A Unified Energy Decomposition and Delocalization Approach to Rare-Gas Excimer Bonding

Marcos Mandado(✉)

Department of Physical Chemistry, University of Vigo, Lagoas-Marcosende s/n, 36310 Vigo, Spain
mandado@uvigo.es

Abstract. The nature of the bonding in rare-gas excimers is examined through the combination of interaction energy decomposition and electron delocalization analysis. Herein, the Deformation Density-based Energy Decomposition Analysis (DD-EDA) framework is extended to the study of intermolecular interactions in electronically excited state complexes. Within this framework the total interaction energy is decomposed into electrostatic, intermolecular exchange, spin repulsion and polarization energies. This interaction energy decomposition is applied to Ne_2 and Kr_2 excimers in their lowest-lying excited states and the results are compared to those obtained for the corresponding geometrically unrelaxed ground-state complexes. Even though all the energy terms increase upon excitation, the polarization energy clearly emerges as the main stabilizing component. Visualization of the polarization density reveals a pattern that differs significantly from that exhibited by highly dispersive interactions in ground state, reflecting the dominant effect of excitonic resonance in the excimer polarization, in agreement with previous works. Analysis of the Domain-Averaged Fermi Hole Density (DAFH) and electron delocalization indices (DIs) reveals the excitonic resonance also leads to a substantial increase in the interatomic electron delocalization, with DI values that agree with a marked covalent character, in contrast with the small negative values obtained in the unrelaxed ground-state complexes. These results show that the strong binding in rare-gas excimers arises from the interplay between enhanced non-covalent interactions and excitation-induced electron delocalization (covalency).

Keywords: Excimers · Excited-State Complexes · Energy Decomposition Analysis · TDDFT · Electron Delocalization

1 Introduction

Excimers are molecular complexes that are bound exclusively in electronically excited states and dissociate upon relaxation to the ground state [1]. This unusual bonding mechanism gives rise to characteristic spectroscopic signatures, including broad and red-shifted emission bands, and plays a central role in many photophysical and photochemical processes [1–6]. Because their stability emerges only upon excitation, excimers provide a unique framework for exploring intermolecular interactions beyond the ground-state paradigm.

© The Author(s), under exclusive license to Springer Nature Switzerland AG 2027
O. Gervasi et al. (Eds.): ICCSA 2026 Workshops, LNCS 16766, pp. 281–290, 2027.
https://doi.org/10.1007/978-3-032-30539-8_21

Rare-gas excimers have been extensively employed in laser technologies [7, 8] and constitute prototypical systems for investigating the nature of excited-state bonding [9–11]. In their ground state, rare-gas atoms interact only weakly through dispersion forces, leading to very shallow potential energy surfaces [12]. Upon excitation, however, they form strongly bound dimers with significantly reduced equilibrium distances and large binding energies [13]. This dramatic change in interaction strength highlights the fundamental role of electronic excitation in modifying intermolecular forces.

Understanding the origin of this stabilization requires a detailed analysis of the different contributions to the interaction energy [11]. Traditional descriptions often emphasize the role of dispersion forces in weakly bound systems. However, in excited states, additional effects arise from electronic exchange, and charge and excitonic resonances between equivalent configurations [14, 15]. These effects can lead to significant electron delocalization between fragments, introducing a degree of covalent character into the interaction.

Previous theoretical studies have shown that helium excimer exhibit strong exchange–correlation energy and bond order, challenging the conventional view of these systems as purely van der Waals complexes and suggesting covalent nature [9, 10]. In particular, the resonance character of the excited-state wavefunction implies that the excitation may be delocalized over both atoms, giving rise to bonding mechanisms that cannot be captured by classical noncovalent interactions alone.

In this work, we present an investigation of the nature of bonding in rare-gas excimers by combining energy decomposition analysis within the DD-EDA framework [16] with complementary descriptors of intermolecular electron delocalization. This approach enables a unified interpretation of excimer stabilization in terms of both energetic contributions and electronic structure, providing new insight into the fundamental mechanisms governing excited-state intermolecular interactions.

