



**QUEEN'S
UNIVERSITY
BELFAST**

Chemical control through dissociative electron attachment - A study on pentafluorotoluene, pentafluoroaniline and pentafluorophenol

Omarsson, B., Bjarnason, E. H., Ingolfsson, O., Haughey, S., & Field, T. A. (2012). Chemical control through dissociative electron attachment - A study on pentafluorotoluene, pentafluoroaniline and pentafluorophenol. DOI: 10.1016/j.cplett.2012.04.059

Published in:
Chemical Physics Letters

Document Version:
Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Contents lists available at [SciVerse ScienceDirect](#)

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Chemical control through dissociative electron attachment – A study on pentafluorotoluene, pentafluoroaniline and pentafluorophenol

Benedikt Ómarsson^a, Elías H. Bjarnason^a, Oddur Ingólfsson^{a,*}, Sean Haughey^b, Thomas A. Field^{b,*}^a Science Institute and University of Iceland, Department of Chemistry, Dunhaga 3, 107 Reykjavik, Iceland^b Queen's University Belfast, Department of Physics and Astronomy, University Road, Belfast BT7 1NN, N. Ireland, United Kingdom

ARTICLE INFO

Article history:

Received 10 March 2012

In final form 27 April 2012

Available online xxxxx

ABSTRACT

In a combined experimental and theoretical study on dissociative electron attachment (DEA) to pentafluorotoluene, pentafluoroaniline and pentafluorophenol in the energy range 0–3 eV we reveal the role of rearrangement and hydrogen bonded intermediates in the DEA process and show that HF formation can be used to enable otherwise inaccessible, efficient low energy DEA processes.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Dissociative electron attachment (DEA) has long been known to play an important role in plasma processing [1] and atmospheric chemistry [2] and more recently the role of DEA in radiation damage to biologically relevant molecules has been the subject of interest of many research groups [3]. In a simplified picture many DEA processes can be fairly well described within the model of a quasi-diatom dissociation by



where a low energy electron attaches to the neutral molecule; AB, to form a transient negative ion (TNI). The TNI; AB^{-*} , can reemit the attached electron (autodetachment) or, if it is energetically above the threshold for dissociation, dissociate to form the neutral fragment; A, and the negative ion; B^- . Electron attachment is a resonant transition from the neutral ground state to the TNI state, and is only accessible in a narrow electron energy range in the Franck–Condon region. In contrast to fragmentation induced by direct electron impact, where excess energy of several eV is required, DEA is very bond selective and can occur close to zero eV electron energy with high efficiency [4] and large cross sections of about 10^{-16} to 10^{-18} m² [1]. Excellent examples of the site selectivity in DEA have been demonstrated for the pyrimidine nucleobases thymine and uracil [5], the amino acid valine [6] and a range of small organic molecules [7], to name a few. It is thus not farfetched to consider DEA by low energy electrons as a method of chemical control at the molecular level.

In DEA, the thermochemical threshold for a specific direct dissociation process is given by the difference between the bond dissociation energy (BDE), here the AB bond, and the electron affinity of the neutral fragment; B, ejected as an anion. Therefore, such

(direct) high efficiency processes can only occur close to 0 eV electron energy if the electron affinity of B is greater than the bond dissociation energy. This is rarely the case except where fragments with high electron affinities, such as Cl, Br, I and CN, are ejected as anions. Good examples of such processes can be found in the review articles [4,8]. More complicated processes with multiple bond ruptures which cannot be described by the quasi-diatom model are however frequently observed in DEA at low incident electron energies. In these processes the energy gained by the formation of new chemical bonds enables the reactions to proceed at low electron energies with high efficiency and selectivity.

Notable examples of such processes include the formation of CN^- from hexafluoroacetone azine [9] and the amino acids valine [10] and glycine [11] as well as multiple fragmentation processes observed close to 0 eV in DEA to the well known explosive TNT [12]. Other examples include those described in DEA studies of trifluoroacetic acid [13] and pentafluorophenylacetonitrile [14]. In both these cases anions consisting of the parent molecule less one fluorine and one hydrogen atom; $[M - HF]^-$, are formed with high efficiency close to 0 eV electron energy. The very low thresholds for these channels, and high efficiencies, are achieved through the formation of neutral HF molecules in the dissociation process, which fuel the reaction by releasing the HF bond energy of ≈ 5.9 eV [15]. Such hydrogen halide formation has also been shown to be a dominating process in DEA to 5-chloro uracil [16], and furthermore, high intensity H₂ loss has been reported close to 0 eV for the nucleobase thymine [17].

