

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## COMMUNICATION

# Reactions of Laser-ablated U Atoms with (CN)<sub>2</sub>: Infrared Spectra and Electronic Structure Calculations of UNC, U(NC)<sub>2</sub>, and U(NC)<sub>4</sub> in Solid Argon

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012Yu Gong,<sup>a</sup> Lester Andrews,<sup>\*a</sup> Benjamin K. Liebov,<sup>a</sup> Zongtang Fang,<sup>b</sup> Edward B. Garner, III,<sup>b</sup> and David A. Dixon<sup>\*b</sup>

DOI: 10.1039/x0xx00000x

www.rsc.org/

**Reactions of laser-ablated U atoms with (CN)<sub>2</sub> produce UNC, U(NC)<sub>2</sub>, and U(NC)<sub>4</sub> as the major products, identified from their Ar matrix infrared spectra and precursors partially and fully substituted with <sup>13</sup>C and <sup>15</sup>N. Mixed isotopic multiplets substantiate product stoichiometries. Band positions and quantum chemical calculations verify the isocyanide bonding.**

Cyanogen, (CN)<sub>2</sub>, is a pseudohalogen with two important differences: (1) the C-C bond energy, 136.7 ± 1.6 kcal/mol, is at least double any of the halogen molecules,<sup>1</sup> and (2) the CN radical can bond at either C or N, leading to cyanides and isocyanides. Different metal centers may prefer one type of bonding over the other. Pyykkö and coworkers<sup>2</sup> proposed that uranium bonding to CN is not favorable because both are σ donors and π acceptors. They hypothesized that the isocyanide arrangement is preferred because the N is a better π donor than the C. They reported electronic structure calculations that showed that it is slightly more exothermic to replace 2 F in UF<sub>6</sub> with 2 NC than with 2 CN groups and that the stretching frequencies are about 200 cm<sup>-1</sup> higher for the cyano ligand than for the isocyanide ligand. Other theoretical investigations of uranyl-CN/NC bonding have been reported.<sup>3,4</sup> Sonnenberg, et al. predicted that the tetra coordinated ion [UO<sub>2</sub>(NC)<sub>4</sub>]<sup>2-</sup> is more stable than the CN isomer, and the reverse holds for the penta-coordinated analogs.<sup>4</sup> These results suggest that the U-CN and U-NC bonding have comparable energies, which depend intimately on the local environment.

There are a number of ligand supported cyanido complexes of uranium most notably from the work of Ephritikhine and coworkers with a variety of substituents.<sup>5,6,7</sup> The local environment of uranium for the isolated complex is different in the gas phase as investigated by computations and the noble gas matrix as studied by infrared spectroscopy of the ligand stretching mode as compared to cyanide compounds such as [Cp\*<sub>2</sub>U(CN)<sub>3</sub>][NEt<sub>4</sub>]<sub>3</sub>.<sup>6</sup> Thus it is reasonable for the NC/CN attachment to the U centers to be different in these cases. So far, the only known uranium isocyanide examples where the bare CN ligand is nitrogen bound to uranium are CH<sub>3</sub>UNC and

CH<sub>2</sub>=U(H)NC prepared by reactions of laser ablated uranium atoms and acetonitrile in argon matrices.<sup>8</sup> We report here the formation of UNC, U(NC)<sub>2</sub>, and U(NC)<sub>4</sub> complexes from the U and cyanogen reaction isolated in argon matrices at 4 K and supporting theoretical calculations.