2 Theoretical Section

2.1 DD-EDA for Excited-State Complexes

Within the DD-EDA framework, the intermolecular interaction energy is decomposed into physically meaningful contributions, namely, electrostatic (elec), intermolecular exchange (exch), spin-repulsion (rep) and polarization:

$$E_{int} = E_{elec} + E_{exch} + E_{rep} + E_{pol} \tag{1}$$

where the polarization term encompasses induction and dispersion contributions. However, a rigorous separation of polarization into induction and dispersion is only possible for weak interactions where second-order perturbation effects are sufficient and higher-order terms are negligible [16]. This is not the case in rare-gas excimers, so that we will not perform the decomposition of the polarization energy into induction and dispersion. Moreover, the sum of the intermolecular exchange and spin-repulsion contributions corresponds to the well-known Pauli repulsion energy, which can be examined separately within the DD-EDA framework [16]. It is worth noting that the term intermolecular exchange denotes the attractive component of the Pauli energy, arising—as

the name suggests—from electronic exchange between different monomers. In contrast, spin-repulsion refers to the repulsive component of the Pauli energy, originating from changes in the one-electron density induced by the Pauli exclusion principle.

The formalism is applicable to both idempotent and non-idempotent density matrices. In the case of excited states described within TDDFT, the density matrix is non-idempotent and can be diagonalized to yield natural orbitals and occupation numbers. This allows the extension of the DD-EDA scheme to excited states without modification of its fundamental structure.

A key aspect of the extension concerns the definition of the non-interacting reference system. For excimers formed by identical fragments (monomers A and B), the excited state is described by a symmetric combination of configurations in which the excitation is localized on either fragment. The corresponding electron density for the non-interacting system is then constructed as an average of ground- and excited-state (GS and ES) monomer densities, ensuring a consistent and physically meaningful reference.

$$\langle \rho \rangle = \frac{1}{2}\left(\left\langle \rho_A^{\mathrm{GS}} \right\rangle + \left\langle \rho_A^{\mathrm{ES}} \right\rangle + \left\langle \rho_B^{\mathrm{GS}} \right\rangle + \left\langle \rho_B^{\mathrm{ES}} \right\rangle\right) \tag{2}$$

The electrostatic energy is evaluated using these averaged densities, while exchange and spin-repulsion contributions are obtained through weighted orthogonalization of the monomers' natural orbitals [16]. This procedure provides a direct and internally consistent way of analyzing intermolecular interactions in excited states.

2.2 Intermolecular Electron Delocalization

To characterize the covalent component of the interaction, intermolecular electron delocalization was analyzed using both qualitative and quantitative descriptors.

Domain-Averaged Fermi Hole (DAFH) densities provide a spatial representation of electron delocalization by describing the extent to which the exchange–correlation hole associated with one fragment extends into the domain of the other. For excited states in this work, the one-electron approximation proposed by Cooper and Ponec based on natural orbitals was employed [17],

$$g_\Omega(\mathbf{r}) = \sum_{i,j} n_{ij}(\Omega)\eta_i(\mathbf{r})\eta_j(\mathbf{r}) \tag{3}$$

where η_i denote the natural orbitals and $n_{ij}(\Omega)$ is the domain occupation matrix, defined as

$$n_{ij} = \sqrt{n_i n_j} \sum_k S_{ik}(\Omega) S_{kj}(\Omega) \tag{4}$$

Here n_i are the natural occupation numbers and S represents the overlap integrals between natural orbitals evaluated within the spatial domain Ω.

Delocalization indices (DIs) were used as quantitative measures of electron sharing between fragments. In the case of rare-gas excimers, DIs were computed between the two atoms forming the dimer. As will be shown in the next section, large positive values

were found for the excited-state dimers, indicating large electron sharing and covalent character, whereas small negative values were obtained for the ground state dimers in the excited state geometries.

Within the one-electron approximation, which is also adopted here for the calculation of DIs in the excited states, delocalization indices are given by

$$\mathrm{DI}_{\Omega,\Omega'} = \sum_{i,j} \sqrt{n_i n_j} S_{ij}(\Omega) S_{ji}(\Omega') \tag{5}$$

2.3 Computational Details

The Ne_2 and Kr_2 excimers were optimized in their lowest-lying excited state (S1) using TDDFT with the M06-2X functional and the aug-cc-pVTZ basis set, including D3 dispersion correction. Basis-set effects were analyzed using the aug-cc-pVXZ series and the basis set superposition error (BSSE) evaluated using the counterpoise (CP) correction [18]. Electronic structure calculations were performed using Gaussian 16 software package [19].