In the context of chemical control through DEA it is thus very interesting to seek ways to exploit highly exothermic bond formation processes, such as the HF formation, as a driving force for dissociation channels that would otherwise not be accessible. Motivated by this concept we have conducted a systematic experimental and theoretical study of DEA to the substituted pentafluorophenyl compounds pentafluorotoluene (PFT); C₆F₅CH₃, pentafluoroaniline (PFA); C₆F₅NH₂ and pentafluorophenol (PFP);

* Corresponding authors. Fax: +354 5528911 (O. Ingólfsson).

E-mail addresses: odduring@hi.is (O. Ingólfsson), t.field@qub.ac.uk (T.A. Field).

C_6F_5OH . We have chosen these compounds as, from a steric point of view, they can all form HF between a hydrogen and a fluorine in the ortho-position but they differ with respect to the polarization of the X–H bonds, which increases in the order $C < N < O$. These compounds are thus excellent candidates to study the role of hydrogen bonding in the HF formation process and we expected a large difference between PFT on one hand and PFA and PFP on the other, as the more electronegative N and O, like F, form hydrogen bonds that may stabilize $X \cdots H \cdots F$ intermediates.

2. Experimental methods

The experimental setup is described in detail elsewhere [18]. In brief, it consists of a trochoidal electron monochromator (TEM) and a time-of-flight (ToF) mass spectrometer. The experiment is pulsed with $\approx 1 \mu s$ electron pulses passing through the source region of the ToF mass spectrometer. When all the electrons have left the source region ($\approx 1 \mu s$) any ions generated are pushed with a 200 V/cm pulsed electric field towards an acceleration field of 400 V/cm, whereafter the ions drift along the ToF Mass Spectrometer towards the ion detector. The mass spectrometer potentials are reversible so that both positive and negative ions can be detected. The electron energy scale is calibrated with respect to the formation of SF_6^- from SF_6 at 0 eV electron energy and the resolution (≈ 140 meV) is estimated from the FWHM of the SF_6^- signal. The samples were introduced through a gas inlet into the high vacuum reaction chamber by sublimation (PFP and PFA) or evaporation (PFT) at room temperature. PFP and PFT were purchased from Sigma–Aldrich (St. Louis, MO, USA) and PFA from Fluorochem (Hadfield, Derbyshire, England). All compounds had stated purity of 99% and were used as delivered.

3. Computational methods

To determine the threshold energies for the individual DEA processes, the geometry of all molecules and fragments was optimized at the B3LYP/6-31G** [19,20] level of theory and vibrational frequency calculations were made to verify the minima. Single point energy calculations were performed for the optimized systems at the B3LYP and B2PLYP [21] levels of theory using the aug-*pc*-2 basis set [22]. The zero-point energy and the thermal vibrational energy at 298 K from harmonic vibrational frequency calculations were added to the systems. In the final step, threshold energies were determined by subtraction of the total energy of the products of the respective DEA processes from the total energy of the corresponding parent molecules. All these calculations were performed with NWChem 6.0 [23].

To explore the role of hydrogen bonding in the DEA process, the minimum energy path for the revolution of the XH_n groups was evaluated at the B3LYP/6-31G** level of theory using the Nudged Elastic Band (NEB) method [24]. These calculations were performed using Chemshell [25] with the NWChem program interfaced as QM code and the DL-FIND [26] interface as geometry optimizer. A total of 18 NEB images were calculated along the reaction paths. In the case of PFA and PFP the XH_n group is rotated 180° between the initial and the final state but in the case of PFT the range is 60° . The resulting transition states and minima were further optimized at the B3LYP/*pc*-2 level of theory to obtain a good estimate for the energy barrier.

4. Results and discussion

Figure 1 shows the negative ion yield curves of all fragments formed through DEA to PFA (a) and PFP (b) in the incident electron energy range from 0 to 3 eV. In this energy range, several DEA