Argon matrix infrared spectra from the reaction of laser ablated uranium atoms and 1.0% cyanogen are illustrated in Figure 1, which shows the major absorptions after sample deposition at 4 K, ultraviolet (uv) irradiation, and annealing to 30 K in trace (a). Details of the experiments are given in the Supporting Material. The sharp band at 2054.2 cm<sup>-1</sup> observed in all of our spectra is due to the precursor isomer CNCN produced by photolysis from the emission plume.<sup>9</sup> Four major uranium dependent product bands were observed on deposition at 2040.6, 2028.5, 2020.0 and 1989.4 cm<sup>-1</sup> (Table 1). It is important to consider the effect of (CN)<sub>2</sub> concentration, using 0.3%, for example. The first band at 2040.6 cm<sup>-1</sup> is clearly stronger relative to the other bands; the 2028.5 and 2020.0 cm<sup>-1</sup> bands track in relative intensity just as they did using 1% reagent, and the lower band at 1989.4 cm<sup>-1</sup> is markedly weaker than the other product absorptions. Annealing had the same band sharpening effect as described for Figure 1, and photolysis again clearly increased the lower bands. In addition, annealing to 20 K also revealed growth of the CN radical at 2044.2 cm<sup>-1</sup> most likely from combination of atoms produced by laser plume photolysis. These spectra show that there are products of three different stoichiometries, which give rise to the first, the second and third, and the lowest band system, respectively.

The isotopically substituted cyanogen spectra in Figure 1 provide the identification for these three products. The first band at 2040.6 cm<sup>-1</sup> shifted to 1999.4 cm<sup>-1</sup> using (<sup>13</sup>CN)<sub>2</sub> with the 1.02061 frequency ratio and exhibited no intermediate mixed isotopic components. Analogous behaviour was found in the (C<sup>14</sup>,<sup>15</sup>N)<sub>2</sub> reaction (not shown) with the pure <sup>15</sup>N component at 2008.8 cm<sup>-1</sup> and ratio 1.01583. These observations show that this vibration involves one C and one N atom. This 2040.6 cm<sup>-1</sup> frequency for UNC may be compared with the 2029.7 cm<sup>-1</sup> value reported for CH<sub>3</sub>UNC.<sup>8</sup>

The next pair of bands at 2028.5 and 2020.0  $\text{cm}^{-1}$  with  $(^{12}\text{CN})_2$  maintain constant relative intensities and arise from the same species, which absorb at 1988.1 and 1979.4  $\text{cm}^{-1}$  with  $(^{13}\text{CN})_2$  and define the 1.02032 and 1.02051 frequency ratios. It is significant that *no* new intermediate bands are observed in the experiment with mixed reagents, trace (c), which for this product is the sum of the pure isotopic spectra. However, using the scrambled reagent, trace (b) with the  $(^{12}\text{CN})(^{13}\text{CN})$  reagent also present, these bands plus two

new bands are observed at 2024.7 and 1983.3  $\text{cm}^{-1}$ , almost at the median of the first band pairs. The latter two bands are due to the mixed isotopic product species  $(^{12}\text{CN})\text{U}(^{13}\text{C})$  and show that U undergoes a concerted reaction with cyanogen. Analogous mixed isotopic bands were observed for  $(\text{C}^{14}\text{N})\text{U}(^{15}\text{NC})$ . Therefore the pair of bands at 2028.5 and 2020.0  $\text{cm}^{-1}$  with  $(^{12}\text{CN})_2$  are due to the symmetric and antisymmetric UN-C stretching modes of  $(^{12}\text{CN})\text{-U}(^{12}\text{C})$  with two equivalent isocyanide ligands.