Interaction energies and their components were evaluated for the excited state complexes, as well as for the geometrically unrelaxed ground state complexes (GS/S1) obtained upon vertical electronic relaxation, using the DD-EDA scheme within a locally modified version of the EDA-NCI software [20] that implements the calculation of excited state complexes. DAFH densities and DIs were computed using local algorithms from natural orbitals obtained in the electronic structure calculations. Both Mulliken and QTAIM atomic domains were employed in the calculations.

Polarization, spin-repulsion and DAFH densities were visualized and the corresponding images created using GaussView 6 [21].

3 Results and Discussion

3.1 Structure and Interaction Energies

The symmetry of the lowest-lying excited state of Ne_2 and Kr_2 corresponds to Σ_u^+. The optimized geometries are in good agreement with previous theoretical studies reporting ab initio high-level calculations, confirming the reliability of the computational approach employed in this work. Thus, the Ne–Ne and Kr-Kr equilibrium distances obtained here are 1.78 and 2.72 Å, respectively, only slightly larger than the values of 1.71 and 2.65 Å reported using the CC2 method [22]. As expected, excitation leads to significantly shorter interatomic distances compared to the ground state, reflecting the emergence of strong attractive interactions.

A critical aspect of the analysis concerns the treatment of basis-set effects. The interaction energies obtained for the aug-cc-pVXZ (with X = 2–5) basis set series with and without CP correction are represented in Fig. 1. The results show that CP correction leads to a systematic underestimation of binding energies in the excited states, yielding values that deviate significantly from the CC2 reference data (−19.60 and −20.98 kcal/mol for Ne_2 and K_2, respectively) [22]. In contrast, uncorrected interaction energies exhibit

only minor variations with basis-set size and are close to the previously reported data, indicating an effective cancellation between BSSE and intrinsic basis-set incompleteness. It must be noticed that BSE arises from the use of finite basis sets, whereas BSSE originates from evaluating the dimer in the full basis while describing the monomers with their individual basis sets. Consequently, BSSE leads to an overestimation of the IE, whereas BSE typically results in its underestimation. All of this suggests that, for rare-gas excimers, the use of CP-uncorrected interaction energies provides a more reliable description of binding, particularly when diffuse basis functions are employed.

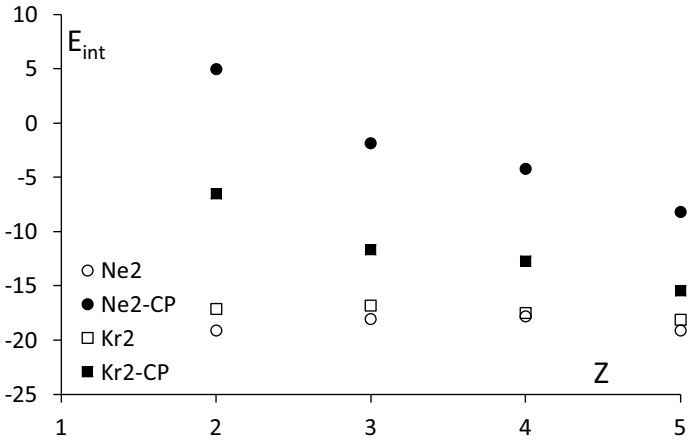

Fig. 1. IEs (in kcal/mol) obtained for the Ne_2 and Kr2 (squares) excimers using the aug-cc-pVXZ basis set series with and without CP correction at the TDDFT/M06-2X-D3 level.

3.2 Energy Decomposition Analysis

The DD-EDA results collected in Table 1 reveal a substantial increase in all interaction energy components upon excitation from GS/S1 to S1. This behavior reflects the increased overlap between the atomic densities in the excited state.

Electrostatic interactions become significantly more attractive, highlighting the importance of charge penetration effects. At the same time, the spin repulsion increases due to enhanced overlap, although this increase is partially offset by a corresponding rise in the attractive intermolecular exchange contribution. This large increase in the spin repulsion energy is qualitatively reflected on the spin repulsion densities depicted in Fig. 1 for the S1 and GS/S1 states. As anticipated, the spin-repulsion density shows a redistribution of electron density away from the intermolecular region—where orbital overlap is greatest—toward the atomic centers. This pattern becomes much more pronounced in the excited states, in line with the corresponding energy trends, which indicate stronger repulsion compared to the ground states. The effect is especially striking in Ne_2, where the depletion of electron density not only occurs between the atoms but also extends into the outer regions surrounding them, underscoring the significant interpenetration of the Ne atoms in the excimer.

