SHORT COMMUNICATION

Croat. Chem. Acta 2017, *90*(*1*), 99–105

DOI: 10.5562/cca3077

Computational Study of the Electron Spectra of Acetamide and *N*-methylformamide

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RECEIVED: January 7, 2017 ✶ REVISED: May 21, 2017 ✶ ACCEPTED: May 22, 2017

THIS PAPER IS DEDICATED TO PROFESSOR LEO KLASINC ON THE OCCASION OF HIS 80TH BIRTHDAY

Abstract: The molecular structures of the three conformers of acetamide are first studied by *ab initio* method of CCSD/cc-pVTZ. Using the optimized geometry of each species, we apply established and/or developing methods to compute several physical properties of acetamide and compare them with available experimental data. The properties include dipole moments, polarizabilities, ionization energies of both valence and core electrons, and absorption spectra of both valence and core electrons. Similar results for *N*-methylformamide are included for comparison.

Keywords: acetamide, *N*-methylformamide, structure, electron spectra.

INTRODUCTION

COMPARISON of the performance of various levels of theory and different basis sets on molecular structure and energies has been reported in several papers. For example, Helgaker *et al.*[1] compared the prediction of bond lengths of 28 small molecules by *ab initio* methods, from Hartree-Fock to coupled cluster singles and doubles (**CCSD**)[2] plus perturbative triples correction (**T**), with large basis sets up to cc-pVQZ; while Bak *et al.*[3] used similar methods with even larger basis set CCSD(T)/cc-pCVQZ on the equilibrium structures (bond lengths and bond angles) of 19 small molecules. For many molecules, the levels of theory such as CCSD(T)/cc-pVQZ will be too demanding computationally. On the other hand, use of small basis sets instead may be inadequate. In the present study, the level of theory CCSD/cc-PVTZ is chosen for the determination of the molecular structure.

Acetamide is an interesting molecule for several reasons. First, it is one of the best models of the peptide bond; secondly, there is the question of whether or not the arrangement of the bonds around the nitrogen atom is planar or pyramidal, the question being common to other nitrogen-containing molecules such as amines, amides, and nitro molecules;[4] thirdly, pyramidization aside, there is the question of the planarity of the heavy atom framework C(CO)N;[5] furthermore, the rotation of the methyl group leads to three conformers;[4] and finally the low methyl rotation barrier leads to an ambiguity of nonplanar equilibrium structures versus an effective planar ground state.[6] Demaison *et al.*[6] made an extensive study of the planarity of the CONH linkage in formamide, cyanamide, acetamide, urea, carbamic acid, methylamine, dimethyl ether, and methyl carbamate. They concluded that the CONH linkage is quite complex. Because of the exceedingly low barriers of the internal rotation of the methyl group, the ground state may be considered planar, in spite of the nonplanar equilibrium structure. Ilyushin *et al.*[7] studied the complicated procedure of the labelling problem in the analysis of their Fourier transform microwave spectrum of acetamide. With the focus of this investigation on the electron spectra of acetamide, we make a simplifying assumption that the electron spectra of acetamide can be approximated by the average of those of the three conformers.

N-methylformamide is an isomer of acetamide and similar results for methylformamide are included for comparison.

In any case, we apply established methods to predict the ionization and excitation spectra of both valence and core electrons using the geometry optimized by CCSD/cc-pVTZ method. The computational predictions agree very well with the rather limited experimental results of the ionization energies, available for outer valence electrons only, and suggest similar reliability of other computational results also. We therefore urge experimentalists to measure (a) ionization energies in the inner valence region. (b) core-electron binding energies, (c) valence shell electron energy loss spectra, and (d) X-ray absorption spectra, of both these interesting molecules acetamide and *N*-methylformamide.