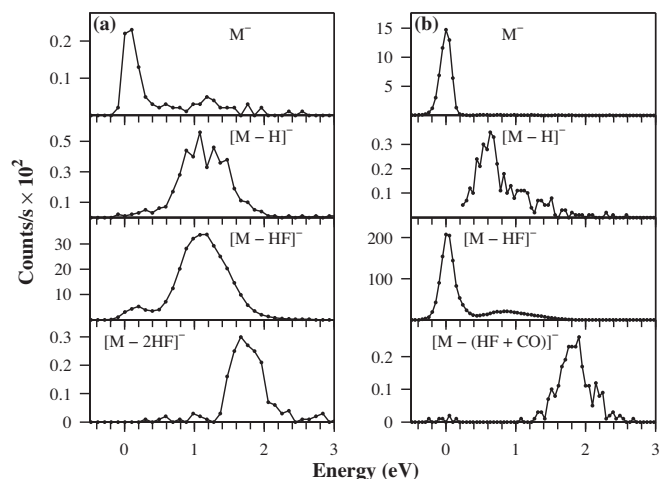


Figure 1. Ion yield from DEA to PFA (a) and PFP (b) in the incident electron energy range from 0 to 3 eV.

products are observed from both PFA (a) and PFP. By contrast, the only negative ion observed from PFT, in this energy range is the parent molecular anion, M^- , which is observed with very low intensity close to 0 eV (not shown here). Hence, no DEA processes are observed from PFT in this energy range.

The most pronounced DEA channels for PFA and PFP lead to the formation of $[M - HF]^-$ through two distinct resonances located close to 0 eV and 0.9 eV, respectively. In PFP the 0 eV resonance dominates whilst the 0.9 eV resonance dominates in PFA. Hydrogen loss from these molecules is about two to three orders of magnitude weaker than HF loss. Loss of HF and CO from PFP leading to the anionic fragment $[M - (HF + CO)]^-$ is observed through the high-energy tail of the 0.9 eV resonance and stretches from about 1.5–2.5 eV. Similarly, the formation of $[M - 2HF]^-$ through the loss of two HF molecules from PFA is observed in the range from about 1 to 2 eV. The anionic products from these processes appear in the ion yield curves with similar intensities as the hydrogen loss. In addition to the DEA products, the molecular anion is observed close to 0 eV from both PFA and PFP, as well as from PFT. From PFP the intensity of M^- is found to be about one tenth of the $[M - HF]^-$ signal, but from PFA the relative contribution from the parent molecular anion is much less pronounced. The ion yield curve for M^- in PFA (Figure 1a) shows traces from the partly overlapping ion yield curve for $[M - H]^-$ at slightly higher energies. This overlap is attributed to metastable fragmentation during the early stage of the ion acceleration.

In order to explore the mechanism behind the HF formation we have calculated the thermochemical threshold energies for the formation of the observed fragments. All the relevant thresholds are given in Table 1. Figure 2 shows the proposed fragmentation mechanism for the main fragmentation channels in PFP (a) and PFA (b), respectively.

For the HF loss from PFP we calculate thresholds of 0.29 and 0.59 eV with B3LYP and B2PLYP, respectively, if we assume that the charged fragment retains its six-membered carbon ring structure and the open shell $C_6F_4O^-$ anion is formed. We find, however, that this reaction is exothermic by 0.36 eV and 0.19 eV with B3LYP and B2PLYP, respectively, if we assume that the loss of HF is associated with a rearrangement of the ion to form a five-membered ring with a terminal CO group, i.e., the open shell $C_5F_4-CO^-$ anion (structure 1 in Figure 2a). The structure of the dominant $[M - HF]^-$ ion from PFP close to 0 eV is thus most likely the five-membered ring structure 1 in Figure 2a. The $[M - HF]^-$ contribution from PFP centred close to 0.9 eV, on the other hand, can originate from

Table 1

Calculated thermochemical threshold energies for the observed fragments, using the B3LYP and B2PLYP density functionals. The fragments signified as 6-memb. and 5-memb. in the table, refer to the reactions where the 6-membered ring is retained and where rearrangement leads to a 5-membered ring, respectively. These are shown in Fig. 2.

Anionic fragment	Neutral fragment	ΔH (eV)	
		B3LYP	B2PLYP
[PFP – HF] [−] 6-memb.	HF	0.29	0.59
[PFP – HF] [−] 5-memb.	HF	−0.36	−0.19
[PFP – (H + F)] [−]	H + F	6.12	6.44
[PFP – (HF + CO)] [−]	HF + CO	1.40	1.63
[PFA – HF] [−] 6-memb.	HF	0.52	0.82
[PFA – HF] [−] 5-memb.	HF	0.76	0.96
[PFA – (H + F)] [−]	H + F	6.36	6.66
[PFP – 2HF] [−]	2HF	0.77	0.96
[PFP – HF] [−]	HF	0.61	0.89
[PFT – (H + F)] [−]	H + F	6.44	6.73

