**PAPER**

Cite this: DOI: 10.1039/c8cp06160b

Ab initio quantum-chemical computations of the absorption cross sections of HgX\(_2\) and HgXY (X, Y = Cl, Br, and I): molecules of interest in the Earth’s atmosphere†

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The electronic-structure properties of the low-lying electronic states and the absorption cross sections (\(\sigma(E)\)) of mercury halides HgCl\(_2\), HgBr\(_2\), HgI\(_2\), HgBrCl, HgClI, and HgBrI have been determined within the UV-vis spectrum range (170 nm \(\leq \lambda_{\text{photon}} \leq 600\) nm) by means of the DKH3-MS-CASPT2/SO-RASSI quantum-chemical methodology (with the ANO-RCC basis set) and a semi-classical computational strategy based on nuclear sampling for simulating the band shapes. Computed band energies show a good agreement with the available experimental data for HgX\(_2\) with errors around 0.1–0.2 eV; theoretical and \(\sigma(E)\) are within the same order of magnitude. For the mixed HgXY compounds, the present computed data allow us to interpret previously proposed absorption bands estimated from the spectra of the parent molecules HgX\(_2\) and HgY\(_2\), measured in methanol solution. The analyses performed on the excited-state electronic structure and its changes around the Franck–Condon region provide a rationale on the singlet–triplet mixing of the absorption bands and the heavy-atom effect of the Hg compounds. Furthermore, the present benchmark of HgX\(_2\) and HgXY absorption \(\sigma(E)\) values together with the previous benchmark of the electronic-structure properties of HgBr\(_2\) [see S. P. Sitkiewicz, et al., J. Chem. Phys., 2016, 145, 244304] has been helpful to set up a methodological and computational protocol which shall be used for predicting the atmospheric absorption and photolysis properties of several Hg compounds present in the atmospheric cycle of Hg.

1 Introduction

Due to its volatile nature, much research on mercury (Hg) has over the past two decades focused on its atmospheric dispersal and cycling. Anthropogenic emissions to the atmosphere are essentially in the elemental Hg(0) form which is oxidized to divalent Hg(II),\(^{1,2}\) the reactive form that is deposited to Earth’s surface mostly by rain and becomes bioaccumulative species. The harmful effects of mercury on the environment are already well known and can affect our health, animal life, and the ecosystems on Earth, as happened in the human disaster of Minimata (Japan) in 1956. Relevant oxidation products are Hg\((n)XY\), with X, Y representing halogen atoms or oxygen species such as BrO, O, OH, or NO\(_2\). These species are reduced in the atmosphere, which competes with deposition. However, the mechanism of the corresponding process is still poorly understood. Literature is scarce on experimental and theoretical information on the kinetics and thermodynamics of atmospheric mercury oxidative processes, and basically absent in the case of the response to irradiation under atmospheric conditions.\(^{3–4}\) This last aspect is highly relevant since a source of reduction could be \(\text{via}\) light absorption. In this context, accurate theoretical methods for computing UV-vis absorption spectra and effective \(\sigma(E)\) of mercury derivatives are necessary in order to predict elemental mercury atmospheric processes.

Among the Hg\((n)XY\) compounds, mercury halides (which from now on we denote as HgX\(_2\) and HgXY, with X, Y = Cl, Br, and I) are probably the systems for which more experimental data have been reported to date regarding electronic-structure and spectroscopic properties. Hence, these systems can be used
in the benchmarks of computational strategies to establish accurate approaches with a predictive character for more complicated systems.

So far, for the mercury species of interest in this work, the gas-phase absorption spectra have been experimentally measured for HgCl₂, HgBr₂, and HgI₂. Their similarities in the visible and near UV part of the energy spectrum are the occurrence of three absorption bands: an initial low-intensity and broad band at low energies (band a), a high-intensity and sharp band at higher energies (band b), and an even sharper band in the close vicinity of band b but at slightly higher energies (band c). These bands are red-shifted upon increasing the atomic number of the halogen atoms in HgX₂. According to the four available experimental studies, the energy positions of the band maxima (nm) for HgCl₂, HgBr₂, and HgI₂, in this order, are the following: (i) 202, 211 225, 229.5/221,9 and 262/271 for band a, (ii) 182, 181 190/197/193/194,9 and 225/219/225 for band b, and (iii) not reported (out of the range of measured energies), 18 1331/183,12 and 2081/201/208 for band c.

For the mixed halide compounds HgBrCl, HgClI, and HgBrI – absorption spectra have been derived from measurements in methanol solutions (not in the gas phase). Griffiths and Anderson calculated the $\sigma(E)$ data of these systems from the measured spectra of mixed methanol solutions of HgX₂ + HgY₂, where the HgXY are formed.13,14 We shall use this data for comparisons with the results obtained in our computations. It can be easily seen in the HgXY experimental spectra, reported only in the range 200–340 nm, that low-intensity absorption signals spread over the two a-type bands of the parent molecules HgX₂ and HgY₂ and a higher-intensity and sharper band appears in between the b-type bands of the parent molecules.13,14

From a theoretical viewpoint, we should emphasize that the study of the excited-state electronic-structure properties of Hg compounds is in general quite complex, especially when spectroscopic accuracy is desired. Firstly, the use of multi-reference methods is required to correctly describe the multi-configurational character of the excited states.15,16 Secondly, relativistic effects in molecules with heavy atoms such as Hg and I have to be accounted for – both scalar relativistic effects (through the choice of a proper Hamiltonian and a suitable basis set), and spin–orbit coupling (SOC) (since this type of interaction is also relevant for the excited states and often ground states).16–21 Most of the computational studies on the mercury halides found in the literature were focused on the ground-state electronic structure,19,20,22–25 with some exceptions such as the work of Wadt published in 1980.13 This author determined the electronic-structure of the ground and low-lying excited states of HgCl₂ and HgBr₂ on the basis of a moderate-size configuration interaction (CI) method, named POL(1) CI, and a double-$\zeta$ plus polarization quality basis set with effective core potentials (ECPs). According to his calculations, bands a, b, and c were assigned to the transition from the $1^2\Sigma^+_u$ ground state to the $1^1\Pi_u$, $1^2\Sigma^+_u$, and $2^2\Sigma^+_g$ singlet states, respectively. However, in his work the SOC effect was not considered and the scalar relativistic effects were accounted for with approximated ECPs. Recently, we carried out an extensive theoretical analysis on the electronic states of IBr and HgBr₂ in order to establish a useful and highly accurate theoretical methodology for predicting vertical absorption energies ($\Delta E$) and associated oscillator strengths ($f$) of the Hg-based systems.16 On the basis of the results, we confirmed some of Wadt’s predictions. In addition, we concluded that, for HgBr₂, band a has a complex nature, originating from several singlet–singlet and singlet–triplet transitions to low-lying coupled $\Sigma$ and $\Pi$ states. Band b corresponds to a pure singlet–singlet transition to the $1^1\Sigma^+_u$ state. Meanwhile, band c occurs due to the transition to the $1^3\Sigma^+_u$ state (contrary to Wadt’s computations, in which such a transition was spin-symmetry forbidden).15,16