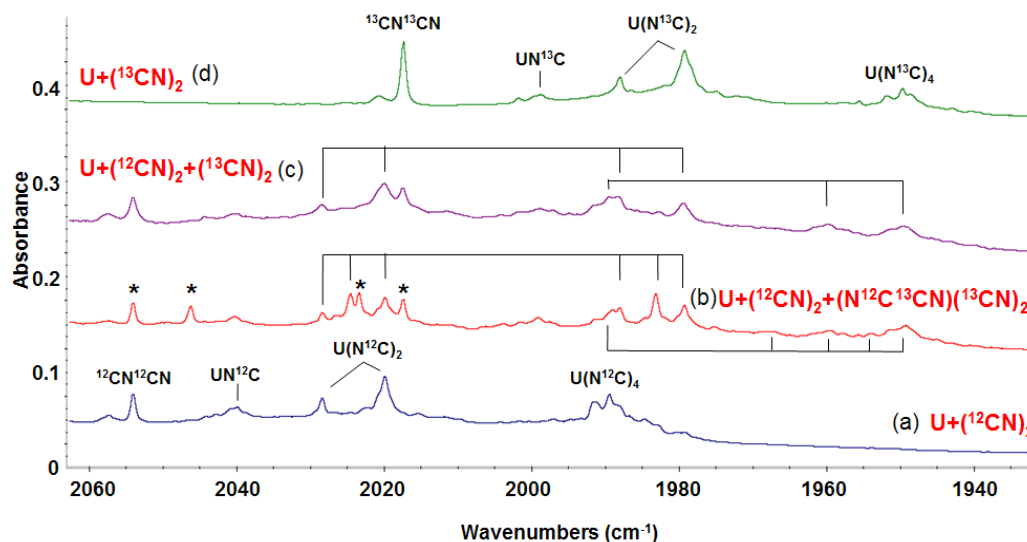


Figure 1. Infrared spectra of laser ablated U and  $(^{12}\text{CN})_2$  and  $^{13}\text{C}$  substituted  $(\text{CN})_2$  reaction products codeposited in argon at 4 K and after uv photolysis and annealing to 30 K to optimize product yield. (a) 1 %  $(^{12}\text{CN})_2$ , (b) 1 %  $(^{12,13}\text{CN})_2$ , (c) 1 %  $(^{12}\text{CN})_2$  and 1 %  $(^{13}\text{CN})_2$  mixed, (d) 1 %  $(^{13}\text{CN})_2$ . The \* denotes the CNCN photoisomer of cyanogen.

Molecule	$(^{12}\text{C}^{14}\text{N})_2$	$(^{13}\text{C}^{14}\text{N})_2$	$(^{12}\text{C}^{14}\text{N})_2 + ^{14}\text{N}^{13}\text{C}^{12}\text{C}^{14}\text{N} + (^{13}\text{C}^{14}\text{N})_2$	$(^{12}\text{C}^{14}\text{N})_2 + (^{13}\text{C}^{14}\text{N})_2$
UNC expt	2040.6	1999.4	2040.6, 1999.4	2040.6 1999.4
$^4\text{UNC}$ calc	2080.6 $\sigma$ (493)	2038.7 $\sigma$	2080.6, 2038.7	2080.6, 2038.7
$\text{U}(\text{NC})_2$ expt	2028.5 2020.0	1988.1 1979.4	2028.5, 2024.7 1988.1, 2020.0 1983.3, 1979.4	2028.5 1988.1 2020.0 1979.4
$^5\text{U}(\text{NC})_2$ calc	2072.3 $b_2$ (681) 2084.0 $a_1$ (171)	2031.2 $b_2$ 2044.3 $a_1$	2072.3, 2036.8 2031.0, 2084.0 2080.9, 2044.3	2072.3 2031.0 2084.0 2044.3
$^4\text{U}(\text{NC})_3$ expt	2015	1975		
$^4\text{U}(\text{NC})_3$ calc	2072.0 $e$ (1453) 2088.7 $a_1$ (54)	2030.0 $e$ 2046.8 $a_1$	2029.9, 2039.3 2033.9, 2072.8 2079.7, 2084.4	
$\text{U}(\text{NC})_4$ expt	1989.4	1949.8	1989.1, 1959.7 1968, 1954 1949.6	1989.4 1959.7 1949.8
$^3\text{U}(\text{NC})_4$ calc	2045.6 $b$ (927) 2046.4 $e$ (2100) 2086.0 $a$ (0)	2004.2 $b$ 2004.9 $e$ 2045.3 $a$	2004.4, 2004.9 2025.3, 2065.9 2010.2, 2045.8 2046.4, 2080.6	2004.5 2017.0 2046.0 2074.3

Table 1. Experimental and DFT (B3LYP) calculated isocyanide N-C stretches (in  $\text{cm}^{-1}$ ) for NC bonded to U from reactions with cyanogen. Calculated intensities in parentheses in  $\text{km}/\text{mol}$ .

