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***Ab initio* quantum–chemical computations of the absorption cross sections in HgX₂ and HgXY (X, Y=Cl, Br, and I): Molecules of interest on the Earth's atmosphere[†]**

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The electronic–structure properties of the low–lying electronic states and the absorption cross sections of mercury halides HgCl₂, HgBr₂, HgI₂, HgBrCl, HgClI, and HgBrI have been determined within the UV–Vis spectrum range ($170\text{ nm} \leq \lambda_{\text{photon}} \leq 600\text{ nm}$) 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 HgX₂ with errors around 0.1–0.2 eV; theoretical and experimental cross sections (σ) are within the same order of magnitude. For the mixed HgXY compounds, the present computed data allow to interpret previously proposed absorption bands estimated from the spectra of the parent molecules HgX₂ and HgY₂, measured in methanol solution. The analyses performed on the excited–state electronic structure and its changes around the Franck–Condon region allow to clearly rationalize the singlet–triplet mixing of the absorption bands and the heavy–atom effect of the Hg compounds. Furthermore, the present benchmark of HgX₂ and HgXY absorption σ values together with the previous benchmark of the electronic–structure properties of HgBr₂ [see S. P. Sitkiewicz, *et al.*, *J. Chem. Phys.*, 2016, **145**, 244304] allow us 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(II)XY, with X, Y representing halogen atoms or oxygen species such as BrO, O, OH, or NO₂. Such 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 the experimental and theoretical information on the kinetics and thermodynamics of atmospheric mercury oxidative processes, and basically absent in the case of the response to the irradiation in the atmospheric conditions.^{3–8} This last aspect is highly relevant since a source of reduction could be via light absorption. In this context, accurate theoretical methods for computing UV–Vis absorption spectra and effective absorption cross sections of mercury derivatives are necessary in order to predict elemental mercury atmospheric processes.

Among the Hg(II)XY compounds, mercury halides (which from now on we denote as HgX₂ and HgXY, with X, Y = Cl, Br, and

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[†] Electronic Supplementary Information (ESI) available: Tables compiling information on the experimental and theoretical bond lengths for the studied compounds; tables compiling information on computed vertical transitions of HgCl₂, HgI₂, HgClI and HgBrI and the nature of the important electronic states; figures displaying simulated absorption spectra of HgCl₂, HgI₂, HgClI, and HgBrI; section on the benchmark of the computational procedure of simulation of UV–Vis spectra of studied compounds. See DOI: 10.1039/b000000x/

I) are probably the systems for which more experimental data have been reported to date regarding electronic-structure and spectroscopy 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 HgCl_2 , HgBr_2 , and HgI_2 .^{9–12} 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*). Those bands are red-shifted upon increasing the atomic number of the halogen atoms in HgX_2 . According to the four available experimental studies, the energy position of the bands maxima (nm) for HgCl_2 , HgBr_2 , and HgI_2 , in this order, are the following: (i) 202,¹¹ 225¹¹/229¹²/221,⁹ and 262⁹/271¹⁰ for band *a*, (ii) 182,¹¹ 198¹¹/197¹²/194,⁹ and 225¹¹/219⁹/225¹⁰ nm for band *b*, and (iii) not reported (out of range of measured energies),¹¹ 183¹¹/183¹², and 208¹¹/201⁹/208¹⁰ 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 absorption cross sections of these systems from the measured spectra of mixed methanol solutions of $\text{HgX}_2 + \text{HgY}_2$, 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 HgX_2 and HgY_2 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 the spectroscopic accuracy is desired. Firstly, the use of multireference methods is required to correctly describe the multiconfigurational character of the excited states.^{15,16} Secondly, the relativistic effects in molecules with heavy atoms such as Hg and I have to be accounted for – both scalar relativistic effect (through the choice of 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 1980.¹⁵ This author determined the electronic-structure of the ground and low-lying excited states of HgCl_2 and HgBr_2 on the basis of a moderate-size configuration interaction (CI) method, named as POL(1) CI, and a double- ζ plus polarization quality basis set with the effective core potentials (ECPs). According to his calculations, bands *a*, *b*, and *c* were assigned to the transition from the $1^1\Sigma_g^+$ ground state to the $1^1\Pi_u$, $1^1\Sigma_u^+$, and $2^1\Sigma_u^+$ singlet states, respectively. However, in his work the spin-orbit