In the present work, we have used the previously established16 high-level multireference multiconfigurational methodology – complete-active-space self-consistent field/multi-state complete-active-space second-order perturbation theory/spin–orbit restricted-active-space state-interaction (CASSCF/MS-CASPT2/ SO-RASSI) – for the electronic-structure computations of the HgXY halides with two objectives. Firstly, the study aims to characterize and interpret the red shifts of the transition bands upon changing the X atom to a heavier halogen atom and the spectral modifications arising for the asymmetric structures (with distinct X and Y halogen atoms) as compared to the $\sigma(E)$ of the symmetric HgX₂ molecules. Secondly, we have gone one step further from the conventional determination of theoretical absorption properties, based on $\Delta E$ and associated $f$ at one (equilibrium) geometry from the Franck–Condon region, and we have computed the absorption-spectra band shapes of the symmetric and asymmetric HgXY molecules in the UV-vis part of the energy spectrum (up to 170 nm) with relevance to atmospheric chemistry. In order to achieve this goal, we have used a nuclear-ensemble computational approach able to predict, with relatively good accuracy, absorption spectra with physically-meaningful band shapes, as proposed by Barbatti and co-workers.26–28 The same computational methodology has been recently used in other work,29 extending the study to other Hg(n)XY species, which has evaluated the impact that efficient atmospheric photoreduction of Hg(n) has over the global Hg cycle. This study together with the present one allows us to conclude that gaseous Hg(n) photolysis can dominate global atmospheric mercury reduction and lead to substantial changes in atmospheric mercury lifetime, transport, and deposition.

2 Computational details

In the first part of this section, details are given on the used CASSCF/MS-CASPT2/SO-RASSI30–32 quantum-chemical methodology for computing the $\Delta E$, which are also named vertical excitation energies, and $f$ between electronic states of HgX₂ and HgXY. In the second part, the nuclear-ensemble computational approach for determining $\sigma(E)$ is described.
2.1 Quantum-chemical methodology

The CASSCF/MS-CASPT2\textsuperscript{31,33–35} methodology with the third-order Douglas-Kroll and Hess (DKH3) Hamiltonian\textsuperscript{38–41} and the atomic-natural-orbital relativistic-correlation-consistent (ANO-RCC) basis set of valence quadruple-\(\zeta\) plus polarization quality (hereafter, ANO-RCC-VQZP)\textsuperscript{42} have been used in the present study as calibrated in our previous work on IBr and HgBr\textsubscript{2}.\textsuperscript{16} Highly accurate \(\Delta E\) and \(f\) were obtained with this methodology showing a good agreement with the experimental values with errors around 0.2 eV. We summarize here the details of the methodology and describe the adaptation done for the presently-studied molecules. Regarding the active-space selection, in our previous work we already discussed the proper CAS for these systems (necessary for the description of transitions in the energetic range of interest).\textsuperscript{16} In this study we have chosen the (12,10) active space corresponding to 12 active electrons distributed over 10 natural orbitals (NOs) of the following character: \(\sigma/\sigma^+\)-type (Hg 6s \(\pm\) Cl 3p/Br 4p/1 5p\(z\)), \(\sigma^\text{nb}\)-type (Cl 3p/Br 4p/1 5p\(z\)), \(\pi^\text{nb}\)-type (Cl 3p\(xy\)/Br 4p\(xy\)/1 5p\(xy\)) and \(\pi\) (Hg 6p\(xy\)) (see Fig. 1; note the additional parity symmetry in the case of HgX\textsubscript{2} systems and also note the asymmetric effects in AO contributions for mixed HgXY molecules). The \(\sigma^+\)-type orbital related to the Hg 6p\(z\) \(\pm\) Cl 3p/Br 4p/1 5p\(z\) atomic orbital contributions was included in the active space, although it was not significantly occupied in any of the excited-state wavefunctions. Two last NOs of non-bonding character, consisting of Br 4d\(xy\) + Br 4d\(xy\) AOs and used in our first benchmark study with CAS(12,12),\textsuperscript{16} were shown to be not necessary for the determination of the absorption spectra and were therefore omitted in the present computations.

The previous benchmark study\textsuperscript{16} included also comparisons of the suitability of all-electron basis sets (ANO-RCC-VQZP\textsuperscript{12} and Sapporo-DKH3-QZF\textsuperscript{43,44}) against basis sets with electron-core potentials (Def2QZVP\textsuperscript{45} and aug-cc-pVQZ-PP\textsuperscript{46–49}), the number of state-average (SA) roots in the SA-CASSCF wavefunction optimizations, the ionization potential electron affinity (IPEA)\textsuperscript{50} parameter of the CASPT2 method and the single- and multi-state approaches of this method. Furthermore, the role of SOC in the computed vertical transitions was also analyzed. The basis sets with ECPs (the first two) provided poor descriptions in some cases with strong SOC, and therefore they are not adequate for an accurate determination of the electronic transitions in the systems studied here. The ANO-RCC basis set was shown to be particularly efficient due to its general contraction scheme, which makes it more flexible in the characterization of the excited states. Meanwhile, 8 state-averaged (SA)-CASSCF roots in all the irreducible representations (IrReps) of the \(D_{2h}\) point group were found to provide a good description of the electronic states of interest. The IPEA shift of 0.25 a.u. of the CASPT2 method improved the transition energies by 0.2–0.4 eV with respect to the results obtained with the non-modified zeroth-order Hamiltonian of CASPT2. The single- and multi-state approaches of CASPT2 gave rise to basically the same energies, although the latter provided a better description of the relative intensity of the absorption bands in HgBr\textsubscript{2}. Finally, the benchmark showed that a description based on the spin–orbit (SO) states rather than spin-free (SF) states is mandatory for these halogen/mercury molecular systems since some bands (such as band c) arise as the result of the SOC. All these established parameters have been also employed in the present study for accurately determining \(\Delta E\) and \(f\) in the HgXY molecules. An imaginary shift with a value of 0.2 a.u. was also used to minimize the effect of weakly-interacting intruder states.\textsuperscript{51} Oscillator strengths \((f)\) were similarly computed as described in the previous work.\textsuperscript{16} All the electronic-structure computations

