Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

Density functional theory study of the electron spectra of formamide vapor

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ARTICLE INFO

ABSTRACT

The ionization and excitation spectra of the valence and core electrons of formamide in the gas phase are studied with density functional theory. The calculated ionization energies of both valence and core electrons agree very well with experiment, with an average absolute deviation of only 0.1 eV from experiment for all twelve MOs, and confirm the nonplanarity of formamide. The theoretical valence-electron absorption spectrum also agrees well with experiment. However, the inner-shell excitation spectra are not as well reproduced by the present calculations and require further study.

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1. Introduction

The near planarity of the amine group in molecules such as nitrosamine, aniline, p-nitroaniline, and formamide, due to partial double-bond character, has been of interest to chemists. Many studies and discussions have been simplified by assuming planarity. In this study, we focus our attention on the formamide molecule, which is the simplest model of the peptide bond.

In 1957, Kurland and Wilson (KW57) [1] reported a planar structure for formamide from their microwave spectrum. However, Costain and Dowling (CD60) [2] disagreed and, with convincing experimental evidence, gave a nonplanar structure, which was supported by more microwave spectroscopic studies [3,4]. In spite of that, both Kitano and Kuchitsu (KK74) [5] and Hirota et al. (H+74) [6] assumed planarity and reported different bonding parameters, as shown in Table 1. We note that some bond lengths and bond angles reported by the four groups are outside the uncertainties of one another.

Our recent density functional theory (DFT) studies of electron spectra of s-triazine [7], naphthalene, azulene [8], and p-benzoquinone [9] confirm that the DFT method abbreviated as ΔPBE0(SAOP) provides excellent vertical ionization energies (VIEs) for valence electrons [10]. By ΔPBE0(SAOP), we mean the total energy difference between the valence-hole cation and the neutral parent molecule calculated with the parameter-free Perdew–Burke–Ernzerhof (PBE0) exchange-correlation functional [11–13], using the electron density obtained with the exchange-correlation potential V_{xc} known as statistical average of orbital potentials (SAOP) [14–16]. Because the $V_{xc} = $ SAOP is asymptotically correct, it is our belief that it leads to a reliable description of valence electrons and good distribution of orbital energies for both occupied and vacant MOs. From the excellent results of VIEs, we draw the tentative conclusion that, given the electron density, the exchange-correlation functional $E_{xc} = $ PBE0 can provide excellent energy differences for valence-electron ionization.

For core-electron binding energies (CEBEs), on the other hand, the procedure ΔPW86-PW91+C_{rel}, first developed in 1999 [17,18], gives reliable results. By ΔPW86-PW91+C_{rel}, we mean the energy difference calculated with the combination of Perdew–Wang 1986 exchange functional [19] with Perdew–Wang 1991 correlation functional [20], plus a small relativistic correction C_{rel} in allometric form derived empirically in 1995 [21]: $C_{rel} = K\, X_{nr}^N$, where $K = 0.2198 \times 10^{-6}$, $N = 2.178$, and X_{nr} is the non-relativistic value. Both C_{rel} and X_{nr} are in units of eV. This method has been shown to provide reliable predictions of CEBEs for many organic and other small molecules [22,23].

The purpose of this work is to use ionization energies predicted by DFT to confirm the nonplanarity of formamide.

2. Computational details

All calculations of ionization and excitation energies were performed on a 3.2 GHz single-CPU Pentium4 desktop computer with the Amsterdam Density Functional (ADF) package [24], using an efficient and high-quality basis set of Slater-type orbitals (STOs) called even-tempered polarized valence quadruple-zeta (et-pVQZ) basis set [25] and unrestricted method for the cations.

In short, the DFT protocol we use in this work can be abbreviated as follows:

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Table 1
Bonding parameters of formamide (bond lengths in angstroms and angles in degrees) at six geometries[a].

	Geometry					
	//KW57 Yes[b]	//CD60 No[b]	//KK74 Yes[b]	//H+74 Yes[b]	//B3LYP/6-311+(d,p) ~Yes[b]	//CCSD(T)/6-311+(d,p) No[b]
R(HN)$_{ave}$	0.995 ± 0.007	1.008 ± 0.005	1.027 ± 0.006	1.0016 ± 0.003	1.0079	1.0106
R(NC)	1.343 ± 0.007	1.376 ± 0.010	1.368 ± 0.003	1.352 ± 0.012	1.3609	1.3753
R(CO)	1.243 ± 0.007	1.193 ± 0.020	1.212 ± 0.003	1.219 ± 0.012	1.2117	1.2154
R(CH)	1.094 ± 0.025	1.102 ± 0.010	1.125 ± 0.012	1.098 ± 0.01	1.1060	1.1073
<HNH	118.98 ± 0.50	118.88 ± 0.67	121.6 ± 1.4	121.6 ± 0.3	119.14	117.09
<NCO	123.58 ± 0.35	123.80 ± 0.67	125.0 ± 0.4	124.7 ± 0.3	124.94	124.64
<NCH	103.9 ± 1.2	113.23 ± 0.67	112.7 fix	112.7 ± 2	112.39	112.48

[a] KW57, Kurland and Wilson [1]; CD60, Costain and Dowling [2]; KK74, Kirchhoff and Johnson [3]; H+74, Hirota et al. [6]. See text for details.
[b] Planar.