COMPUTATION DETAILS

In this study, we use two computer program packages: Gaussian09[8] and ADF13.[9] No new methods are used in this work. As mentioned in the introduction, the method of geometry used is CCSD/cc-pVTZ, available in the Gaussian09 program. The Gaussian basis set cc-pVTZ is abbreviated as Basis C in this work. For dipole moments and static polarizabilities, we prefer the exchange-correlation potential V_{xc} known as statistical averaging of orbital potentials (SAOP)[10–12] available in the ADF package, in the belief that use of V_{xc} = SAOP will lead to better description of the electron density. In the ADF package, there is an efficient basis set of even-tempered Slater-type orbital called et-pVQZ,[13] which is abbreviated at Basis Q. Therefore, the dipole moment and static polarizabilities are calculated by the method of SAOP/Basis Q//CCSD/Basis C.

For vertical ionization energies (VIEs) of valence electrons, also known as vertical ionization potentials (VIPs), we use the method ΔPBE0(SAOP)/et-pVQZ, which was developed in 2009[14] and has been applied to many molecules. The abbreviation means the total energy difference between the neutral parent molecule and the valence-hole cation calculated with the parameter-free Perdew-Burke-Ernzerhof (PBE0) exchange-correlation functional[15,16] for the electron density obtained with V_{xc} = SAOP. For core-electron binding energies (CEBEs) of *C* to *F*, we recommend the method developed much earlier in 1999,[17] namely ΔPW86x-PW91c+C_{rel}, which stands for the total energy difference calculated with the combination of Perdew-Wang 1986 exchange functional[18] and Perdew-Wang 1991 correlation functional.[19] A small relativistic correction C_{rel} derived empirically in 1995[20] is added. The correction C_{rel} is in the form of:

$$C_{rel} = K \cdot X_{nr}^{N}$$

where $K = 0.2198 \times 10^{-6}$ and $N = 2.178$ when the nonrelativistic value X_{nr} and the correction C_{rel} are both in units of eV. This method for CEBEs of organic and other small molecules have been tested on many systems.[21,22]

For excitation of valence electrons, the procedure of time-dependent density functional theory (TDDFT) using V_{xc} = SAOP has been tested in many molecules. The TDDFT procedure produces excited singlet states with oscillator strengths as well as triplet states. The procedure for core electron excitations is more complicated. Blind application of TDDFT(SAOP) would be met with disaster because we would need to perform a configuration interaction (CI) calculation with a very large number of singly excited configurations. Stener *et al.*[23] proposed a shortcut by allowing only excitations from the core orbitals for the TDDFT calculation. Such a "reduced window" approximation is somewhat analogous to the usual separation of rotations and vibrations. We have gained some experience with this shortcut. Although such a shortcut greatly reduces the size of the CI calculation, such an approximation leads to two disadvantages: (a) The excitation energies are too low by tens of electron volts, and (b) the intensities are only qualitatively correct. To overcome (a), we can shift the entire X-ray absorption spectra (XAS) by a value determined from the difference between one of the TDDFT triplet energies and the one calculated by the method of ΔPW86-PW91+C_{rel}. The state for the evaluation of this shift is chosen to be the triplet state which corresponds to the singlet with the most intensity. Because of (b), we must realize that XAS spectra computed by convolution of the calculated energies and intensities would also be unreliable.

Finally, the energies of non-resonant X-ray emission spectra (XES) are simply the differences between VIEs of valence and core orbitals, while the energies of resonant XES are the differences between valence and core excitation energies. The intensities of XES are more complicated and are outside the scope of the present study.

RESULTS AND DISCUSSION

Following Samdal,[4] we call the three conformers of acetamide by the names syn, anti, and perp. In Table 1, we summarize the energies, rotational parameters, dipole moment, and static polarizabities of the three conformers. The three conformers have very similar energies (with perp being the lowest). It is therefore quite likely that the Boltzmann distribution is not far from 1/3 for each conformer and so our simplifying assumption would not be far wrong. Our average A and C rotational parameters are close to those of Samdal's calculation, while the B parameter is close to the observed value. Corresponding results on *N*-methylformamide included for comparison are very similar to those for acetamide.