Fig. 1. Selected (12,10) active space for the symmetric HgX\textsubscript{2} (top) and asymmetric HgXY (bottom) compounds. In HgXY, note the small polarization of the \(\pi^\text{nb}\) (\(\pi^\text{nb}\)) orbital toward the more (less) electronegative halogen, represented with the green (brown) ball.
were carried out using the MOLCAS 8 quantum-chemistry software.25

2.2 Semi-classical spectrum simulations using geometry ensembles

Whereas the main features of a typical UV-Vis spectrum normally come from the electronic transitions from the ground state to the excited states at the Franck–Condon equilibrium geometry, the actual shape of the observed electronic absorption bands originates from more subtle transitions between vibrational states of different electronic states.29,53,54 For such band-shape determination, detailed information on the vibrational part of the wavefunction corresponding to each of the excited states is required. Some approaches are available to determine the rovibrational patterns of one or a few low-lying electronic states in diatomic and triatomic molecules.55 However, we are interested in a huge number of SO states (see Section 2.1) spanning all the wavelengths of relevance in the atmosphere (170 nm ≤ λphoton ≤ 600 nm), and it must be taken into account that the electronic-structure determinations of the studied mercury compounds require one to account for relativistic effects such as scalar relativity and SOC. In addition, we pursue a common and general approach valid also for molecules in which the number of degrees of freedom do not allow us to determine the full dimensionality of the PES, such as those studied in a related study.29 Therefore, the vibrational states and couplings can only be estimated by using approximate strategies. An adequate computational strategy, which was previously used in other theoretical studies by Barbatti and co-workers and which has been also employed here, is based on generating a representative ensemble of sampled geometries \( \mathbf{R}_k \) around the ground-state equilibrium structure and combining the computed \( \Delta E \) and \( f \) (obtained separately for each geometry) to build up the bands26,27,56,57. A semi-classical approach was then used (based on an average of the data obtained from the ground-state geometrical ensemble), which allows to approximate the vibrational structure of the absorption bands. No nuclear wavefunction of the excited electronic states is required and high-level quantum-chemistry methodologies such as CASSCF/MS-CASPT2/SO-RASSI can be used in the electronic-structure calculations, which was a mandatory condition in our study as described above. Furthermore, such methodology allows for the automation of the computations which is of great importance for carrying out the present study and upcoming works on Hg compounds with larger molecular size.

Hence, the absorption cross sections \( \sigma(E) \) were computed for each photon energy \( E \) separately, by using the following equation:26

\[
\sigma(E) = \frac{1}{N_p} \frac{\pi e^2}{2m c \hbar} \sum_k \int_{f E_0}^{f E_0 + \Delta E_0} f_\omega(R_k) g(E - \Delta E_0(R_k), \delta) \]  

(1)

where \( e \) and \( m \) are the charge and mass of the electron, respectively, \( c \) is the speed of light in a vacuum, \( \nu_0 \) is the vacuum permittivity, \( N_p \) is the number of sampled geometries, and \( N_{\text{exc}} \) is the number of excited states. Calculated separately for each sampled geometry \( R_k \), \( f_\omega \) is the oscillator strength of the transition from the ground state to the \( l \)-th excited state and \( g(E - \Delta E_0(R_k), \delta) \) is the Gaussian-type shape function that accounts for the broadening of the resonant lines of the spectra and depends on the nature of the transition (in our case, the electronic excitations from the ground to the excited states):26

\[
g(E - \Delta E_0(R_k), \delta) = \left( \frac{2}{\hbar} \right)^{1/2} \frac{1}{\delta} \exp \left( \frac{-2}{\delta^2} (E - \Delta E_0(R_k))^2 \right) \]  

(2)

On the energetic scale \( E \), each of the Gaussian functions is centered at the vertical transition energy to a particular \( l \)-th excited state, \( \Delta E_0(R_k) \), and \( \delta \) is the phenomenological broadening. These computations do not take into account the temperature or the refractive index of the medium. Thus, vibrationally cold molecules in the gaseous phase are considered. In the present work, the statistical error of the sampling \( \delta \sigma(E) \) is measured as the standard deviation for the particular sampled photon energy \( E \), in a slightly different manner to the one presented in the study of Crespo-Otero and Barbatti:26,27

\[
\delta \sigma(E) = \sqrt{\frac{\sum_{l=1}^{N_p} (\sigma_l(E) - \sigma(E))^2}{N_p(N_p - 1)}} \]  

(3)

where \( \sigma_l(E) \) is the signal at photon energy \( E \) obtained from a particular geometry \( R_k \):

\[
\sigma_l(E) = \frac{\pi e^2}{2m c \hbar} \int_{f E_0}^{f E_0 + \Delta E_0} f_\omega(R_k) g(E - \Delta E_0(R_k), \delta) \]  

(4)

Sampling of the nuclear coordinates \( R_k \) was done according to the Wigner distribution58 for the optimized ground spin-free (SF) states and using the corresponding vibrational harmonic frequencies of the normal modes.26,27,59 The optimization and vibrational analysis were carried out numerically, at the same level of theory used in the electronic-structure calculations of the excited states [DKH3-CASPT2(12,10)/ANO-RCC-VQZP] with the MOLCAS 8 program. The sampled geometries \( R_k \) were generated with the 1.4 NEWTON-X program,26,60,61 using the obtained information on the equilibrium structures, whereas the calculation of \( \sigma(E) \) was done with an in-house program. At each of the sampled geometries, the MS-CASPT2 computations of \( \Delta E \) and \( f \) were performed with the \( C_s \) symmetry constraint on the wavefunction (all three atoms were placed in the XOY plane). For each of the IrRep belonging to the \( C_s \) point group, \( A' \) and \( A'' \), we chose \( N_p = 10 \) for the number of SF states in the CASSCF/CASPT2 computations because it includes all relevant SF transitions up to 170 nm. Finally, \( N_p = 100 \) geometries were used along with a broadening of the Gaussian shape functions of \( \delta = 0.05 \text{ eV} \), adequate for the triatomic systems studied in this work.