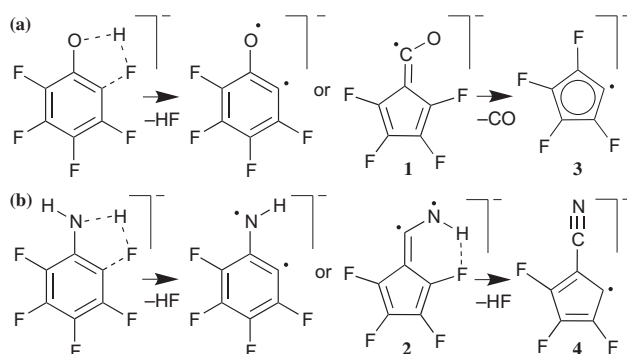


Figure 2. Proposed fragmentation mechanism for the formation of; (a) [M – HF][−] and [M – (HF + CO)][−] from PFP and (b) [M – HF][−] and [M – 2HF][−] from PFA.

the intact six-membered ring as well as the five-membered ring structure **1**.

For the HF abstraction from PFA, thresholds of 0.52 eV and 0.82 eV are calculated with B3LYP and B2PLYP, respectively, if it is assumed that the negatively charged fragment retains the initial six-membered ring structure. Marginally higher values of 0.76 and 0.96 eV are calculated with B3LYP and B2PLYP if it is assumed that the product ion has a five-membered ring and a terminal CNH group, i.e., the C₅F₄–CNH[−] anion shown with structure **2** in Figure 2b. These calculations predict that both these channels are accessible in PFA throughout the higher energy resonance, but cannot explain the observation of [M – HF][−] ions from PFA close to 0 eV. Through harmonic vibrational frequency calculations of the neutral PFA we observe vibrational modes which could aid in the formation of HF. Three of these modes; ν_5 , ν_6 and ν_7 , are soft bending modes of the N–H and C–F bonds which, through a linear combination, can be described as the stretch of an unformed H–F bond. The vibrational energy of these three modes is around 35 meV so the higher vibrational levels are quite populated even at room temperature. In fact, for ν_5 , ν_6 and ν_7 , the occupation ratio for the first excited vibrational state versus the ground state was found to be about 0.26:1. Therefore, there may be additional energy available from these vibrational modes, which will effectively reduce the incident electron energy required to reach the threshold for this DEA channel. Furthermore, energy in other vibrational modes may be redistributed through intramolecular vibrational energy redistribution (IVR) into modes that aid formation of HF. Looking at the shape of the [M – HF][−] signal it is clear that the maximum (≈ 1 eV) is very close to the thresholds calculated here. From the present experimental results and calculations it appears most likely that the low energy contribution from PFA close to 0 eV is due to ‘hot-band transitions’, hence a part of the energy required

for the DEA process comes from the vibrational energy of the molecule. At room temperature the fraction of molecules with sufficient energy for the DEA process will drop considerably as the incident electron energy drops from 1 eV to about 0 eV. However, the electron attachment cross section should rise fairly steeply with decreasing electron energy, and thus offset some of this drop.

For the [M – HF][−] formation from PFT we calculate the threshold values 0.61 eV and 0.89 eV with B3LYP and B2PLYP, respectively, if we assume the final geometry to be a six-membered ring. Rearrangement of the negatively charged molecular ion product is not found to give a lower threshold. The thermochemical threshold for this channel is thus comparable for PFT and PFA, though no [M – HF][−] formation is observed from PFT.

As mentioned above, our calculations showed the most stable form of the [M – HF][−] from PFP as a cyclic C₅F₄ with an exocyclic CO group (1). If we assume that the formation [M – (HF + CO)][−] from PFP proceeds through a sequential loss of HF and CO leading to the aromatic perfluorocyclopentadien anion, C₅F₄[−], as shown with structure **3** in Figure 2a, we derive a threshold value of 1.40 eV and 1.63 eV with B3LYP and B2PLYP, respectively. The experimental threshold for this process is about 1.2 eV, and considering the electron energy resolution and the accuracy of the calculations the agreement is good. Similarly, if we assume a sequential mechanism for the formation of [M – 2HF][−] from PFA leading to the formation of the C₅F₃–CN[−] anion as shown with structure **4** in Figure 2b, our calculations give thresholds of 0.77 and 0.96 eV with B3LYP and B2PLYP, respectively. Within experimental errors and the accuracy of the calculations, this is in good agreement with the observed experimental threshold of about 1.1 eV for this reaction. If, however, we assume the [M – 2HF][−] fragment from PFA to retain the six-membered ring and to be formed by simple abstraction of two HF molecules, we derive a threshold of 3.09 eV and 3.52 eV with B3LYP and B2PLYP, respectively. It is thus reasonable to assume a sequential HF loss leading to the formation of a five-membered ring with an exocyclic CN group (4).