The situation is different for the last band at 1989.4  $\text{cm}^{-1}$  which contains one new band at 1959.7  $\text{cm}^{-1}$  in trace (c) and two additional new bands in trace (b) at 1968 and 1953  $\text{cm}^{-1}$ . This shows that two precursor molecules are involved in this product molecule. The weak band at 2015  $\text{cm}^{-1}$  has the proper  $^{13}\text{C}$  isotopic counterpart to be due to an N-C mode, but we cannot obtain any mixed isotopic data for this band. On the basis of the calculations described below, we tentatively assign the weak 2015  $\text{cm}^{-1}$  band to  $\text{U}(\text{NC})_3$ . Finally, we can assign the 1989.4  $\text{cm}^{-1}$  band to  $\text{U}(\text{NC})_4$  where we are able to observe three of the mixed isotopic components. The band at 1991.9  $\text{cm}^{-1}$  could be assigned as the matrix site splitting of the 1989.4  $\text{cm}^{-1}$  band or to the *b* mode of  $^3\text{U}(\text{NC})_4$  in  $S_4$  symmetry as discussed below based on the computational results.

In order to better understand the energetics of the various structures identified in the matrix and to assist in the IR spectral assignments, density functional theory (DFT) with the B3LYP hybrid exchange-correlation functional<sup>10</sup> was used with the aug-cc-pVTZ basis set<sup>11</sup> on C and N and the ECP60MWB effective core potential and ECP60MWB\_SEG [10s,9p,5d,4f,3g] basis set on U.<sup>12</sup> The calculations were done in the spin unrestricted formalism. As a test of the functional, calculations on the states of UCN and UNC were also performed with the PBE and PW91 functionals which gave the same energy ordering and similar frequencies. The B3LYP calculated frequencies are shown in Table 1. The Gaussian09 program system was used for the DFT calculations.<sup>13</sup> The relative

energetics are given in the Supporting Material as are the complete list of frequencies.

The lowest energy structure for addition of a single ligand to U is  ${}^4\text{UNC}$  with  ${}^6\text{UCN}$ , 29 kcal/mol higher in energy. The intense UN-C stretching mode of  ${}^4\text{UNC}$  is predicted to be  $40\text{ cm}^{-1}$  above the experimentally observed value consistent with the fact that the calculated values are harmonic and the experimental ones contain an anharmonic component. The  ${}^6\text{UCN}$  is predicted to have a much weaker UC-N stretching mode at a higher frequency of  $2169\text{ cm}^{-1}$  (12 km/mol), and there is no observed absorption in this region. The electron configuration of the  ${}^4\text{UNC}$  ground state is  $7s^25f^3$  (see Table S1 for the NBO populations.<sup>14</sup>) There is about 0.3 e spin paired on the 6d. The spin densities are shown in Figure 2. The details of the spin populations are given in the Supporting Material.

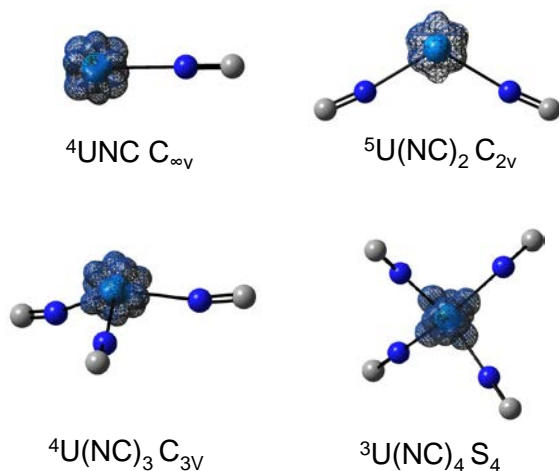


Figure 2. Spin densities of the lowest energy uranium isocyanides for 1 to 4 NC groups with a contour level of 0.02