Benchmark computations were also carried out varying the number of sampled geometries and the method used to generate the ground-state minimum geometry and associated frequencies. Thus, nuclear ensembles of 20, 50, 75, and 100 geometries were generated from the CASPT2 equilibrium structure and...
frequencies and tested. In addition, absorption spectra were also computed, using sampling based on the equilibrium structures and frequencies obtained with the coupled-cluster method including single and double excitations (CCSD) and density functional theory (DFT) with the PBE0 functional, both with the Def2ZVP basis set and using the Gaussian09 (revision C.01) program.62 The atomic masses of the Hg, Cl, Br, and I atoms used in the computations are 201.9706, 34.9688, 78.9183, and 126.9045 Da, which correspond to the most abundant isotopes. For both tests, see a short discussion presented in Section SII of the ESL†.

3 Results and discussion

In this section, we firstly present the computed geometrical parameters (bonds and angles) and vibrational frequencies of the normal modes for the compounds studied in this work and compare them with data from the literature.19,20,63,64 Secondly, the electronic structures of the low-lying SF and SO electronic states are analyzed and discussed in detail, focusing separately on the symmetric HgX2 and mixed HgXY halides (X, Y = Cl, Br, and I). Finally, the computed $\sigma(E)$ are compiled and compared with the experimental spectra.

3.1 Equilibrium ground-state structures

The theoretical and experimental data available in the literature for the mercury–halogen bond distances ($R_{HgX}$) together with those computed in this work with the CASPT2/ANO-RCC-VQZP methodology are compiled in Tables SI and SII (see ESL†). In this section, we will focus only on the main trends. For the HgX2 molecules, experimental measurements using the electron diffraction technique and compiled by Hargittai give rise to equilibrium geometries with Hg–X bond lengths of 2.240, 2.374, and 2.558 Å for X = Cl, Br, and I, respectively. Other experimental data deviate by up to 0.04 Å.63 In contrast, for the mixed molecules (HgXY), the values of $R_{HgY}$ slightly overestimates the bond distances, while CASPT2 underestimates them.

In general, all methodological approaches considered here predict linear structures for the ground-state equilibrium of the HgXY compounds, which is in agreement with the experimental observations.16,19,20,63 The behaviour is different for some low-lying excited states which show bent structures.15,16 This is the case of the low-lying singlet and triplet $\Sigma_1^+$ and $\Pi_1$ electronic states, which become $A_1$ and $B_1/B_2$ states in $C_{2v}$ symmetry, respectively, with bond angles around 90°.15,16

From the comparison of the different bond distances compiled in Tables S1 and SII (ESI†), heavy atom effects can be quantified. The Hg–X bond length in the symmetric compounds (HgX2) increases by 0.13 Å from X = Cl to Br and by 0.17 Å from X = Br to I. For the mixed molecules (HgXY), the change in the Y atom slightly affects the distance of the Hg–X bond and the resulting differences are of order ±0.01 Å.

Regarding the vibrational normal modes, the documented experimental data correspond to UV, Raman, and IR measurements.65–76 The symmetric stretching ($v_{sym}$), asymmetric stretching ($v_{asym}$), and bending ($v_{bend}$) normal modes frequencies are compiled in Tables S1 and SII (ESI†) together with the corresponding theoretical values from the literature (selected DFT19,20 and CC19 methods) and those computed in this study with the CASPT2 method. In general, CASPT2/ANO-RCC-VQZP values of $v_{sym}$, $v_{asym}$, and $v_{bend}$ are larger than the best estimations obtained with the CCSD(T) method. Both theoretical findings are slightly larger than the experimental data. However, the differences are not qualitatively significant and therefore the trends are the same in all cases. It can be easily seen that vibrational frequencies decrease upon increasing the atomic number of the halogen atom. The $v_{bend}$ normal mode is much less affected than $v_{sym}$ and $v_{asym}$. In the HgX2 molecules, substitution of the Hg–Cl bonds with Hg–Br implies a decrease of all frequencies almost twice bigger than that obtained by changing Br for I. This trend is also observed in the case of the mixed HgXY halides for the $v_{bend}$ normal mode, whereas it is not found for $v_{sym}$ and $v_{asym}$, most probably because the last two frequencies are much more affected by the other halogen atom.

3.2 Vertical electronic transitions

Tables 1 and 2 compile the electronic-structure data obtained for the symmetric HgBr2 and asymmetric HgBrCl molecules, respectively, at the DKH3-SOC-MS-CASPT2 [12,10]/ANO-RCC-VQZP level of theory. Analogous tables for the other compounds can be found in the ESL† (see Tables SIII–SVI). In the corresponding calculations, the highest Abelian symmetry point-group of the electronic-structure properties of the HgBr2 molecule as compared to the Def2ZVP and aug-cc-pVQZ-PP basis sets containing ECPs.16 SOC was not considered for the geometry determination due to the negligible effect for the ground-state geometrical parameters. As compared with the best estimations obtained in the literature at the CCSD(T)/CBS(TQ) level and including CV, SO, and SR corrections, the CASPT2 results show in all cases shorter bond lengths with an average difference of 0.014 Å. As compared with the experimental data, CCSD(T)
occupied and lowly-occupied molecular orbitals which are
(X = Cl, Br, and I) gives rise to the following relevant highly-
nation of the Hg and X atoms in the linear HgX₂ molecules

To facilitate comparisons between non-mixed and mixed
Data corresponding to other secondary and non-allowed elec-
important SO states for the absorption spectra are also added.