Table 1. Calculated energies (in hartrees), rotational parameters (in MHz), dipole moments (in debyes), and static polarizabilities (in au) of the three conformers of acetamide(g) and *N*-methylformamide

	Acetamide							*N*-methylformamide
	syn	anti	perp	Average	Observed	MP2(c)	B3LYP(c)	
CCSD + 208	–0.856707	–0.856650	–0.856846					–0.839698
CCSD(T) + 208	–0.889818	–0.889819	–0.890009					–0.873144
A	10840	10902	10842	10861	10173(a)	10860	10872	19545
B	9379	9330	9359	9356	9342(a)	9457	9281	6343
C	5191	5188	5191	5190	5144(a)	5218	5167	4935
μ, debyes	4.163	4.152	4.088	4.134	3.68±0.03(b)	4.20	3.82	4.268
α_{ave}, au	38.39	38.54	38.57	38.50				38.61
$\Delta\alpha$, au	13.95	14.27	13.95	14.06				17.95

(a) Average experimental values of Kojima,[24] Suenram,[25] Yamaguchi,[26] and Iayushin.[7]

(b) From Stark effect.[24]

(c) Samdal[4] with cc-pVTZ basis.

Table 2. Bond lengths (in Angstroms) of acetamide and *N*-methylformamide

	Method	Ref.	conformer	CC	CN	CO	NH_c	NH_t	CH	CH	CH
Expt	Electron	[27]		1.53	1.36	1.21	(1.02)	(1.02)	(1.09)	(1.09)	(1.09)
	diffraction	**[28]**		**1.519**	**1.380**	**1.220**	**1.022**	**1.022**	**1.124**	**1.124**	**1.124**
Calc	MP2/6-31+G**	[5]		1.511	1.371	1.232	1.007	1.005	1.085	1.088	1.089
	Pulay force field	[29]		1.5182	1.3633	1.2187	0.9918	0.9943	1.0830	1.0771	1.0771
	MP2/6-31+G**	[30]	syn	1.5137	1.3693	1.2334	1.0070	1.0046	1.0901	1.0851	1.0851
	MP2/cc-pVTZ	[4]	perp	1.5040	1.3597	1.2163	1.0021	0.9991	1.0812	1.0840	1.0856
			anti	1.5046	1.3579	1.2164	1.0022	0.9984	1.0835	1.0835	1.0835
	MP2/pVQZ+corr	[6]	perp	1.509	1.362	1.216	1.003	1.000	1.082	1.085	1.086
	CCSD/cc-pVTZ	This	syn	1.5139	1.3640	1.2126	1.0018	0.9995	1.0832	1.0902	1.0902
		work	anti	1.5141	1.3619	1.2131	1.0022	0.9989	1.0884	1.0881	1.0881
			perp	1.5133	1.3688	1.2118	1.0033	1.0011	1.0853	1.0892	1.0908
			average	1.5138	1.3649	1.2125	1.0025	0.9998	1.0856	1.0892	1.0897
NMF(a)	CCSD/cc-pVTZ	This			1.4502	1.2118		1.0008	1.0870	1.0890	1.0998
		work			1.3522						

(a) *N*-methylformamide.

The bond lengths from our CCSD/cc-pVTZ computations are compared with previous calculations and experimental values in Table 2. It can be seen that our CCSD/cc-pVTZ procedure underestimates all bond lengths of acetamide.

The results of our computation of vertical ionization energies are compared with experiment in Tables 3 and 4.