The lowest energy structure with two ligands is  ${}^5\text{U(NC)}_2$  in  $C_{2v}$  symmetry with  ${}^5\text{U(CN)}_2$ , 11 kcal/mol higher in energy. Note that the UNC bonding arrangement is not quite linear (See Figure 2). The intense UN-C antisymmetric  $b_2$  stretching mode of  ${}^5\text{U(NC)}_2$  is predicted to be  $52\text{ cm}^{-1}$  above the experimentally observed value with the higher intensity. The weaker  $a_1$  band for the symmetric stretch is predicted to be at a higher frequency of  $2084\text{ cm}^{-1}$ ,  $56\text{ cm}^{-1}$  above the weaker experimental band at  $2028\text{ cm}^{-1}$ . The higher energy  ${}^5\text{U(CN)}_2$  structure has two weak computed bands at  $2213$  and  $2215\text{ cm}^{-1}$  which are not consistent with the observed spectral features. The CN stretches for the U-CN bonding arrangement increase with increasing numbers of CN in contrast to the decrease predicted for the isocyanide bonding arrangement and the decrease observed experimentally. The ground state is  $7s^15f^3$  with about 0.5 e donated to the 6d from the NBO populations. The 0.54 e is spin polarized with 0.41 e  $\alpha$  spin and 0.14 e  $\beta$  spin.

The ground state  ${}^4\text{U(NC)}_3$  in  $C_{3v}$  symmetry is more stable than the lowest energy  ${}^4\text{U(CN)}_3$  structure by 18 kcal/mol. The  ${}^4\text{U(NC)}_3$  is predicted to have an intense  $e$  antisymmetric stretch band,  $57\text{ cm}^{-1}$  higher than the one tentatively assigned at  $2015\text{ cm}^{-1}$ . The higher energy  $a_1$  symmetric stretch is predicted to have a much lower intensity (factor of  $\sim 25$ ). The ground state is  $5f^3$  with about 0.5 e donated to the 6d from the NBO populations. The 0.54 e in the d is essentially spin paired so it does not contribute to the spin state. Weak bands at  $2219\text{ cm}^{-1}$  (195 km/mol) for the  $e$  mode and  $2221\text{ cm}^{-1}$  (17 km/mol) for the  $a$  mode are predicted for  ${}^4\text{U(CN)}_3$ .

The  ${}^3\text{U(NC)}_4$  in  $S_4$  symmetry is more stable than the lowest energy  ${}^3\text{U(CN)}_4$  structure in  $C_{2v}$  ( $\sim$ tetrahedral) symmetry by 30 kcal/mol. A very intense degenerate  $e$  stretch band at  $2046\text{ cm}^{-1}$  with

an additional intense band of  $b$  symmetry within  $1\text{ cm}^{-1}$  is predicted for  ${}^3\text{U(NC)}_4$  consistent with the assignment of the experimental band at  $\sim 1990\text{ cm}^{-1}$ . The difference between the calculated and experimental values is  $56\text{ cm}^{-1}$ , consistent the differences given above. Three stretching bands for  ${}^3\text{U(CN)}_4$  are predicted to be at  $\sim 2220$  each with an intensity of  $\sim 210\text{ km/mol}$ . The electron configuration is essentially  $f^2$  with 2.41 e in the 5f (the excess is spin paired) and 1.0 e spin paired in the 6d.

The geometry results in the Supporting Information show that the CN bond distance is shorter in the cyanide compounds and longer in the isocyanides consistent with the higher CN stretch in the former. Coupled with this is the fact that the U-C bond distance is 0.12 to 0.15 Å longer than the U-N bond distance showing that the U is interacting more strongly with the isocyanide than with the cyanide. In addition, the positive charge on the U (Supporting Material) in the isocyanides is larger than on the cyanides except for  $n=1$  where they are comparable. Thus there is more negative charge on the NC in the isocyanides than on the CN in the cyanides. The isocyanides are highly polarized with a charge of about -1.0 e on the N and a positive charge of 0.28 to 0.37 on the C. In contrast, the charges on the C and N are both about equal and negative. Thus the electrostatic and dipolar interactions are larger in the isocyanides than in the cyanides. As a consequence, the isocyanide bonding interactions are larger than in the cyanides and the isocyanides are more stable with shorter U-N bond lengths and longer NC bond distances. The prior results<sup>2,3,4</sup> are focused on the addition of  $\text{CN}^-/\text{NC}^-$  to U(VI) in contrast to the current work which focuses on the addition of  $\text{CN}^-/\text{NC}^-$  to U(I) to U(IV) with no other ligands present. The differing results for whether isocyanide or cyanide bonding to U is preferred clearly depend on the charge on the U and the nature of any other ligands that are present.

