Understanding London Dispersion Effects in Molecular Materials[1]

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The *Gecko* can walk up a glass window because of the adhesion in hydrophobic setae on its toes that convey van der Waals (vdW) interactions with the surface.[2] The attractive part of such vdW-interactions is an electron correlation effect referred to as *London dispersion*. Its role in the formation of condensed matter has been known since the work of van der Waals[3] and London[4] who related dispersion to polarizability. London dispersion has been underappreciated in molecular chemistry as a key element of structural stability, chemical reactivity, and catalysis. This negligence is due to the notion that dispersion is weak, which is only true for *one* pair of interacting atoms. For increasingly larger structures, the overall dispersion contribution grows rapidly and can amount to tens of kcal mol^{-1}. This presentation shows selected examples that emphasize the importance of inter- and intramolecular dispersion for molecules consisting mostly of first row atoms.[5] We note the synergy of experiment[6] and theory that now has reached a stage where dispersion effects can be examined in fine detail. This forces us to re-consider our perception of steric hindrance and stereoelectronic effects, and even the transferability of chemical bond parameters from one molecule to another.

(1) **Review:** Wagner, J. P.; Schreiner, P. R. *Angew. Chem. Int. Ed.* **2015**, *54*, 12274.

(2) Autumn, K.; Sitti, M.; Liang, Y. A.; Peattie, A. M.; Hansen, W. R.; Sponberg, S.; Kenny, T. W.; Fearing, R.; Israelachvili, J. N.; Full, R. J. *Proc. Natl. Acad. Sci.* **2002**, *99*, 12252.

(3) van der Waals, J. D., doctoral thesis, Leiden University, 1873.

(4) London, F. *Z. Phys.* **1930**, *63*, 245.

(5) a) Fokin, A. A.; Gerbig, D.; Schreiner, P. R. *J. Am. Chem. Soc.* **2011**, *133*, 20036; b) Grimme, S.; Schreiner, P. R. *Angew. Chem. Int. Ed.* **2011**, *50*, 12639; c) Schreiner, P. R.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Schlecht, S.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A. *Nature* **2011**, *477*, 308; d) Fokin, A. A.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Dahl, J. E. P.; Carlson, R. M. K.; Schreiner, P. R. *J. Am. Chem. Soc.* **2012**, *134*, 13641; e) Wagner, J. P.; Schreiner, P. R. *J. Chem. Theory Comput.* **2014**, *10*, 1353; f) Wang, C.; Mo, Y.; Wagner, J. P.; Schreiner, P. R.; Jemmis, E. D.; Danovich, D.; Shaik, S. *J. Chem. Theory Comput.* **2015**, *11*, 1621; g) Prochazkova, E.; Kolmer, A.; Ilgen, J.; Schwab, M.; Kaltschnee, L.; Fredersdorf, M.; Schmidts, V.; Wende, R. C.; Schreiner, P. R.; Thiele, C. M. *Angew. Chem. Int. Ed.* **2016**, *55*, 15754; h) Wagner, J. P.; Schreiner, P. R. *J. Chem. Theory Comput.* **2016**, *12*, 231; i) Rösel, S.; Balestrieri, C.; Schreiner, P. R. *Chem. Sci.* **2017**, *8*, 405; j) Rösel, S.; Quanz, H.; Logemann, C.; Becker, J.; Mossou, E.; Cañadillas-Delgado, L.; Caldeweyher, E.; Grimme, S.; Schreiner, P. R. *J. Am. Chem. Soc.* **2017**, *139*, 7428.

(6) a) Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *ACS Nano* **2017**, *11*, 9459; b) Ebeling, D.; Šekutor, M.; Stiefermann, M.; Tschakert, J.; Dahl, J. E. P.; Carlson, R. M. K.; Schirmeisen, A.; Schreiner, P. R. *Nat. Commun.* **2018**, *9*, 2420.