Table 1. Interaction energy decomposition analysis performed within the DD-EDA framework for the Ne_2 and Kr_2 complexes in their lowest-lying excited state (S1) and in the unrelaxed ground state obtained upon vertical electronic emission (GS/S1).

	Ne_2		Kr_2	
	S1	GS/S1	S1	GS/S1
Electrostatic	−46.29	−12.45	−60.73	−20.28
Pauli	116.03	38.64	129.57	51.73
Exchange	−71.91	−46.28	−60.72	−47.02
Repulsion	187.94	84.92	190.29	98.75
Polarization	−87.81	−4.52	−85.68	−11.61
Total	−18.07	21.67	−16.84	19.84

However, the most significant change is observed in the polarization energy, which increases dramatically and becomes the dominant stabilizing term. The relative increase in polarization is particularly pronounced in Ne_2, where it exceeds an order of magnitude compared to the ground-state configuration. In Kr_2, a similar trend is observed, although the relative increase is somewhat smaller due to the already significant polarization present in the ground state.

This large increase in the polarization energy in the excited state cannot be attributed solely to purely dispersion forces. Instead, it reflects the influence of the resonance character of the excited-state wavefunction, including exciton and charge-transfer resonance forms. Thus, when the wavefunction—and consequently the reference electron density defined in Eq. 2—is fully relaxed to that of the complex, the resulting polarization densities shown in Fig. 2 are obtained. For both Ne_2 and Kr_2 excimers, these densities display features that deviate from those typical of purely dispersive interactions with an accumulation and depletion of electrons in the intermolecular and intramolecular regions, respectively. This is, however, observed for the Kr_2 dimer in the GS/S1 state. Consistent with the ALMO-EDA study by Ge and Head-Gordon [11]—which identified exciton splitting as the leading contribution to the interaction energy in rare-gas excimers—our results reveal clear signatures of this effect in the polarization density. In Ne_2, the influence is particularly strong, as electron density shifts away from the bond axis into regions perpendicular to it, extending this intratomic electron redistribution into the interatomic region. This reflects the role of exciton resonance in shaping the polarization density. For Kr_2, in addition to this behavior, a faint sandwich-like redistribution appears within the interatomic region: electron density accumulates at the center while depletion occurs on either side, consistent with a small purely dispersion contribution.

These results suggest that the stabilization of rare-gas excimers is governed primarily by polarization effects arising from excitation-induced charge redistribution, rather than by dispersion alone. The strong binding is also assisted by an increase in the attractive first-order terms—namely electrostatic and intermolecular exchange interactions—which partially offset the significant rise in spin repulsion associated with the close interatomic distances in the excimers.

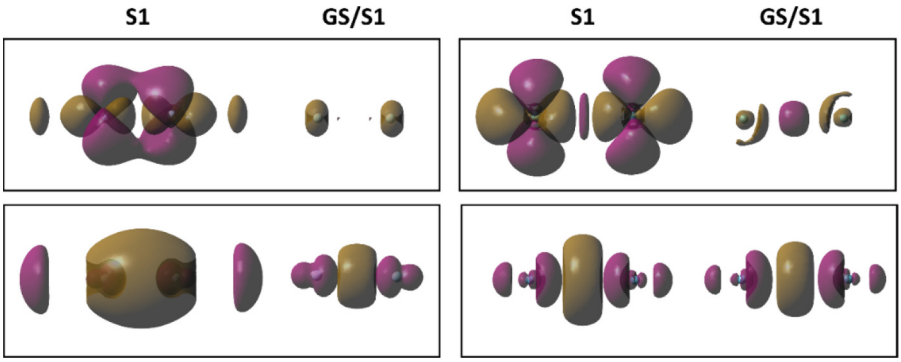

Fig. 2. Polarization (upper panels) and spin-repulsion (bottom panels) densities obtained for the lowest-lying excited state (S_1) and unrelaxed ground state (GS/S_1) complexes of Ne_2 (left panels) and Kr_2 (right panels). Brown and magenta colours represent negative and positive densities, respectively. The plots are represented using an isosurface value of $2{\cdot}10^{-3}$ au.