Triplet states which mix with singlet SF states or which give rise to
mixing. It can be readily seen that for equivalent states, singlet–
energy order, the predicted lowest-energy electronic transition is
and p from the
Similarly, σ’nab → πₐ generates Σ''₄, Π₆, and Σ''₄ states. At high energies (see Table 1), 2¹Σ''₄, which mainly corresponds
to σ’nab → σ''₄ excitation plus some contribution from the σ’nab → πₐ one, is the most probable transition. The 1¹Σ''₄ and
1¹Π₄ states follow, with a decrease of f of one order of magnitude each. Taking into account now the distinct multiplici-
to be readily seen that for equivalent states, singlet–
energy order, the predicted lowest-energy electronic transition is

HgX₂/HgXY molecules was used, the D₂h/C₂ᵥ point group
in SA-CASSCF procedures 8 roots per IrRep were used). The point
The only difference observed is an average decrease of 0.6 eV for
strongly mixed. While the latter dominates the low-energy 1¹Σ''₄ state, the former has a higher weight in the low-energy triplet 1³Σ''₄, which gives rise to the 1¹Π₄ state. Next, σ’nab → σ''₄ gives rise to 1¹Π₄. πₐ → πₐ produces a set of three electronic states Σ₄, Π₅, and Σ₄. Similarly, σ’nab → πₐ generates Σ''₄, Π₆, and Σ''₄ states. At high energies (see Table 1), 2¹Σ''₄, which mainly corresponds
to the σ’nab → σ''₄ excitation plus some contribution from the σ’nab → πₐ one, is the most probable transition. The 1¹Σ''₄ and
1¹Π₄ states follow, with a decrease of f of one order of magnitude each. Taking into account now the distinct multiplici-
to be readily seen that for equivalent states, singlet–
energy order, the predicted lowest-energy electronic transition is

3.2.1 HgX₂. Within the Hartree–Fock picture, the combina-
nation of the Hg and X atoms in the linear HgX₂ molecules
(X = Cl, Br, and I) gives rise to the following relevant highly-
the main SF state contributing to the SO state is indicated
in which the main SF state contributing to the SO state is indicated
in which the focus is only on the Ω number and the
energetic order of the states (for example, 1¹Π₄ and (2)1₄, respectively; see more details in our previous work).¹⁶

Table 1 Symmetry-allowed vertical electronic transitions of HgBr₂ computed at the DKH₃-SOC-MS-CASPT2(12,10)/ANO-RCC-VQZP level of theory at
the ground-state equilibrium geometry, including vertical excitation energies in eV (ΔE) and oscillator strengths (f) for the spin-free (SF) and spin–orbit (SO) states (left and right parts, respectively), the main natural orbital excitations which characterize the SF states (columns 2 and 3, only weights larger than 10% are given, for more information see Table SVIII, ESI), and the main SF states contributing to the SO states (columns 8 and 9, only weights larger than 2% are provided)

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<th>SF state</th>
<th>Weight [%]</th>
<th>Excitation</th>
<th>ΔE [eV]</th>
<th>f [a.u.]</th>
<th>SO state/Ω state</th>
<th>Weight [%]</th>
<th>SF state</th>
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<td>σⁿab → σ''₄</td>
<td></td>
<td></td>
<td>1¹Π₄u</td>
<td>19</td>
<td>1¹Π₄</td>
<td>5.39</td>
<td>0.09004</td>
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<tr>
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<td>23</td>
<td>πⁿab → πₐ</td>
<td>6.36</td>
<td>0.09646</td>
<td>2¹Σ₂⁺u</td>
<td>99</td>
<td>1¹Σ₂⁺</td>
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<tr>
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<td>6.45</td>
<td></td>
<td>2¹Π₄u</td>
<td>68</td>
<td>2¹Π₄</td>
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<tr>
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<td>89</td>
<td>πⁿab → πₐ</td>
<td>6.59</td>
<td></td>
<td>1¹Π₄u</td>
<td>100</td>
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<td>68</td>
<td>1¹Π₄</td>
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<td>σⁿab → σ''₄</td>
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<td>2.52704</td>
<td>2¹Σ₂⁺u</td>
<td>97</td>
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<td>2¹Σ₂⁺</td>
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<td>3¹Π₄u</td>
<td>3</td>
<td>3¹Π₄</td>
<td></td>
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In terms of SO electronic states, it can be seen in Table 1 and Tables SIII, SIV (ESI†) that 11Πu, 1′Σν, and 2′Σν contribute predominantly to (2)1u, (2)0u, and (4)0u, respectively. While (2)0u and (4)0u arise mainly from the respective singlet SF states, (2)1u presents a large participation of triplet states, in particular 1′Σν and 1′Πu. In addition, new probable transitions (with non-negligible f-values) appear mainly arising from triplet states (which are forbidden without SOC). This is the case of (1)1u, (1)0u, (3)1u, and (3)1u, with f values of 0.004–0.007. The comparison of the SO data for the distinct halogen compounds allows us to analyze the heavy-atom effect, which contributes by increasing the SOC or singlet-triplet mixing. This can be easily seen by analyzing the contributions of singlet and triplet SF states to the SO states. Thus, greater mixing appears in Hgl₂ as compared to HgBr₂ and HgCl₂, which in some cases makes transitions more probable and in other cases less probable depending on the relative contribution of singlet and triplet SF states. Significant changes of several orders of magnitude in the f values can be seen, for example, in the transition to the (1)0u state, with f = 0.00001, 0.00645, and 0.04102 for HgCl₂, HgBr₂, and HgI₂, respectively. The (3)1u SO state also has higher f values for Hgl₂ and HgBr₂ than for HgCl₂. Meanwhile, the transition to the (5)1u SO state with a pure triplet character is also more probable for the Hgl₂ compound than for HgBr₂ and is very small in HgCl₂.

