	NCN bend
10				3983	3809	143	3999	3765	100	O−H asym stretch H_2O
11				3835	3587	249	3870	3640	35	O−H sym stretch H_2O
12				1652	1582	116	1625	1587	111	H_2O bend
13				470	731	189	377	548	38	
14				249	407	70	274	585	246	
15				131	124	4	206	445	128	
16				68	420	145	196	238	14	
17				33	207	4	89	408	31	
18				27	114	14	34	150	18	

the more stable complex (H_2O hydrogen bonding with one of the N−H bonds) displays merely a slight red shift of the C≡N stretch (~6 cm^{-1}), while complexation with H_2O at the C≡N side of the cyanamide leads to the blue shift of this frequency. However, the calculations involve only one H_2O molecule, whereas the measurements were of nitriles surrounded by H_2O, which may be the reason for this discrepancy. Hydrogen bonding with the C≡N group (complex (a), $H_2N{-}C{\equiv}N{\cdots}H_2O$) causes its strengthening rather than weakening, and therefore the blue shift of the C≡N stretch. This effect is opposite to the more common hydrogen-bonding effects on single O−H and N−H bonds, found previously in amino acid−water complexes.[5] Such effects are present in cyanamide−water complexes as well. The $N{-}H{\cdots}OH_2$ hydrogen bonding in complex (b) leads to a large red shift of the N−H stretch (more than 100 cm^{-1}), and its intensity is increased significantly (from 55 to 433 km/mol). The O−H stretch of water elongated by hydrogen bonding in complex (a) also shifts to the red by about 100 cm^{-1}, and its intensity increases 50 times. It should be noted that intensities of all water vibrations in both complexes increase significantly compared to those of the isolated water molecule.

(b) Acetonitrile ($CH_3{-}C{\equiv}N$) and Its Complexes with Water. Acetonitrile is one of the most common and well-studied nitriles. Equilibrium geometries of acetonitrile and its complexes with one water molecule are shown in Figure 2. In the lowest energy complex (a), the water molecule is bound to the C≡N end of the nitrile molecule through a hydrogen bond formed by one of the O−H bonds of the water molecule and the terminal nitrogen of acetonitrile. The effects of this complexation on the geometrical parameters of acetonitrile are very minimal (e.g. it leads to the shortening of the C≡N and C−C bonds by only about 0.001 Å). The effect on the O−H bond of the water molecule is larger (elongation by 0.005 Å). The hydrogen bond is slightly longer than in the case of a similar complex with cyanamide (~2.14 Å vs ~2.11 Å), and the elongation of the water O−H bond is also slightly less significant, which shows that the hydrogen bond with water is somewhat weaker in the case of acetonitrile than in the case of cyanamide. The second complex (b) has two very weak hydrogen bonds (see Figure 2), and its geometrical parameters are also very similar to those of the isolated molecules. The calculated binding energies of the two complexes are 5.05 and 4.88 kcal/mol, which reduce to 3.76 and 3.62 kcal/mol when zero-point energy corrections are added (Table 1). Such relatively small binding energies also support the conclusion of weaker hydrogen bonds formed by acetonitrile with water as compared to cyanamide−water complexes.