In the case of PFT the calculated threshold for the formation of [M – HF][−] is found to be 0.61 eV and 0.89 eV with B3LYP and B2PLYP, respectively, but formation of [M – HF][−] from PFT is not observed in the experiment. The absence of [M – HF][−] may be because PFT does not have the higher energy resonance observed for PFA and PFP in the energy range from about 0.5 to about 2 eV. We, however, consider it more likely that this resonance is also present in PFT, but the coupling to the reaction coordinates for HF loss is much weaker and, thus, autodetachment dominates. Sterically, the formation of HF from PFT is just as probable as from PFA and PFP. The polarization of the C–H bond in PFT, however, is considerably less than that of the N–H and O–H bonds in PFA and PFP, respectively. Both neutral PFA and PFP may be stabilized through X–H...F hydrogen bonding. The transition states (X...H...F; see Figure 2) in the dissociation of the TNI may also be stabilized by hydrogen bonding. By contrast, any hydrogen bonding stabilization of the neutral or of the dissociation intermediate of the TNI will be significantly weaker in PFT due to the weaker C–H polarization compared to N–H and O–H.

Intramolecular hydrogen bonding in phenol- and other benzene derivatives has been described in both computational and spectroscopic studies [27–29] and although the interaction is weak, intramolecular hydrogen bonds in these systems contribute significantly to the geometry of the aromatic ring [27].

To further explore the role of hydrogen bonding and geometrical constraints we have calculated the minimum energy path for the rotation of the XH_n substituent group in all three compounds using the Nudged Elastic Band (NEB) method. Figure 3 shows the results for a 360° revolution of the XH_n group in PFA, PFP and PFT.

Figure 3 shows clearly in the case of PFA and PFP the existence of an energy barrier to rotation, but virtually no barrier is found for

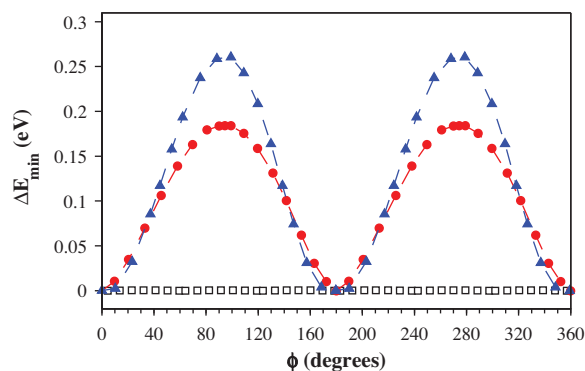


Figure 3. Calculated energy path for the 360° rotation of the XH_n substituent group in PFT (squares), PFA (circles) and PFP (triangles).

PFT. The optimized values for the energy barrier of PFA and PFP at the B3LYP/pc-2 level of theory were found to be 0.26 eV and 0.13 eV, respectively, after the addition of the thermal vibrational energy. In the case of PFT on the other hand we observe a quasi-free rotation of the CH_3 group with a rotational energy barrier of only 0.4 meV. It is clear in the case of PFT that little attractive force exists between the methyl hydrogen and the neighbouring fluorine atom, which confirms the expectation of virtually no hydrogen bonding in PFT. This in turn explains the lack of $[M - HF]^-$ fragment formation from PFT. In the cases of PFA and PFP the rotational barriers have two major causes; the delocalized π -bonding in the molecule and intramolecular hydrogen bonding between H and F. The restricted rotation of the anilinic and phenolic hydrogen atoms will restrict them in the vicinity of the ortho fluorine atoms on the aromatic ring and promote the loss of HF.

5. Conclusions

In the light of these results we conclude that HF formation from both PFA and PFP is most likely coupled to rearrangement of the carbon ring and that the further loss of CO from PFP, and another HF from PFA, is sequential and follows an initial HF loss. Furthermore, it is likely that intramolecular hydrogen bonding plays a pivotal role in the HF excision from PFA and PFP. By suitable choice of substituents the formation of HF can be used to fuel DEA channels at low incident electron energies, where the attachment cross sections are commonly very high. Such reactions have the potential of enabling otherwise inaccessible electron induced reactions at surfaces and in the gas phase and could also prove valuable in the production of relatively high intensity neutral and negative ion beams.