Table 2 Symmetry-allowed vertical electronic transitions of HgBrCl computed at the DKH3-SOC-MS-CASPT2(12,10)/ANO-RCC-VQZP level of theory at the ground-state equilibrium geometry, including vertical excitation energies in eV (ΔE) and oscillator strengths (f) for the spin-free (SF) and spin–orbit (SO) states (left and right parts, respectively), the corresponding SF states of Dₐu symmetry in HgX₂, the main natural orbital excitations which characterize the SF states (columns 3 and 4, only weights larger than 10% are given, for more information see Table S5, ESI), and the main SF states contributing to the SO states (columns 9 and 10, only weights larger than 2% are provided).
3.2.2 HgXY. Electronic-structure properties of the mixed halides can be related to those of the pure mercury–halogen compounds. The following trends are observed in such a HgX2–HgXY comparison.13 Firstly, transitions to the $1^1\Pi$ state, which correspond to $\pi_{\pi}^{nb} \rightarrow \sigma^{+\nu}$ orbital excitations, are close in energy to the corresponding $1^1\Pi_u$ state ($\pi_u^{nb} \rightarrow \sigma^{+\nu}$) of the parent halide with the highest electronegativity halogen atom (similarly for the gerade-like $1^1\Pi$ state, which involves $\pi_{\pi}^{nb} \rightarrow \sigma^{+\nu}$ excitations and is related to the $1^1\Pi_u$ state of the parent compounds mainly formed by the $\pi_u^{nb} \rightarrow \sigma^{+\nu}$ excitations). Secondly, electronic transitions to $4^3\Sigma^+$ ($\sigma_g \rightarrow \sigma^{+\nu}$) related to $3^3\Sigma^+$ ($\sigma_g \rightarrow \sigma^{+\nu}$) show the opposite behaviour and they appear closer to the corresponding states of the non-mixed halide with the lowest electronegativity halogen atom (higher atomic number). Meanwhile, transitions to the set of $2^3\Sigma^-$, $1^3\Delta$, and $1^1\Sigma^-$ states, which correspond to $\pi_u^{nb} \rightarrow \pi$ NO excitations and are related to the set of $2^3\Sigma_u$, $1^3\Delta_u$, and $1^1\Sigma_u$ states, respectively, with $\pi_u^{nb} \rightarrow \pi_u$ relevant excitations, appear in between the corresponding transitions of the parent halides (similarly for the gerade-like states $3^1\Sigma^+$, $2^1\Delta$, and $2^1\Sigma^- (\pi_u^{nb} \rightarrow \pi)$ related to $2^3\Sigma_u$, $1^3\Delta_u$, and $1^1\Sigma_u (\pi_u^{nb} \rightarrow \pi_u$ states of HgX2)).

In general, there are five relevant vertical electronic transitions in the SF description of the mixed halides, ascribed to the energetically ordered $1^1\Pi$, $2^1\Pi$, $2^3\Sigma^+$, $3^3\Sigma^+$, and $4^3\Sigma^-$ states. The most intense is the last one, whereas distinct relative intensities appear when the other transitions are compared in the three compounds. In particular, while $3^3\Sigma^+$ is more intense than $2^3\Sigma^+$ in HgClI, their relative intensity decreases in HgBrI, and the opposite trend is found for HgBrCl.

Regarding the energy splitting between related singlet and triplet states, the gaps are higher than those obtained for the non-mixed halides. Singlet–triplet energy splittings are around 0.1 eV for the $\Delta$ and $\Sigma^-$ states and 0.3 eV for the $\Pi$ states. As can be seen in Table 2 and Tables SV, SVI (see ESI†), $\Sigma^+$ states show a strong mixture of the $\pi_{\pi}^{2\nu}/C_0 \rightarrow \pi$ and $\sigma_g/\sigma^{+\nu}/C_0 \rightarrow \sigma^-$ configuration state functions, producing, in general, larger gaps. Similarly to the parent HgX2 compounds, inclusion of a less electronegative halogen atom gives rise to a decrease in $\Delta E$, with an average difference of $0.3 \text{ eV}$ between HgBrCl and HgClI, of $0.3 \text{ eV}$ between HgClI and HgBrI, and of $0.6 \text{ eV}$ between HgBrCl and HgBrI. A proportional shift of 0.3 eV is then obtained when changing one halogen atom in the HgXY (X, Y = Cl, Br, and I) halides.

In the SO description of the absorption spectra, many transitions become probable, which arise not only from dominant singlet SF states but also from singlet–triplet mixture and even dominant triplet SF states. As can be seen by comparing Table 2 and Tables SV, SVI (ESI†), this mixing is more pronounced in HgBrI due to the heavy-atom effect. The brightest transition computed corresponds to the $3^3\Pi$ state which is mainly generated by the singlet $4^3\Sigma^+$ SF state. The other singlet SF states $1^1\Pi$, $2^1\Pi$, $2^3\Sigma^+$, and $3^1\Sigma^+$ give rise mainly to the $(2^1, (5)^1, (4)^0, \text{and} (6)^0$ SF states, respectively. In general, mixing with other triplet SF states is largely increased in the cases of HgBrI and HgClI. At low energies, below that of the important “singlet” $4^3\Pi$ state, the relevant transitions to SO states with dominant triplet character are $(2^3, (3)^3, \text{and} (6)^3$ for HgBrCl and $(2)^3, (3)^3, (3)^0, \text{and} (4)^3$ for HgBrI. The SO states $(2)^3, (3)^3, \text{and} (3)^0$, are basically pure triplet $1^3\Pi$ and $2^3\Pi$ SF states, respectively. Meanwhile, at higher energies, significant transitions characterized by strong triplet components are $(7)^0, \text{and}(8)^0$, for HgClI and HgBrI. They are mainly formed from the $3^3\Pi$ or $2^3\Sigma^-$ SF states.

3.3 Simulated absorption cross sections

As described above in Section 2, benchmark computations were carried out in this work to establish an accurate semi-classical approach for determining the absorption band shapes of the representative HgBr2 and HgXY molecules. We analyzed the effect of the type of method used for determining the ground-state optimized geometries (and corresponding vibrational modes frequencies), which are required for the generation of the set of nuclear configurations, and the effect of considering a different number of configurations in the nuclear sampling (see eqn (1)). An extended analysis of such benchmarks can be found in Section III of the ESL†. In summary, negligible changes are obtained by comparing the $\sigma(E)$ values obtained by using DFT/PBE0, CCSD, or CASPT2 starting geometries and frequencies (see Fig. S1, ESI†). For the second test, since the studied molecular systems have a small number of degrees of freedom, 100 configurations are clearly enough to produce an averaged absorption spectrum (see Fig. S2, ESI†) which compares the spectra generated by sampling 25, 50, 75, and 100 geometries). On the other hand, the $\delta$ value that seems to be more reliable and appropriate is 0.05 eV, since higher values might introduce unphysical band shapes. Also the apparent vibrational resolution that can be obtained with lower $\delta$ values is not reliable because the exact vibronic couplings are not computed here with the semi-classical approximation.