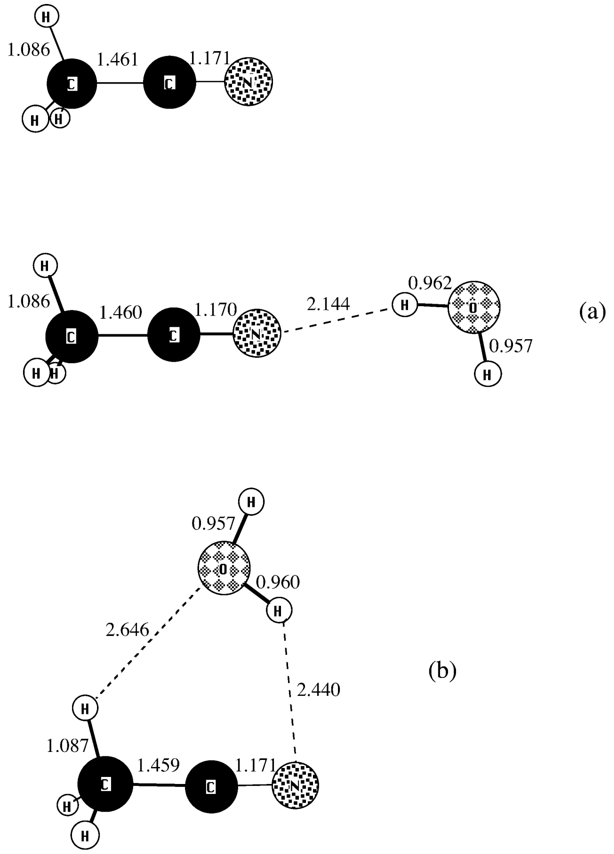

Figure 2. MP2/TZP geometrical structures of acetonitrile and its complexes with water (bond lengths are in Å).

The calculated vibrational frequencies (both harmonic and anharmonic) and infrared intensities of acetonitrile and its complexes with water are presented in Table 3. It can be seen from the table that the harmonic and anharmonic (CC-VSCF) values of the C≡N stretching frequency in the uncomplexed acetonitrile are 2224 and 2177 cm^{-1}, respectively. This is again somewhat lower than experimentally observed values: 2251 cm^{-1} in the crystalline phase[1], 2258 cm^{-1} in Ar matrix,[2] and 2267 cm^{-1} in the gas phase.[18] As in the case of $H_2N{-}C{\equiv}N{\cdots}H_2O$, this frequency shifts to the blue by about 15−20 cm^{-1}