coupling (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 HgBr_2 in order to establish a useful and highly accurate theoretical methodology for predicting vertical absorption energies and associated oscillator strengths of the Hg-based systems.¹⁶ On the basis of the results, we confirmed some of the Wadt's predictions. In addition, we concluded that, for HgBr_2 , band *a* has a complex nature, originated from several singlet-singlet and singlet-triplet transitions to low-lying coupled Σ and Π 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 $1^3\Sigma_{u0}^+$ state (contrary to Wadt's computations, in which such 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 has been aimed to characterize and interpret the red shifts of the transition bands upon changing the X atom to a heavier halogen atom and the spectra modifications arising in the asymmetric structures (with distinct X and Y halogen atoms) as compared to the absorption cross sections of the symmetric HgX_2 molecules. Secondly, we have gone one step further from the conventional determination of theoretical absorption properties, based on vertical transition energies and associated oscillator strengths 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 in atmospheric chemistry. In order to achieve this goal, we have used a nuclear-ensemble computational approach able to predict, with relatively good accuracy, absorption cross sections with physically-meaningful band shapes, as proposed by Barbatti and co-workers.^{26–28} The same computational methodology has been recently used in another work,²⁹ extending the study to other Hg(II)XY species, which has evaluated the impact that an efficient atmospheric photoreduction of Hg(II) has over the global Hg cycle. This study together with the present one allows to conclude that gaseous Hg(II) 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-RASSI^{30–32} quantum-chemical methodology for computing the vertical transition energies (ΔE), which are also named as vertical excitation energies, and oscillator strengths (*f*) between electronic states of HgX_2 and HgXY . In the second part, the nuclear-ensemble computational approach for determining the absorption cross sections is described.

2.1 Quantum-chemical methodology

The CASSCF/MS-CASPT2^{31,33–35}/SO-RASSI^{36,37} methodology with the third-order Douglas-Kroll and Hess (DKH3) Hamiltonian^{38–41} and the atomic-natural-orbital relativistic-correlation-consistent (ANO-RCC) basis set of valence quadruple- ζ plus polarization quality (hereafter, ANO-RCC-VQZP)⁴² have been used in the present study as calibrated in our previous work on IBr and HgBr₂.¹⁶ Highly accurate ΔE 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. Starting from the active-space selection, in our previous work we already discussed on the proper CAS for these systems (necessary for the description of transitions in the energetic range of interest).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: σ/σ^* -type (Hg $6s \pm \text{Cl } 3p_z / \text{Br } 4p_z / \text{I } 5p_z$ and Hg $6p_z \pm \text{Cl } 3p_z / \text{Br } 4p_z / \text{I } 5p_z$), σ^{nb} -type (Cl $3p_z / \text{Br } 4p_z / \text{I } 5p_z$), and π^{nb} -type (Cl $3p_{x/y} / \text{Br } 4p_{x/y} / \text{I } 5p_{x/y}$ and Hg $6p_{x/y}$) (see Fig. 1; note the additional parity symmetry in case of HgX₂ systems and also note the asymmetric effects in AO contributions for mixed HgXY molecules). The σ^* -type orbital related to the Hg $6p_z \pm \text{Cl } 3p_z / \text{Br } 4p_z / \text{I } 5p_z$ atomic orbitals contributions was included in the active space, although it was not significantly occupied in none of the excited-state wavefunctions. Two last NOs of non-bonding character, consisting of Br $4d_{xz/yz} + \text{Br } 4d_{xz/yz}$ AOs and used in our first benchmark study with a CAS(12,12),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 study¹⁶ included also comparisons of the suitability of all-electron basis sets (ANO-RCC-VQZP⁴² and Sapporo-DKH3-QZP^{43,44}) against basis sets with electron-core potentials (Def2QZVP⁴⁵ and aug-cc-pVQZ-PP^{46–49}), the number of state-average (SA) roots in the SA-CASSCF wavefunction optimizations, the ionization potential electron affinity (IPEA)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 the CASPT2. The single- and multi-state approaches of the CASPT2 gave rise to basically the same energies, although the latter provided a better description of the relative intensity of the absorption bands in HgBr₂. Finally, the benchmark showed that a