Acknowledgements

The authors acknowledge financial support from the Icelandic Centre for Research (RANNIS), the University of Iceland Research Fund, the EPSRC and the Royal Society. B.O., E.H.B. and O.I. acknowledge support for a visit to Belfast by the European Network ITS-LEIF. Special thanks goes to Ragnar Bjornsson for technical assistance concerning calculations. This work was conducted within the framework of the COST action CM0601 on electron controlled chemical lithography.

References

- [1] L.G. Christophorou, J.K. Olthoff, *Appl. Surf. Sci.* 192 (2002) 309.
- [2] Lu. Qing-Bin, *Phys. Rep.* 487 (2010) 141.
- [3] I. Baccarelli, I. Bald, F.A. Gianturco, E. Illenberger, J. Kopyra, *Phys. Rep.* 508 (2011) 1.
- [4] I. Bald, J. Langer, P. Tegeder, O. Ingólfsson, *Int. J. Mass Spectrom.* 277 (2008) 4.
- [5] S. Ptasińska, S. Denifl, V. Grill, T.D. Märk, E. Illenberger, P. Scheier, *Phys. Rev. Lett.* 95 (9) (2005) 093201.
- [6] H. Flosadóttir et al., *Angew. Chem. Int. Ed.* 46 (2007) 8057.
- [7] V.S. Prabhudesai, A. Kelkar, D. Nandi, E. Krishnakumar, *Phys. Rev. Lett.* 95 (2005) 143202.
- [8] O. Ingólfsson, F. Weik, E. Illenberger, *Int. Rev. Phys. Chem.* 15 (1996) 133.
- [9] I. Bald, I. Dbkowska, E. Illenberger, O. Ingólfsson, *Phys. Chem. Chem. Phys.* 9 (2007) 2983.
- [10] P. Papp, J. Urban, Š. Matejčík, M. Stano, O. Ingólfsson, *J. Chem. Phys.* 125 (2006) 204301.
- [11] A. Mauracher et al., *Phys. Chem. Chem. Phys.* 9 (2007) 5680.
- [12] P. Sulzer, F. Rondino, S. Ptasińska, E. Illenberger, T.D. Märk, P. Scheier, *Int. J. Mass. Spectrom.* 272 (2008) 149.
- [13] J. Langer, M. Stano, S. Gohlke, V. Foltin, Š. Matejčík, E. Illenberger, *Chem. Phys. Lett.* 419 (2006) 228.
- [14] I. Dbkowska, H.D. Flosadóttir, M. Orzol, S. Ptasińska, I. Bald, O. Ingólfsson, E. Illenberger, *Phys. Chem. Chem. Phys.* 11 (2009) 5323.
- [15] Yu-Ran Lue, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, New York, 2007.
- [16] S. Denifl, Š. Matejčík, B. Gstir, G. Hanel, M. Probst, P. Scheier, T.D. Märk, *J. Chem. Phys.* 118 (2003) 4107.
- [17] S. Denifl, S. Ptasińska, M. Probst, J. Hrusak, P. Scheier, T.D. Märk, *J. Phys. Chem. A* 108 (2004) 6562.
- [18] T.A. Field, A.E. Slattery, D.J. Adams, D.D. Morrison, *J. Phys. B: At. Mol. Opt. Phys.* 38 (2005) 255.
- [19] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [20] C.T. Lee, W.T. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [21] S. Grimme, *J. Chem. Phys.* 124 (2006) 034108.
- [22] F. Jensen, *J. Chem. Phys.* 115 (2001) 9113.
- [23] M. Valiev et al., *Comput. Phys. Commun.* 181 (2010) 1477.
- [24] H. Jónsson, G. Mills, K.W. Jacobsen, *Classical and Quantum Dynamics in Condensed Phase Simulations*, World Scientific, Singapore 385, 1998.
- [25] ChemShell, A Computational Chemistry Shell. Available from: <www.chemshell.org>.
- [26] J. Kaestner, J.M. Carr, T.W. Keal, W. Thiel, A. Wander, P. Sherwood, *J. Phys. Chem. A* 113 (2009) (1865) 11856.
- [27] A. Kovacs, I. Macsari, I. Hargittai, *J. Phys. Chem. A* 103 (1999) 3110.
- [28] A. Kovacs, A. Szabo, I. Hargittai, *Acc. Chem. Res.* 35 (2002) 887.
- [29] A. Kovacs, V. Izvekov, G. Keresztury, C.J. Nielsen, P. Klæboe, *Chem. Phys.* 335 (2007) 205.