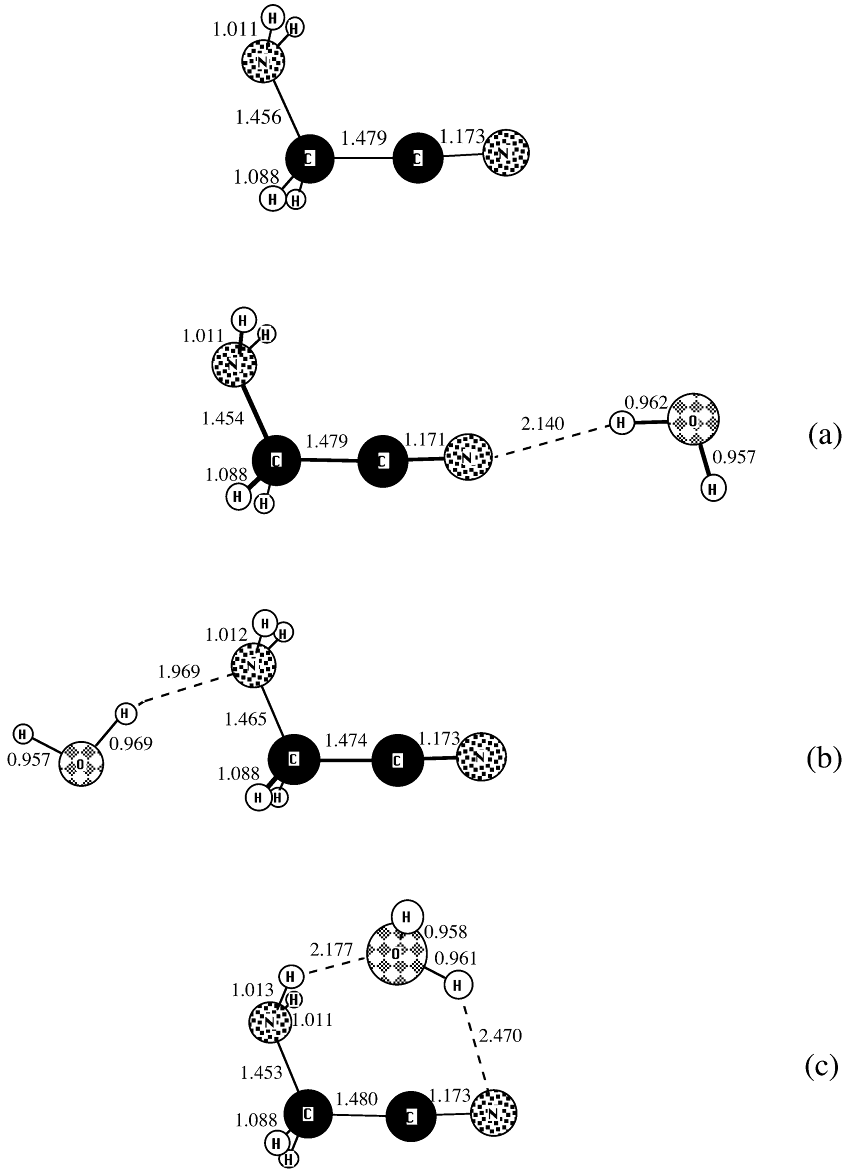

Figure 3. MP2/TZP geometrical structures of aminoacetonitrile and its complexes with water (bond lengths are in Å).

TABLE 3: Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of Acetonitrile and Its Complexes with Water

	$CH_3-C\equiv N$			$CH_3-C\equiv N\cdots H_2O$ (a)			$CH_3-C\equiv N\cdots H_2O$ (b)			
mode	harm	cc-vscf	intens	harm	cc-vscf	intens	harm	cc-vscf	intens	description
1	3215	3016	4	3218	3041	2	3221	2993	1	C−H asym stretch
2	3215	2986	4	3218	3014	2	3216	2953	4	C−H asym stretch
3	3120	2952	6	3121	2956	3	3120	2952	6	C−H sym stretch
4	2224	2177	17	2236	2200	32	2223	2192	28	C≡N stretch
5	1519	1474	12	1517	1473	13	1522	1540	13	CH_2 bend
6	1519	1474	12	1517	1473	13	1515	1535	10	CH_2 bend
7	1445	1420	0.6	1445	1424	0.5	1439	1416	1	CH_3 umbrella
8	1080	1067	0.7	1080	1069	1	1082	1101	3	CCH bend
9	1080	1066	0.7	1080	1069	1	1082	1099	1	CCH bend
10	935	919	8	938	921	12	935	918	9	C−N stretch
11	354	360	0.5	362	384	3	366	395	0	NCCH tors
12	354	358	0.5	357	383	3	357	388	7	NCCH tors
13				3985	3763	139	3996	3797	99	O−H asym stretch H_2O
14				3843	3617	223	3857	3675	24	O−H sym stretch H_2O
15				1650	1607	122	1612	1564	131	H_2O bend
16				447	679	192	300	654	150	
17				239	458	91	246	492	143	
18				126	197	35	122	138	2	
19				33	117	5	93	574	161	
20				33	117	2	69	124	30	
21				8	67	56	66	298	1	

TABLE 4: Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of Aminoacetonitrile and Its Complexes with Water

	$H_2N-CH_2-C\equiv N$		complex (a)		complex (b)		complex (c)		
mode	freq	intens	freq	intens	freq	intens	freq	intens	description
1	3676	8	3679	10	3654	13	3663	36	N−H asym stretch
2	3573	3	3576	4	3557	10	3560	40	N−H sym stretch
3	3186	7	3187	5	3197	2	3185	8	C−H asym stretch
4	3132	14	3133	12	3144	5	3131	16	C−H sym stretch
5	2194	7	2206	17	2198	7	2189	15	$C\equiv N$ stretch
6	1694	37	1695	38	1686	38	1704	31	NH_2 bend
7	1506	8	1503	8	1504	11	1501	8	CH_2 bend
8	1411	0	1411	0	1412	0	1424	2	
9	1398	17	1398	18	1404	17	1393	16	
10	1209	0	1211	0	1202	0	1226	3	
11	1135	16	1137	15	1127	21	1149	23	$C(H_2)-N(H_2)$ stretch
12	950	178	940	191	997	203	972	218	C−C stretch
13	911	0	911	0	916	5	916	7	
14	853	63	851	65	886	25	872	20	
15	563	13	567	13	569	8	574	10	
16	379	18	382	44	376	1	329	87	
17	265	52	268	36	278	13	309	123	
18	208	15	205	10	248	16	220	25	
19			3986	146	3969	100	3991	108	O−H asym stretch H_2O
20			3842	248	3689	439	3850	27	O−H sym stretch H_2O
21			1647	114	1640	104	1619	136	H_2O bend
22			436	188	710	148	432	67	
23			244	108	429	189	267	67	
24			122	3	159	7	161	149	
25			33	56	80	112	146	17	
26			24	5	68	10	106	7	
27			24	37	16	51	56	13	