Table 3. Vertical ionization energies (in eV) of acetamide

Experiment					This work					
Meeks 1975[31]	McGlynn 1975[32]	Asbrink 1981[33]	Kishimoto 2001[34]	best estimate	MO	syn	anti	perp(a)	average	ave - best
9.95	9.95	10.0	9.86	**9.92**	13a’	9.85	9.85	9.91	**9.87**	–0.05
10.34	10.34	10.4	10.32	**10.33**	3a”	10.38	10.37	10.47	**10.41**	0.08
12.98	12.98	13.0	13.01	**12.99**	2a”	12.94	12.90	12.94	**12.93**	–0.06
		14.1	14.08	**14.08**	12a’	13.82	13.32	14.06	**13.73**	–0.35
14.12	14.12	≈14.5	14.43	**14.22**	11a’	14.05	14.04	14.08	**14.06**	–0.16
15.4	15.42	15.4	15.39	**15.41**	1a”	15.20	15.14	15.21	**15.18**	–0.23
16.0	16.02	16.0	16.13	**16.08**	10a’	15.65	15.69	15.69	**15.68**	–0.40
18.0	17.96	18.0	18.09	**18.03**	9a’	18.11	18.15	18.04	**18.10**	0.07
19.3	19.46	19.4	19.34	**19.40**	8a’	19.26	19.30	19.18	**19.25**	–0.15
		23.9			7a’	23.60	23.59	23.61	**23.60**	
					6a’	28.34	28.36	28.36	**28.35**	
					5a’	31.95	31.92	32.00	**31.96**	
					4a’ (C^*H_3)	291.21	291.22	291.23	**291.21**	
					3a’ ($C^*=O$)	293.88	293.87	293.90	**293.88**	
					2a’ (N1s)	406.21	406.25	406.23	**406.23**	
					1a’ (O1s)	537.20	537.14	537.25	**537.20**	
							Mean absolute deviation			0.17

(a) For MOs 16a to 5a.

Table 4. Vertical ionization energies (in eV) of *N*-methylformamide

Experiment				This work		
Brundle 1969[35]	Keller 1986[36]	Li 2016[37]	best estimate	MO	DFT	DFT - best
9.87 π	10.1 π	≈9.86	**9.87**	3a″	9.96	0.09
10.05	10.1	≈10.06	**10.05**	13a′	10.03	−0.02
13.2	13.3 π	≈13.71	**13.2_5**	2a″	13.18	-0.0_7
	14.1	≈14.16	**14.1**	12a′	13.76	-0.3_4
14.3	14.5		**14.4**	11a′	14.30	−0.1
15.7	15.6		**15.6_5**	10a′	15.34	-0.3_1
15.7	15.6 π		**15.6_5**	1a″	15.41	-0.2_4
18.3	18.13		**18.13**	9a′	18.03	−0.10
≈20				8a′	1943	
				7a′	22.88	
				6a′	28.75	
				5a′	31.94	
				4a′ (C*H$_3$)	291.22	
				3a′ (C*=O)	293.59	
				2a' (N1s)	406.33	
				1a' (O1s)	537.29	
				Mean absolute deviation		0.1_6

The mean absolute deviation (MAD) is 0.17 eV for acetamide (that for the perp conformer is marginally smaller at 0.13 eV) and 0.1_6 eV for *N*-methylformamide. We could not find experimental values for the inner valence or core region. It would be interesting to find out how reliable our DFT procedures are for those vertical ionization energies.

Acetamide and *N*-methylformamide involve methyl substitution of different hydrogen atoms of formamide. All three molecules have the O=C−N linkage. The calculated CEBEs of the carbonyl carbon are: 294.19,[38] 293.88, and 293.59 eV for formamide, acetamide, and *N*-methylformamide, respectively. The values indicate the electron-donating effect of methyl leading to a lowering of the CEBE of carbonyl carbon by 0.3 eV. Similarly, the CEBEs of N1s are 406.55,[38] 406.23, and 406.33 eV for formamide, acetamide, and *N*-methylformamide, respectively, providing a lowering of 0.2 eV for the electron donating effect of methyl substitution on the CEBE of N. The effects are quite small compared to the much larger increase of the CEBEs of O, which are 517.78,[38] 537.20 and 537.29 eV, respectively, due to effects other than simple potential from inductive charges.