Fig. 2 displays the $\sigma(E)$ of all the HgXY halide compounds, computed in the present study with the DKH3-SOC-MS-CASPT2(12,10)/ANO-RCC-VQZP level of theory and the semi-classical approximation for the nuclear sampling. Spectra of the HgBr2 and HgBrCl representatives are displayed in Fig. 3 and 4, respectively, along with the experimental absorption spectra reported in the literature.9,11–13 The analogous figures for the remaining compounds were moved to the ESI† for the sake of a more appropriate organization of the work. Note that for the symmetric HgX2 molecules, experimental spectra correspond to gas-phase data,9–12 whereas for the mixed halides they are obtained from measurements in methanol solution.12 Therefore, for HgXY, the simulated spectra in vacuo are not strictly comparable to the experimental spectra. Dipole moments, which are helpful for a rough qualitative analysis on the possible effects of polar solvents on the band shifts, are compiled in Table SXVI of the ESI†. In general, excited states of HgXY are characterized by larger dipole moments than that of the ground state. This is in part related to the asymmetric AO contributions to the excitations from the halogen atoms to Hg (see Fig. 1). Consequently, general solvatochromic shifts to the red might be expected especially in highly polar solvents.
Finally, we shall focus in this section on the UV-vis absorption spectra of interest up to around 170 nm, which includes electronic transitions with energies up to those of the $\text{Hg}^+\text{Cl}^+$ and $\text{Hg}^+\text{Br}^+$ states for $\text{HgX}_2$ and $\text{HgXY}$, respectively. This corresponds to the bands a, b, and c of $\text{HgCl}_2$ discussed in Section 1. At higher energies, Rydberg states are present according to the experimental observations. These states might interact with the valence states and affect the computed electronic-transition properties of the latter. Computation of Rydberg states requires basis sets with extra diffuse functions and inclusion of the Rydberg orbitals in the active space, which is out of the scope of our work focused on an accurate determination at lower energies.

### 3.3.1 $\text{HgX}_2$

In general, the energy positions and shapes of the bands are reproduced well, as compared with the experimental data, especially for $\text{HgCl}_2$ and $\text{HgBr}_2$. In $\text{HgI}_2$, discrepancies appear between distinct reported experimental spectra (see Fig. S4, ESF†) and for this system, our simulations show a better agreement with the spectrum measured by Maya. Band intensities do not show such good agreement with the experimental data, which might be a consequence of the approximation employed for sampling the nuclei. However, experiments show also here different intensities, as can be seen in the case of $\text{HgBr}_2$ in Fig. 3. The best agreement with our simulated spectra is reached for the data from Frantom. In any case, both experimental and theoretical intensities results appear within the same order of magnitude, which implies reasonable simulations taking into account that the relative intensities are well reproduced.

As described in the Introduction, three main bands characterize the UV absorption spectra of the three halogen–mercury...
compounds (bands a, b, and c). The lowest-energy one (band a) is broad with low intensity. Our computations predict band maxima at approximately 6.20 eV (200 nm), 5.55 eV (223 nm), and 4.95 eV (250 nm) for HgCl₂, HgBr₂, and HgI₂, respectively, which are mainly produced by transitions to 1P₁₁, 1P₁₀, 1P₁₉, and 1Σ⁺₁ SO states (see Table 1 and Tables SIII, SIV, ESI†). Therefore, band a involves a certain degree of SOC. For HgCl₂, the most intense transition is related to the 1P₁₁ state with dominant singlet character (1Σ⁺₁). The second most intense transition corresponds to 1P₁₀, which has mainly triplet character (1P₁₀). In HgBr₂, the transition to the “singlet” 1P₁₁ state is still the most intense but now three SO states with triplet dominance have similar σ values: 1P₁₁, 1P₁₀, and 1Σ⁺₁. Finally, in HgI₂, the “triplet” 1P₁₉ becomes the most probable transition, and the “singlet” 1P₁₁ has a similar f to 1P₁₀ and 1Σ⁺₁. Such intense triplet absorptions are the consequence of SOC and heavy-atom effects which are evident by comparing the spectra generated by SF and SO states (see differences in Fig. 3 and Fig. S3, S4, ESI†). Whereas the SF and SO descriptions are similar in HgCl₂ and no significant SOC role can be interpreted from the spectra, band a is clearly more prominent in the SO spectra than in the SF spectra for HgI₂.

Band b is much sharper and more intense than band a and, according to our simulations, it has band maxima at 6.85 eV (181 nm), 6.34 eV (196 nm), and 5.88 eV (211 nm) for HgCl₂, HgBr₂, and HgI₂, respectively. This band mainly originates from the electronic transition to the 1Σ⁺₀ SO state. As can be seen in Table 1 and Tables SIII, SIV (ESI†), this state is mainly formed by the singlet 1Σ⁺₀ SF state with small contributions from states of triplet character (1Σ⁻₀ for HgCl₂ and HgBr₂ and this state plus 1P₁₀ for HgI₂). The “singlet” nature of band b and the increasing “triplet” nature of band a in the series Cl, Br, and I allows us to interpret the distinct relative intensity of the two analyzed bands observed experimentally (a large relative intensity difference in HgCl₂ and small in HgI₂). This is another clear manifestation of the higher SOC for the heavy atom.

In the high-energy part of the spectra, an even sharper band arises (band c), with band maxima at 7.34 eV (169 nm), 6.75 eV (184 nm), and 6.16 eV (201 nm) for HgCl₂, HgBr₂, and HgI₂, respectively. The σ values of this band are the largest in the spectrum of HgCl₂, largely decrease for HgBr₂, and become very low in HgI₂. Band c can be related to the 1Σ⁺₀ SO state, which is mainly formed by the triplet 1Σ⁺₀. However, subtle contributions seem to affect the band intensity. Firstly, in HgCl₂, there is an 8% contribution of the 1Σ⁺₀ state which according to the SF properties has very large σ value (see Table SIII, ESI†). In HgBr₂, the small contribution of the singlet 1Σ⁺₀ state in the ground-state optimized geometry (only 1%; see Table 1) seems to underestimate the intensity of the band in the corresponding spectrum in Fig. 3. For HgI₂, even though the contribution of the 1Σ⁺₀ SF state to the 1Σ⁺₀ SO state is higher (2%; see Table SIV, ESI†), this band almost disappears in the absorption spectrum (see Fig. S4, ESI†). Such findings point to greater mixing of the singlet 1Σ⁺₀ state in HgBr₂ due to the nuclear sampling and a shorter interaction in HgI₂. The triplet nature of band c becomes evident when comparing the spectra with and without the SOC effect. It fully disappears in the SF simulated spectra. This confirms our predictions on the nature of this band (which are contrary to Wadt’s first predictions).15,16 Finally, it is also worth noticing that in HgI₂ a close-lying band at 6.06 eV (205 nm) is present related to the transition to the (5)1g SO state (which is a pure triplet 1Δg). The peak corresponding to this transition cannot be identified in the spectra of the other symmetrical halide compounds.