upon complexation with water. The rest of the calculated fundamental frequencies of acetonitrile (anharmonic values) are in very good agreement with the gas-phase data[18] (with the average error of only 16 cm^{-1}), and they do not change significantly upon complexation with one water molecule. Estimation of overtone and 1−1 combination excitations shows no bands with large infrared intensities. Combination of acetonitrile modes 7 and 10, which has the closest calculated position to the region of the $C\equiv N$ fundamental (2338 cm^{-1}), is found to have an intensity of only 0.59 km/mol (which is much smaller than that of the fundamental $C\equiv N$ stretch: 17 km/mol). Therefore, our conclusion is that the second band observed for acetonitrile at 2298 cm^{-1} in matrix experiments[2] is due to matrix effects, rather than due to a combination band.

(c) Aminoacetonitrile ($H_2N-CH_2-C\equiv N$) and Its Complexes with Water. Equilibrium geometries of aminoacetonitrile and its complexes with water are shown in Figure 3. Three complexes are found to be minima on the aminoacetonitrile−water potential energy surface. Complex (a), in which a water molecule is bound through a hydrogen bond with the $C\equiv N$ group, is the least stable conformer with the binding energy of $D_e = 4.94$ kcal/mol ($D_0 = 3.68$ kcal/mol, see Table 1). This complex is similar in structure to complex (a) of acetonitrile−water, where it was the lowest in energy. Due to the presence of the NH_2 group in aminoacetonitrile, the other two conformers, (b) and (c), have lower relative energies. The strength of the hydrogen bond and the binding energy of complex (a) are similar to the corresponding values in the acetonitrile−water complex (a). On the other hand, the binding in complexes (b) and (c) is weaker than that in complex (b) of cyanamide−water. Complexation with water at the $C\equiv N$ end, again, leads to a slight strengthening of the $C\equiv N$ triple bond. Other significant effects of complexation with water present in complex (b) are elongation of the single C−N bond by almost 0.01 Å and shortening of the C−C bond by 0.005 Å.

Harmonic vibrational frequencies of isolated aminoacetonitrile and its three complexes with water are listed in Table 4, while anharmonic (CC-VSCF) frequencies are given in Table 5. Comparison with experimental (Ar matrix) and theoretical (B3LYP/6-31+G(d)) data for uncomplexed aminoacetonitrile,[3] as well as with its gas-phase experimental measurements,[19] shows good overall agreement between all the methods. The estimated average error between the CC-VSCF anharmonic frequencies and the gas-phase data is about 24 cm^{-1}. As can be seen from Tables 4 and 5, anharmonic corrections are especially important for the highest frequency N−H and C−H stretching vibrations.

It was mentioned in the previous aminoacetonitrile study[3] that several peaks observed experimentally (in the regions between 772 and 721 cm^{-1}, and between 1035 and 895 cm^{-1}) do not correspond to any of the theoretically computed fundamentals and may result from either overtone or combination excitations. First and second overtones, as well as all 1−1 combinations, were estimated in this study at the anharmonic level. However, they were found to have very low intensities. The 1−1 combination of modes 16 and 17, located between 700 and 800 cm^{-1}, and that of modes 14 and 18 in the region of 1000 cm^{-1} have intensities of only 0.20 and 0.23 km/mol and, therefore, are not likely to have been observed.

The calculations show that the fundamental $C\equiv N$ stretch excitation (characteristic for nitrile compounds) has lower intensity for aminoacetonitrile than for the other nitriles studied here (only 7 km/mol compared to 17 and 152 km/mol for acetonitrile and cyanamide, respectively). For this reason, the $C\equiv N$ vibration has not been observed in the matrix experiments.[3] Its calculated position is 2194 (harmonic) and 2144 cm^{-1} (anharmonic), which is lower than that observed for liquid aminoacetonitrile (2236 cm^{-1}).[19] The $C\equiv N$ stretching frequency of aminoacetonitrile shifts to the blue by about 12 cm^{-1} in complex (a). This shift increases to 22 cm^{-1} when anharmonic corrections are taken into account at the CC-VSCF level (Table 5). These values are very similar to the blue shifts observed for the analogous complexes (a) of acetonitrile and cyanamide. Thus, strengthening of the $C\equiv N$ bond and the blue shift of the