## Conclusions

The laser ablated uranium atom reaction with cyanogen during condensation with excess argon at 4K produces three major products which are identified as the isocyanides UNC,  $\text{U(NC)}_2$  and  $\text{U(NC)}_4$  from experimental mixed isotopic spectra, the spectral region of the absorptions, and B3LYP product energy and frequency calculations. The analysis of the charges and the geometries shows that the isocyanides bond more strongly to the U in the +I to +IV oxidation states than the cyanides when no other ligands are present.

## Notes and references

<sup>a</sup> University of Virginia, Department of Chemistry, Charlottesville, VA, USA. 22904-4319 E-mail: [lsa@virginia.edu](mailto:lsa@virginia.edu)

<sup>b</sup> The University of Alabama, Department of Chemistry, Tuscaloosa, AL, 35487-0336, USA E-mail: [dadixon@ua.edu](mailto:dadixon@ua.edu).

### Acknowledgement:

We gratefully acknowledge financial support from DOE Grant No. DE-SC0001034 to LA. DAD acknowledges the Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences, Heavy Element Program for support via a subcontract from Argonne National Laboratory. DAD also thanks the Robert Ramsay Chair Endowment, University of Alabama, for support.

Electronic Supplementary Information (ESI) available: Experimental details. NBO Population Analysis with the B3LYP Functional for the lowest energy states of  $\text{U(NC)}_n$  for  $n=1$  to 4. Total energies and geometries ( $x, y, z$  Cartesian coordinates in Å) for the lowest energy states of  $\text{U(NC)}_n$  and  $\text{U(CN)}_n$  for  $n=1$  to 4. See DOI: 10.1039/c000000x/

- 1 Y.-R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Taylor and Francis Group, 2007.

- 2 M. Straka, M. Patzschke and P. Pyykkö, *Theor. Chem. Accts.* 2003, **109**, 332-340.
- 3 C. Clavaguera-Sarrio, S. Hoyau, N. Ismail, C. J. Marsden, *J. Phys. Chem. A* 2003, **107**, 4515-4525.
- 4 J. L. Sonnenberg, P. J. Hay, R. L. Martin, B. E. Bursten, *Inorg. Chem.* 2005, **44**, 2255-2262.
- 5 J.-C. Berthet, P. Thuéry and M. Ephritikhine, *Chem. Commun.*, 2007, 604-606.
- 6 J. Maynadić, N. Barros, J. C. Berthet, P. Thuéry, L. Maron and M. Ephritikhine, *Angew. Chem. Int. Ed.* 2007, **46**, 2010-2012.
- 7 J.-C. Berthet, P. Thuéry and M. Ephritikhine, *Organometallics* 2008, **27**, 1664-1666.
- 8 H. G. Cho and L. Andrews, *Organometallics* 2012, **31**, 535-544.
- 9 M. E. Jacox and W. E. Thompson, *J. Chem. Phys.* 2007, **126**, 054308.
- 10 (a) A. D. Becke *J. Chem. Phys.* 1993, **98**, 5648-5652; (b) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785-789.
- 11 R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison *J. Chem. Phys.* **1994**, **96**, 6796-6806.
- 12 <http://www.theochem.unistuttgart.de/pseudopotentials/index.en.html>;  
(b) X. Cao, M. Dolg, and H. Stoll *J. Chem. Phys.* **2003**, **118**, 487-496;  
(c) X. Cao and M. Dolg *J. Mol. Struct. (Theochem)*, **2004**, **673**, 203-209.
- 13 Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010
- 14 F. Weinhold, and C. R. Landis *Valency and Bonding: A Natural Orbital Perspective*, Cambridge University Press, Cambridge, UK, 2005; A. E. Reed, L. Curtiss, and F. Weinhold *Chem. Rev.* **1988**, **88**, 899-926; E. D. Glendening, C. R. Landis, and F. Weinhold, *J. Comp. Chem.* **2013**, **34**, 1429-1437; E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold, F. (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); <http://nbo6.chem.wisc.edu/>.