3.4 HgXY

An intense band is found in the high-energy part of the absorption spectra of HgBrCl, HgClI, and HgBrI with band maxima at 6.52, 6.25 and 6.10 eV, respectively (see Fig. 2). As can be seen by comparing the spectra of the non-mixed and mixed compounds, the energy position of the band for the HgXY molecules is located in between those for the parent HgX₂ and HgYZ systems. Such bands correspond to transitions to the (4)0 SO state with a clearly dominant singlet nature from the 2Σ⁺ SF state, which mainly involve σ²⁻/Cl, Br, and I orbital excitations similarly to the parent compounds (1Σ⁺₀₊, 1Σ⁺₀₋). Therefore, band a involves a certain degree of SOC. For HgXY, two mainly singlet states, 1Π₀ and 2Π₁, contribute to the low-energy part of the spectrum, and one “triplet” state, 1Π₁, appears although with low σ values. For HgClI, two “triplet” SO states, 1Π₀ and 2Π₁, have similar intensities to 2Π₁. In the case of HgBrI, four “triplet” states, 1Π₀, 2Π₁, 2Π₂, and 1Σ⁺₁, and one “singlet” state, 2Π₁, are responsible for the low-energy signals.

Regarding the low-energy part of the spectra, signals have in general lower intensity and are spread over the range of the low-energy band of the parent non-mixed halides. A lack of differences between the SF and SO simulated spectra clearly indicates that this part of the spectra is not very affected by triplet states in HgBrCl (see Fig. 4) while for the other two compounds, HgClI and HgBrI, there are significant triplet contributions (see Fig. S3 and S6, ESI†). Thus, in HgBrCl, two mainly singlet states, 1Π₁ and 2Π₁, contribute to the low-energy part of the spectrum, and one “triplet” state, 1Π₀, appears although with low σ values. For HgClI, two “triplet” SO states, 1Π₀ and 2Π₁, have similar intensities to 2Π₁. In the case of HgBrI, four “triplet” states, 1Π₀, 2Π₁, 2Π₂, and 1Σ⁺₁, and one “singlet” state, 2Π₁, are responsible for the low-energy signals.

Finally, as in the case of HgCl₂ and HgBr₂, the spectra of HgBrCl and HgClI are also characterized by almost pure triplet bands (sharp bands at around 6.7–7.0 eV in the last two compounds). The corresponding electronic transitions are already described in detail in Section 3.2.2 and their nature is once more clearly understood by comparing the SF and SO spectra of Fig. 4 and Fig. S5 (ESI†).

4 Conclusions

In this study, we have extended our previous analysis16 on the nature of the electronic transitions of HgBr₂ to analogous analyses for the HgX₂ and HgXY mercury halides (with X and Y representing the halogen atoms Cl, Br, and I) within the UV-vis range of the energy spectrum up to around 170 nm, followed by simulations of physically meaningful σ(E).

In the first part of the work, in the same manner as in the HgBr₂ study, we have assigned the main electronic bands on the basis of ΔE and f computed at the Franck–Condon geometry.
We have adapted the previously benchmarked CASSCF/MS-CASPT2/2SO-RASSI methodology using the DKH3 Hamiltonian for treating the scalar relativistic effects of the inner electrons and the relativistic-correlation-consistent ANO-RCC-VQZP basis set. The main results of this part confirm the experimental trends observed in the HgX₂ and HgXY UV-vis spectra and provide new information on the nature of the electronic transitions:

1. Electronic excitations (up to 170 nm) are almost of the same nature, and upon increasing the atomic number of the halogen atoms (X or Y) in the series Cl, Br, and I, ΔE systematically decreases by 0.3 and 0.6 eV for the HgXY and HgX₂ halides, respectively.

2. The low-energy part of the absorption spectra with low-intensity signals (band a) has some mixing of singlet and triplet states. The sharp band b, which follows at higher energy, corresponds mainly to singlet states, and band c is basically the electronic transition to a pure triplet state (appearing only with SOC corrections).

3. Stronger singlet–triplet mixing (due to SOC) affects the energetics of the excited states of HgXY halides containing I atoms.

In the second part of this work, we have presented theoretically simulated σ(E) of the studied mercury compounds, which were generated with the semi-classical approach based on computations of ΔE and f for the probed set of geometries (sampled according to the Wigner distribution). This approach has allowed the determination of the general shapes of the electronic bands (and intensities), while keeping a high-level methodology for the electronic-structure computations of the vibrational frequencies for generating the Wigner ensemble.

The results of the benchmarking on the simulations related to the choice of geometrical ensembles have shown the correct applicability of the semi-classical approach. It seems to be invariant to the method employed in the geometry optimizations (and computed vibrational frequencies) for generating the Wigner ensemble. This has been useful in simulations of UV-vis spectra of larger mercury-based compounds, for which computationally cheaper methods (for example DFT) could be chosen for producing the geometrical ensembles.

Overall, the methodological and computational approaches presented in this paper and applied to the HgX₂ and HgXY compounds have allowed us to clearly establish the nature of the UV absorption bands of these molecules (orbital excitations, singlet-triplet mixing, and heavy-atom effects) and systematically relate the bands of the HgXY to those of the parent HgX₂ and HgY₂ compounds. Furthermore, this work has been proved worthy in recent σ(E) predictions in mercury compounds with no available experimental spectra.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
S. P. S. acknowledges the Basque Government for funding through a predoctoral fellowship (PRE 2017 0403). D. R.-S. is thankful to the Spanish MINECO/FEDER for financial support through project CTQ2017-87054-C2-2-P and the Ramón y Cajal fellowship with Ref. RYC-2015-19234.

References