TABLE 5: Anharmonic (CC-VSCF) Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of Aminoacetonitrile and Its Complexes with Water

	$H_2N{-}CH_2{-}C{\equiv}N$		complex (a)		complex (b)		complex (c)		
mode	freq	intens	freq	intens	freq	intens	freq	intens	description
1	3416	8	3468	10	3433	12	3420	36	N−H asym stretch
2	3367	4	3394	5	3356	10	3350	39	N−H sym stretch
3	2960	7	3022	5	3015	2	2990	8	C−H asym stretch
4	2951	14	2965	12	2967	4	2949	16	C−H sym stretch
5	2144	7	2166	16	2165	7	2148	15	$C{\equiv}N$ stretch
6	1642	36	1652	38	1653	38	1660	31	NH_2 bend
7	1473	8	1474	8	1490	12	1475	8	CH_2 bend
8	1373	0	1380	0	1385	0	1392	2	
9	1365	17	1365	18	1375	17	1362	16	
10	1190	0	1198	0	1192	0	1207	3	
11	1113	16	1116	15	1111	22	1128	23	$C(H_2){-}N(H_2)$ stretch
12	944	176	935	187	990	198	958	212	C−C stretch
13	909	0	919	0	938	5	925	7	
14	852	60	859	63	885	25	867	20	
15	565	13	569	13	570	8	574	10	
16	418	17	478	43	482	1	425	83	
17	322	45	485	36	514	13	530	118	
18	219	14	413	10	261	15	258	25	
19			3775	160	3754	109	3760	106	O−H asym stretch H_2O
20			3612	206	3497	386	3633	27	O−H sym stretch H_2O
21			1581	111	1551	106	1580	136	H_2O bend
22			948	187	898	144	525	65	
23			640	107	814	187	471	62	
24			126	3	170	7	509	107	
25			231	61	463	117	212	14	
26			118	4	136	10	146	6	
27			175	40	103	51	161	13	

corresponding stretching frequency upon formation of the hydrogen bond between the $C{\equiv}N$ group and a water molecule is found to be a common feature for all nitriles studied here. This is an important feature of nitrile−water complexes that has to be taken into consideration when analyzing data from astronomical observations. In the other two complexes of aminoacetonitrile with water, (b) and (c), the $C{\equiv}N$ stretching frequency is also shifted to the blue (at the anharmonic level), but even less significantly than in complex (a). Additional theoretical studies are required to elucidate the behavior of the aminoacetonitrile $C{\equiv}N$ stretch in the bulk water environment. However, it is clear that the behavior of the $C{\equiv}N$ bond is very different from the trend known for O−H and N−H single bonds (for example, those of amino acids), which are weakened very significantly by complexation with water.

IV. Conclusions

In this study, geometrical structures, binding energies, and harmonic and anharmonic vibrational spectra are calculated for several nitrile molecules (cyanamide, acetonitrile, and aminoacetonitrile) and their complexes with one water molecule. Two isomers are found on the potential energy surfaces of both cyanamide−water and acetonitrile−water complexes, and three isomers are found to exist for aminoacetonitrile−water. The geometries and binding energies of these complexes are estimated at the MP2/TZP ab initio level, and their differences and similarities are discussed. In addition, effects of complexation with water on geometries and vibrational spectra of nitriles are investigated. Calculated MP2/TZP potentials are combined with the correlation-corrected Vibrational Self-Consistent Field (CC-VSCF) method to obtain anharmonic vibrational spectra. The main spectroscopic feature that results from the complexation of nitriles with water is the blue shift of the $C{\equiv}N$ stretch. This is very different from the effects of the hydrogen bonding found earlier for amino acids where complexation with water caused very significant red shifts of the carboxyl group (O−H and C═O) stretching frequencies. The effects of the complexation with water found in this study should be helpful in assigning experimentally observed bands to nitrile−water fragments.

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