The excitations of valence electrons are presented in Tables 5 and 6. Excitations of valence electrons to lower excited states have very low oscillator strengths. The observable excitations occur in the vacuum ultraviolet region. In any case, the TDDFT(SAOP) procedure gives very

Table 5. Excited states (singlet absorption maxima in nm and triplet energies in eV) of the conformers of acetamide calculated by TDDFT(SAOP)/Basis Q//CCSD/Basis C

	Excited state	syn	anti	perp[a]	Average (sum)	Obs[b]	CASPT2[c]	MRCI[d]
Singlets	1 A″	212 (0.001)	211 (0.000)	214 (0.001)	212 (0.002)		1 A″ 224 (0.002)	1 A″ 209
	2 A′	201 (0.026)	202 (0.026)	200 (0.026)	201 (0.078)		2 A″ 194 (0.022)	2 A″ 206
	2 A″	181 (0.009)	181 (0.010)	178 (0.012)	180 (0.031)		2 A′ 194 (0.018)	2 A′ 197
	3 A′	173 (0.021)	172 (0.012)	173 (0.019)	173 (0.052)		3 A″ 177 (0.001)	3 A′ 177
	4 A′	164 (0.146)	165 (0.024)	163 (0.114)	164 (0.284)	166	3 A′ 174 (0.060)	3 A″ 174
	5 A′	161 (0.047)	161 (0.181)	161 (0.076)	161 (0.304)		4 A′ 172 (0.292)	4 A′ 171
	3 A″	158 (0.006)	157 (0.005)	156 (0.008)	157 (0.019)	158	5 A′ 169 (0.013)	5 A′ 170
	4 A″	154 (0.003)	152 (0.000)	153 (0.012)	153 (0.015)	155	6 A′ 168 (0.009)	4 A″ 169
	6 A′	151 (0.004)	151 (0.047)	150 (0.009)	151 (0.060)		4 A″ 165 (0.000)	5 A″ 168
	5 A″	149 (0.000)	151 (0.011)	148 (0.025)	149 (0.036)		5 A″ 160 (0.004)	6 A′ 151
	7 A′	148 (0.035)	144 (0.039)	148 (0.009)	147 (0.083)		7 A′ 155 (0.000)	
Triplets	1 A″	5.42	5.49	5.38	5.43		5.24	
	1 A′	5.84	5.88	5.85	5,86		5.57	
	2 A′	6.11	6.08	6.12	6.10		6.37	
	2 A″	6.69	6.68	6.78	6.72		6.21	

[a] The states are 2 A to 12 A for singlets and 1 A to 4 A for triplets.

[b] Kaya 1967.[39]

[c] Serrano-Andres 1996[40] for the syn conformer.

[d] Hirst 1997[30] for the syn conformer.

Table 6. Excited states (singlet absorption maxima in nm and triplet energies in eV) of *N*-methylformamide calculated by TDDFT(SAOP)/Basis Q//CCSD/Basis C

	Excited state	TDDFT	Obs(a)	CASPT2(b)	MRCI(c)
Singlets	1 A″	210 (0.002)			1 A″ 215
				1 A″ 225 (0.002)	
	2 A′	194 (0.018)		2 A' 204 (0.007)	2 A″ 209
	2 A″	188 (0.001)	(190)(d)	2 A" 190 (0.003)	2 A′ 195
	3 A′	176 (0.246)	178	3 A′ 185 (0.315)	3 A″ 182
	3 A″	169 (0.023)	172	3 A″ 175 (0.007)	3 A′ 179
	4 A′	169 (0.190)	168	4 A″ 174 (0.001)	4 A″ 177
	5 A′	161 (0.052)	164	4 A′ 174 (0.025)	4 A′ 173
	4 A″	155 (0.004)		5 A′ 170 (0.017)	5 A′ 171
	6 A′	153 (0.057)		5 A″ 168 (0.008)	5 A″ 169
	5 A″	152 (0.003)		6 A′ 168 (0.009)	6 A′ 161
Triplets	1 A″	5.44		6.98	
	1 A′	5.44		6.96	
	2 A′	6.27		7.34	
	2 A″	6.49		6.29	

(a) Kaya 1967.[39]

(b) Serrano-Andres 1996.[40]

(c) Hirst 1997.[30]

(d) Absorption maximum in cyclohexane solution reported by Nielsen 1997.[41]

nice prediction of the UV absorption spectrum, as shown in Tables 5 and 6. The low excitations to triplet states are included in Tables 5 and 6, for the benefit of workers measuring valence shell electron loss spectra.