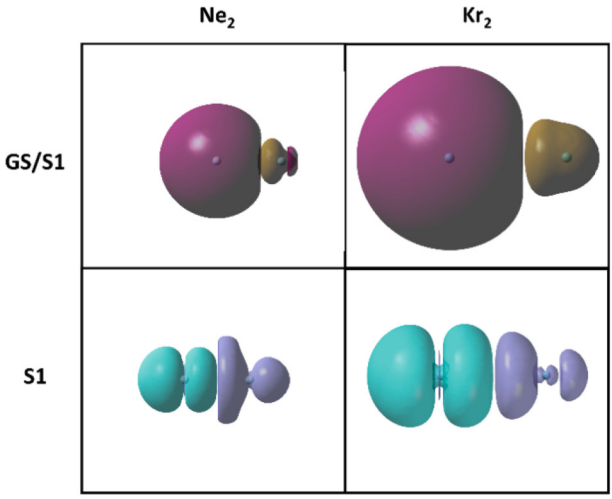

Fig. 3. DAFH density plots for the GS/S_1 states of Ne_2 and Kr_2 dimers (upper panels) and DAFH density difference upon excitation to the S_1 state (bottom panels). Magenta and violet colours represent positive density whereas brown and aquamarine blue colours represent negative density. The plots are represented using an isosurface value of $2{\cdot}10^{-3}$ au.

3.3 Intermolecular Electron Delocalization

The analysis of electron delocalization provides compelling evidence for the emergence of covalent character in rare-gas excimers strongly linked to the exciton resonance mechanism [15].

DAFH densities are depicted in Fig. 3. In order to highlight the bonding changes associated to the excitation, in Fig. 3 we have represented for the excited states the difference of the DAFH densities with respect to the unrelaxed ground states. They

show a pronounced increase in electron sharing upon excitation, with electron density associated with one atom extending significantly into the region of the other. This effect is absent in the unrelaxed ground-state configurations, where electron delocalization is negligible or even slightly antibonding.

Quantitative analysis through delocalization indices confirms this picture (see Table 2). In the excited states, DIs take large positive values, indicating strong electron sharing and a significant degree of covalent interaction. In contrast, the unrelaxed ground-state configurations exhibit small negative values, consistent with non-bonding or antibonding character.

Table 2. DIs for the Ne_2 and Kr_2 complexes in their lowest-lying excited state (S1) and in the unrelaxed ground state obtained upon vertical energy relaxation (GS/S1).

	S1		GS/S1	
	QTAIM	Mulliken	QTAIM	Mulliken
Ne-Ne	0.614	0.480	−0.013	−0.019
Kr-Kr	0.764	0.601	−0.033	−0.045

These results demonstrate that excitation induces a transition from weak, noncovalent interactions to strongly delocalized bonding characterized by significant electron sharing.

4 Conclusions

This work presents a thoroughly study of the bond strength in rare-gas excimers based on interaction energy decomposition and electron delocalization analysis. The results of the energy decomposition indicate that although vertical electronic excitation from the hypothetical geometrically unrelaxed ground-state complexes leads to a significant enhancement of all interaction energy components, polarization energy clearly emerges as the dominant stabilizing contribution. Contrary to intermolecular ground-state complexes formed by non-polar systems, the enhancement of polarization energy cannot be explained solely by an increase of dispersion forces. Conversely, the polarization density reflects the large influence of excitonic resonance on the electron charge redistribution upon complexation, in agreement with previous works where excitonic splitting was pointed out as the main stabilizing factor [11].

Both qualitative (DAFH densities) and quantitative (DIs) analyses reflect a large increase of interatomic electron delocalization upon electronic excitation, revealing a significant covalent character in the excimers. This contrasts with the weak and even antibonding character observed in the corresponding unrelaxed ground-state complexes, associated with small and negative values of DIs.

In summary, excitation-induced electron delocalization in rare-gas excimers, arising from excitonic resonance effects, produces a large enhancement of the polarization energy, largely stabilizing the complexes in the excited state. This stability is also

assisted by the increase of other attractive energy components, such as electrostatic and intermolecular exchange, which partially offset the significant enhancement of the spin repulsion energy.

The findings presented in this work provide a physically grounded picture of bonding in rare-gas excimers and contribute, in general, to our understanding of intermolecular interactions in excited state complexes.