(1) ΔPBE0(SAOP)/et-pVQZ for valence-electron ionizations, and
(2) ΔPW86-PW91/et-pVQZ+C$_{rel}$ for core-electron ionizations.

For degenerate valence MOs of nonperhalo molecules in procedure (1), choosing integer MO occupations leads to better predicted VIEs than preserving molecular symmetry. For procedure (2) for core electrons, localized core-hole must be used [26]. Later, we shall also study excitation spectra of both core and valence electrons with less established procedures:

(3) TDDFT(SAOP)/et-pVQZ for excitations of valence electrons, and

(4) ΔPW86-PW91/et-pVQZ+C$_{rel}$ for core-electron excitation energies, with approximate f-values obtained by truncated TDDFT(SAOP)/et-pVQZ, following the proposal of Stener et al. [27], which allows only excitations from core MOs. It should be mentioned that to obtain the energy of a core-excited singlet state requires three runs: first a restricted DFT calculation with the desired occupations, followed by a non-iterative run with β spins electrons in both open-shell MOs, and another non-iterative run with α and β electrons in them [28]. Then, by using the so-called multiplet approximation [29,30], we can get an estimate of the excited singlet.

Besides the four experimental geometries, we also wish to determine the quality of predicted VIEs of both valence and core electrons at geometries optimized by DFT with the popular exchange-correlation functional B3LYP [31], and by ab initio theory at the level of coupled clusters method with singles and doubles plus perturbative triples abbreviated as CCSD(T). Both optimizations are performed with the Gaussian'03 program package [32] using the internal basis set called 6-311+G(d,p). The bond parameters from our optimizations are included in Table 1. Following common practice, we use the // symbol to indicate geometry.

Because the nonplanarity is small, we use symmetry labels for planar molecules: The 1a–9a MOs for nonplanar formamide ~ 1a′–9a′ for C$_s$ symmetry; 10a and 11a~1a″ and 2a″; 12a~10a′. For virtual MOs, 13a~3a", 14a–17a ~11a′–14a′; 18a~4a″, etc.

3. Results and discussion

3.1. Preliminary results

First, we calculate the DFT energy E_{xc}(PBE0) of formamide from the electron density obtained with V_{xc} = SAOP on each of the six different geometries. The geometries are also used to compute the energy based on CCSD(T) with the 6-311+G(d,p) basis set. The results are compared in Table 2, which includes the energies relative to formamide at the B3LYP/6-311+G(d,p) geometry. The relative energies ΔPBE0(SAOP)/et-pVQZ are plotted against ΔCCSD(T)/6-311+G(d,p) in Fig. 1, which confirms our tentative conclusion that ΔPBE0(SAOP) can provide excellent approximation to relative energies.

Because the calculated energies are so similar, we cannot state which geometry best represents the formamide molecule. However, the results on the dipole moment, also presented in Table 2, suggest that the nonplanar geometry reported by CD60 or the one optimized in this work with CCSD(T)/6-311+G(d,p) may be more appropriate.

3.2. Vertical ionization energies

Since 1969, there have been several investigations of the ionization energies of formamide. In Table 3, we summarize the experimental results and present our best estimate based on them. Some values of VIEs from different studies are quite different from one another, especially the CEBE of O 1s. Therefore, although most

Table 2
Comparison of preliminary results on formamide at various geometries[a].

		μ[b] (D)	E[c] (eV)	ΔPBE0 (SAOP) (eV)	E[d] (au)	ΔCCSD(T) (eV)
Geometry	//KW57	2.479	−44.2417	0.177	−169.532332	0.173
	//CD60	3.972	−44.2551	0.163	−169.532317	0.173
	//KK74	4.199	−44.3777	0.041	−169.537857	0.022
	//H+74	4.300	−44.4130	0.005	−169.538299	0.010
	//B3LYP/6-311+G(d,p)	4.239	−44.4185	(0)	−169.538675	(0)
	//CCSD(T) /6-311+G(d,p)	4.091	−44.3910	0.027	−169.539194	−0.014
Expt	KW57	3.714				
	Handbook	3.73				

[a] See footnote a of Table 1.
[b] Calculated with SAOP/et-Pvqz.
[c] PBE0(SAOP)/et-pVQZ, relative to spherical atoms.
[d] CCSD(T)/6-311+G(d,p).