Finally, the prediction of X-ray absorption spectra, as shown in the last two columns in Tables 7 and 8, is more complicated. The shift must be added to the TDDFT results obtained by the reduced window approximation. For example, the triplet excitation energy of O1s to 4a″ for the syn conformer of acetamide is 508.33 eV by TDDFT with reduces energy window and 531.67 eV by ΔPW86-PW91 (both before approximate relativistic correction C_{rel} is

Table 7. X-ray absorption spectra of acetamide calculated by TDDFT(SAOP) with reduced energy window and shifts needed based on Δ(PW86PW91). Absorption energies are given in eV and *f*-values, in parentheses

			syn	anti	perp	Average (sum)(a)	Shifted	Rel. intensity
CK	A″	4a′ to 4a″	268.77 (0.0002)	268.83 (0.0001)	268.72 (0.0001)	268.77 (0.0004)	284.88	0.004
	A′	4a′ to 14a′	269.39 (0.0006)	269.39 (0.0009)	269.40 (0.0006)	269.39 (0.0020)	285.50	0.022
	A′	4a′ to 15a′	270.45 (0.0031)	270.51 (0.0033)	270.49 (0.0031)	270.48 (0.0095)	286.59	0.102
	A′	4a′ to 16a′	270.85 (0.0013)	270.73 (0.0047)	270.85 (0.0020)	270.81 (0.0080)	286.92	0.086
	A′	4a′ to 17a′	271.36 (0.0006)	271.38 (0.0023)	271.28 (0.0075)	271.34 (0.0104)	287.49	0.112
	A″	4a′ to 5a″	271.28 (0.0080)	271.43 (0.0054)	271.41 (0.0002)	271.37 (0.0136)	287.53	0.146
	A″	3a′ to 4a″	271.61 (0.0439)	271.66 (0.0451)	271.55 (0.0039)	271.61 (0.0929)	287.63	(1)
		shift	16.13	16.25	15.81	16.06		
NK	A″	2a′ to 4a″	380.60 (0.0073)	380.74 (0.0093)	380.57 (0.0072)	380.64 (0.0238)	401.95	0.98
	A′	2a′ to 14a′	381.22 (0.0017)	381.22 (0.0020)	381.24 (0.0020)	381.23 (0.0057)	402.54	0.23
	A′	2a′ to 15a′	382.19 (0.0033)	382.29 (0.0033)	382.23 (0.0034)	382.24 (0.0100)	403.55	0.41
	A′	2a′ to 16a′	382.67 (0.0089)	382.55 (0.0070)	382.67 (0.0085)	382.63 (0.0244)	403.94	(1)
	A″	2a′ to 5a″	382.99 (0.0036)	383.19 (0.0025)	383.00 (0.0033)	383.06 (0.0104)	404.37	0.43
	A′	2a′ to 17a′	383.10 (0.0001)	383.18 (0.0021)	383.29 (0.0021)	383.19 (0.0043)	404.50	0.18
		shift	21.54	21.42	20.67	21.21		
OK	A″	1a′ to 4a″	508.80 (0.0206)	508.76 (0.0184)	508.76 (0.0194)	508.77 (0.0584)	532.32	(1)
	A′	1a′ to 14a′	509.05 (0.0003)	508.97 (0.0003)	509.09 (0.0012)	509.04 (0.0018)	532.59	0.031
	A′	1a′ to 15a′	510.08 (0.0014)	510.07 (0.0012)	510.13 (0.0013)	510.09 (0.0039)	533.64	0.067
	A′	1a′ to 16a′	510.56 (0.0004)	510.33 (0.0006)	510.57 (0.0006)	510.49 (0.0016)	534.04	0.027
	A′	1a′ to 17a′	511.12 (0.0001)	511.04 (0.0002)	510.98 (0.0014)	511.05 (0.0017)	534.60	0.029
	A″	1a′ to 5a″	510.96 (0.0027)	511.06 (0.0017)	511.21 (0.0001)	511.08 (0.0045)	534.63	0.077
		shift	23.33	23.41	23.34	23.36		

(a) Average of XAS energies (sum of *f*-values), including approximate relativistic corrections of 0.05, 0.10, and 0.19 eV for excitations form C1s, N1s, and O1s, respectively.