Acknowledgments. This study was funded by Ministerio de Ciencia e Innovación (grant number PID2022-138023NB-I00) and Xunta de Galicia (grant number GRC2024/27).

Disclosure of Interests. The authors have no competing interests to declare that are relevant to the content of this article.

References

1. Birks, J.B.: Excimers. Rep. Prog. Phys. **1975**(38), 903–974 (1975)
2. Birks, J.B.: Photophysics of Aromatic Molecules. Wiley, London (1970)
3. Förster, T., Kasper, K.: Ein Konzentrationsumschlag der Fluoreszenz des Pyrens. Z. Phys. Chem. **1**, 275–277 (1954)
4. Valeur, B., Berberan-Santos, M.N.: Molecular Fluorescence: Principles and Applications, 2nd edn. Wiley-VCH, Weinheim (2012)
5. Winnik, F.M.: Photophysics of preassociated pyrenes in aqueous polymer solutions and in other organized media. Chem. Rev. **93**, 587–614 (1993)
6. Turro, N.J., Ramamurthy, V., Scaiano, J.C.: Modern Molecular Photochemistry of Organic Molecules. University Science Books, Los Angeles (2010)
7. McCusker, M.: The rare gas excimers. In: Rhodes, C.K. (ed.) Excimer Lasers Topics in Applied Physics, vol. 30, pp. 47–86. Springer, Berlin, Heidelberg (1979)
8. Basting, D., Marowsky, G. (eds.): Excimer Laser Technology. Springer, Berlin, Heidelberg (2005)
9. Casals-Sainz, J.L., Jara-Cortés, J., Hernández-Trujillo, J., Guevara-Vela, J.M., Francisco, E., Martín Pendás, A.: Exotic bonding regimes uncovered in excited states. Chem. Eur. J. **25**, 12169–12179 (2019)
10. Jara-Cortés, J., Manuel Guevara-Vela, J., Martín Pendás, A., Hernández-Trujillo, J.: Chemical bonding in excited states: energy transfer and charge redistribution from a real space perspective. J. Comput. Chem. **38**, 957–970 (2017)
11. Ge, Q., Head-Gordon, M.: Energy decomposition analysis for excimers using absolutely localized molecular orbitals within time-dependent density functional theory and configuration interaction with single excitations. J. Chem. Theory Comput. **14**, 5156–5168 (2018)
12. Laschuk, E.F., Martins, M.M., Evangelisti, S.: Ab initio potentials for weakly interacting systems: homonuclear rare gas dimers. Int. J. Quantum Chem. **95**, 303–312 (2003)
13. Jones, A.C., Loeff, T.F., Heath, B.J., Goerigk, L.: Rare-gas excimers and exciplexes: surprising challenges for time-dependent density functional theory approaches. Polyhedron. **280**, 117678 (2025)
14. Morrison, A.F., You, Z.-Q., Herbert, J.M.: Ab initio implementation of the Frenkel-Davydov exciton model: a naturally parallelizable approach to computing collective excitations in crystals and aggregates. J. Chem. Theory Comput. **10**, 5366–5376 (2014)
15. Li, X., Parrish, R.M., Liu, F., Kokkila Schumacher, S.I., Martínez, T.J.: An ab initio exciton model including charge-transfer excited states. J. Chem. Theory Comput. **13**, 3493–3504 (2017)

16. Mandado, M.: Electron Density-Based Energy Decomposition Analysis: from QM to QM/MM Calculations, pp. 1–38. Springer, Berlin Heidelberg (2025)
17. Cooper, D.L., Ponec, R.: A one-electron approximation to domain-averaged Fermi hole analysis. Phys. Chem. Chem. Phys. **10**, 1319–1329 (2008)
18. Boys, S.F., Bernardi, F.: The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Mol. Phys. **19**, 553–566 (1970)
19. Frisch, M. J., et al: Gaussian16 Revision C.01. (2016)
20. Mandado, M., Van Alsenoy, C.: EDA-NCI: Energy decomposition analysis of non-covalent interactions. https://github.com/marcos-mandado/EDA-NCI. Last Accessed 30 Mar 2025
21. Dennington, R., Keith, T.A., Millam, J.M.: GaussView, Version 6. Semichem Inc., Shawnee Mission, KS (2016)
22. Huenerbein, R., Grimme, S.: Time-dependent density functional study of excimers and exciplexes of organic molecules. Chem. Phys. **343**, 362–371 (2008)