Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Study of the electronic structure of some N-heterocyclic carbenes (NHC) by variable energy photoelectron spectroscopy

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To estimate the usability and error limits of the presently used unrestricted TD-CAMB3LYP//mixed basis set approach for calculating the direct shake-up excitation energies and intensities within the sudden limit approximation, we here present the comparison between the calculated and experimental[1] shake-up spectrum of benzene. The C1s cross sections and shake-up spectra of benzene are much-studied[1-3] and comparatively well-understood and can therefore serve as a benchmark. Considering that the IMes carbene contains one imidazole and two mesitylene rings benzene is also a prototype chromophore of special relevance to the shake-up satellites of IMes. On basis of the results displayed in Table S1 we conclude the following:

(1) The excitation energies of the monopole allowed transitions correlate well with the experimental ones, and the agreement is within the error limits generally expected from the unrestricted TD-DFT approach.[4] The description of the higher lying transitions (> 7.5 eV) is potentially complicated by the involvement of the double (or higher) and/or diffuse (Rydberg) excitations. These cannot be described adequately by the current approach, which relies on the TD-DFT CIS wavefunctions and the basis sets that lack diffuse basis functions. Therefore, somewhat better agreement for the two high-lying transitions (8.4 and 9.8 eV) seen with the STO-3G basis set compared with the cc-pVDZ on the H atoms must be considered fortuitous.

(2) The cc-pVDZ(H) and STO-3G(H) levels of theory exhibit entirely negligible relative differences with regards to both the excitation energies and monopole intensities up to around 8 eV (Table S1). Furthermore, despite the denser cc-pVDZ(H) spectrum (i.e. the larger number of excitations per energy range), the monopole allowed excitations all emerge as closely similar. Therefore, substituting the originally proposed cc-pVDZ basis[5] set on the hydrogen atoms with the minimal STO-3G again appears entirely justified and is expected to have only a negligible bearing on the modeled IMes spectrum.

(3) Currently, we consider the shake-up spectrum of IMes up to about 6.5 eV above the corresponding C1s core-hole mainlines. Therefore, the last excitation below this limit in benzene as the parent chromophore is actually the one lying at ~5.8 eV (Table S1). Furthermore, the two lowest excitations at 3.9 and 4.8 eV are attributed to the “triplet” shake-up states because they each exhibit nearly the order of magnitude lower intensities in the experimental spectrum.[1] Consequently, the calculated monopole amplitudes for these spin-forbidden transitions are insufficient to describe them, and so are currently disregarded in the “scaled I” column of Table S1 (the “scaled I” values are simply derived from the predicted relative intensity (I_{rel}) values by multiplying the latter by the factor (4.35) which minimizes the sum of the squared deviations between the predicted and experimental relative intensities). Because of the spin contamination inherent to the unrestricted formalism, it is difficult to assign the <S^2> value to the calculated excited states (the <S^2> expectation values are not reported in the GAMESS-US output).

Overall, while the U-TD-CAM-B3LYP excitation energies are reasonably close to the experimental shake-up satellites, the correlation between the predicted monopole and experimental intensities is more problematic, notably for the most intense 7.15 eV satellite. However, these monopole intensities are not worse than those typically reported in the theoretical studies of the benzene shake-up spectrum.[1-3] The errors can be attributed to the shortcomings of considering only the single excitations (via the TD-DFT CIS auxiliary wavefunctions) and the lack of diffuse functions in the mixed basis set. As expected, these deficiencies begin to tell in particular with the higher-lying transitions. Unfortunately, in case of IMes the possibility of inclusion of higher excitations and/or diffuse basis functions is far from a feasible option given the size of the molecule and the number of the symmetry inequivalent core-holes. More importantly, however, the range of the currently modeled IMes shake-up spectrum (up to ~6.5. eV) is well below the observed problematic limit in benzene, and so we expect the currently used approach to still provide a reasonably well description of the low-energy portion of the IMes shake-up spectrum.

Table S1. Calculated (level of theory: U-TD-CAMB3LYP/cc-pwCVTZ($C_{\text{core-hole}}$)/mcp-dzp(C_{rest})/cc-pVDZ(H) and U-TD-CAMB3LYP/cc-pwCVTZ($C_{\text{core-hole}}$)/ mcp-dzp(C_{rest})/STO-3G(H)) and experimental shake-up excitation energies and monopole intensities for benzene. The compared transitions are shown in boldface.

	cc-pVDZ(H)		**STO-3G(H)**			**experimental (sudden limit)**	
state	*E*/eV	I_{rel}	*E*/eV	I_{rel}	scaled *I*	*E*/eV	*I* (% of the C1s mainline)
1	3.359	0.0000	3.359	0.0000			
2	**3.726**	**0.4947**	**3.727**	**0.4907**		**3.9 ± 0.1** (“triplet”)	**0.16**
3	**4.461**	**0.6994**	**4.463**	**0.6959**		**4.8 ± 0.1** (“triplet”)	**0.83**
4	5.221	0.0000	5.233	0.0000			
5	5.840	0.0000	5.846	0.0000			
6	**6.156**	**0.7257**	**6.167**	**0.7205**	**3.13**	**5.8 ± 0.1**	**2.21**
7	6.685	0.0000	6.737	0.0000			
8	6.878	0.0000	6.924	0.0000			
9	7.175	0.0000	7.217	0.0000			
10	7.215	0.0000	7.260	0.0000			
11	**7.280**	**0.4680**	**7.303**	**0.4668**	**2.03**	**7.15 ± 0.05**	**5.52**
12	7.682	0.0000	7.702	0.0000			
13	**7.702**	**0.7653**	**7.713**	**0.7644**	**3.33**	**8.4 ± 0.1**	**4.47**
14	7.992	0.0000	8.043	0.0000			
15	8.033	0.0000	8.099	0.0000			
16	8.258	0.0000	8.415	0.0000			
17	8.371	0.0000	8.553	0.0000			
18	8.465	0.0000	8.670	0.0000			
19	8.502	0.0000	9.039	0.0000			
20	8.650	0.0000	9.342	0.0000			
21	8.971	0.0000	9.535	0.0000			
22	9.278	0.0000	9.590	0.0000			
23	9.279	0.0000	9.620	0.0000			
24	9.469	0.0000	**9.795**	**1.0000**	**4.35**	**9.8 ± 0.1**	**2.01**
25	9.531	0.0000	9.870	0.0000			
26	9.558	0.0000	9.953	0.0000			
27	9.696	0.0000	10.048	0.0000			
28	**9.775**	**1.0000**	10.259	0.0000			
29	9.805	0.0000	**10.358**	**0.1965**	**0.85**	**10.9 ± 0.1**	**3.42**
30	9.910	0.0000	10.378	0.0000			

References:

1. E.E. Rennie, B. Kempgens, H.M. Köppe, U. Hergenhahn, J. Feldhaus, B.S. Itchkawitz, A.L.D. Kilcoyne, A. Kivimäki, K. Maier, M.N. Piancastelli, M. Polcik, A. Rüdel, A.M. Bradshaw, *J. Chem. Phys.*, 2000, **113**, 7362.

2. B. Brena, S. Carniato, Y. Luo, *J. Chem. Phys.*, 2005, **122**, 184316.

3. L. Yang, H. Ågren, *Chem. Phys.*, 1997, *222*, 139.

4. F. Wang, T. Ziegler, *Mol. Phys.* 2004, **102**, 2585.

5. J. Shim, M. Klobukowski, M. Barysz, J. Leszczynski, *Phys.Chem. Chem. Phys.*, 2011, **13**, 5703.