Table 8. X-ray absorption spectra of *N*-methylformamide calculated by TDDFT(SAOP) with reduced energy window and shifts needed based on Δ(PW86PW91). Absorption energies are given in eV and *f*-values, in parentheses

			ΔE (*f*-value)	Shifted[a] (rel int)
CK	1 A″	4a′ to 4a″	269.47 (0.000)	287.39 (0.001)
	2 A′	4a′ to 14a′	270.21 (0.002)	288.13 (0.059)
	3 A′	4a′ to 15a′	271.09 (0.001)	289.01 (0.021)
	2 A″	3a′ to 4a″	271.27 (0.039)	289.19 (1)
	4 A′	4a′ to 16a′	271.59 (0.002)	289.51 (0.060)
	5 A′	3a' to 14a'	271.62 (0.001)	289.54 (0.038)
	5 A′	4a′ to 17a′	271.88 (0.006)	289.80 (0.162)
	3 A″	4a′ to 5a″	271.98 (0.004)	289.90 (0.106)
		shift	17.87	
NK	A″	2a′ to 4a″	380.90 (0.012)	402.13 (1)
	A′	2a′ to 14a′	381.59 (0.005)	402.82 (0.383)
	A′	2a′ to 15a′	382.20 (0.002)	403.43 (0.179)
	A′	2a′ to 16a′	382.92 (0.000)	404.15 (0.017)
	A′	2a′ to 17a′	383.20 (0.001)	404.43 (0.059)
	A″	2a′ to 5a″	383.23 (0.000)	404.46 (0.037)
		shift	21.13	
OK	A″	1a′ to 4a″	508.87 (0.022)	538.36 (1)
	A′	1a′ to 14a′	509.27 (0.001)	538.76 (0.006)
	A′	1a′ to 15a′	509.96 (0.000)	539.45 (0.001)
	A′	1a′ to 16a′	510.64 (0.000)	540.13 (0.017)
	A″	1a′ to 5a″	511.03 (0.000)	540.52 (0.000)
	A″	1a′ to 6a″	511.81 (0.000)	540.5 2 (0.012)
		shift	29.29	

[a] Including approximate relativistic corrections of 0.05, 0.10, and 0.20 eV for excitations form C1s, N1s, and O1s, respectively.

added), leading to a shift of 23.33 eV. The predicted XAS for O1s and N1s shows a typical pattern, with a relatively intense excitation to the lowest unoccupied orbital, followed by less intense peaks. In contrast, the predicted XAS for C1s excitations is unexpected, with the most intense excitation given by C1s of the carbonyl carbon to 4a”.

SUMMARY

In the study, we propose a simplifying assumption that the properties of acetamide can be approximated by the average of the three conformers. The focus of this work is on the electron spectra of acetamide, including the ionization and excitation spectra of both the valence and core electrons. Results for *N*-methylformamide are included for comparison. It is amazing how much alike the spectra of the two isomers are. The computational predictions agree well with the rather limited experimental results of the ionization energies, available for outer valence electrons only. We urge experimentalists to measure the other types of electron spectra, including the energies of excited triplet states by electron energy loss spectroscopy, of both interesting molecules acetamide and *N*-methylformamide.

Acknowledgment. The author is grateful for the support of Scientific Computing & Modeling, and to the reviewers for valuable suggestions. He also appreciates the vast contributions of Professor Leo Klasinc in the field of photoelectron spectroscopy and is grateful for the opportunity to celebrate his 80th birthday with this paper.

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