Fig. 1 Selected (12,10) active space for the symmetric HgX₂ (top) and asymmetric HgXY (bottom) compounds. In HgXY, note small polarization of π_1^{nb} (π_2^{nb}) orbital toward more (less) electronegative halogen, represented with green (brown) ball.

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 ΔE and f in the HgXY molecules. The imaginary shift with a value of 0.2 a.u. was also used to minimize the effect of weakly-interacting intruder states.⁵¹ Oscillator strengths were similarly computed

as described in the previous work.¹⁶ All the electronic-structure computations were carried out using the MOLCAS 8 quantum-chemistry software.⁵²

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.^{53,54} For such band-shape determination, a detailed information on the vibrational part of the wavefunction corresponding to each of the excited state 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 ($170 \text{ nm} \leq \lambda_{\text{photon}} \leq 600 \text{ nm}$), and it must be taken into account that the electronic-structure determinations of the studied mercury compounds require to account for relativistic effects such as scalar relativity and spin-orbit coupling. In addition, we pursue a common and general approach valid also for molecules in which the number of degrees of freedom do not allow to determine the full dimensionality of the PES, 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 ΔE and f (obtained separately for each geometry) to build up the bands.^{26,27,56,57} 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 equation²⁶:

$$\sigma(E) = \frac{1}{N_p} \sum_k \frac{\pi e^2}{2mc\epsilon_0} \sum_{l \neq 0}^{N_{fs}} f_{0l}(\mathbf{R}_k) g(E - \Delta E_{0l}(\mathbf{R}_k), \delta) \quad (1)$$

where e and m are the charge and mass of the electron, c is the speed of light in vacuum, ϵ_0 is the vacuum permittivity, N_p is a number of the sampled geometries, and N_{fs} is the number of excited states. Calculated separately for each sampled geometry $\mathbf{R}_k$,

f_{0l} is the oscillator strength of the transition from the ground state to the l -th excited state and $g(E - \Delta E_{0l}(\mathbf{R}_k), \delta)$ 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:

$$g(E - \Delta E_{0l}(\mathbf{R}_k), \delta) = \left(\frac{2}{\hbar}\right)^{1/2} \frac{\hbar}{\delta} \exp\left(-\frac{2(E - \Delta E_{0,l}(\mathbf{R}_k))^2}{\delta^2}\right) \quad (2)$$

On the energetic scale E , each of the Gaussian functions is centered at the vertical transition energy to a particular l -th excited state, $\Delta E_{0,l}(\mathbf{R}_k)$, and δ is the phenomenological broadening. These computations do not take into account the temperature or the refraction index of the medium. Thus, vibrationally cold molecules in gaseous phase are considered. In the present work, the statistical error of the samplings ($\delta\sigma(E)$) 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}

$$\delta\sigma(E) = \sqrt{\frac{\sum_{k=1}^{N_p} (\sigma_k(E) - \sigma(E))^2}{N_p(N_p - 1)}} \quad (3)$$

where $\sigma_k(E)$ is the signal at photon energy E obtained from a particular geometry $\mathbf{R}_k$:

$$\sigma_k(E) = \frac{\pi e^2}{2mc\epsilon_0} \sum_{l \neq 0}^{N_{fs}} f_{0l}(\mathbf{R}_k) g(E - \Delta E_{0l}(\mathbf{R}_k), \delta) \quad (4)$$

Sampling of the nuclear coordinates $\mathbf{R}_k$ 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 $\mathbf{R}_k$ were generated with the 1.4 NEWTON-X program^{28,60,61}, using the obtained information on the equilibrium structures, whereas the calculation of the absorption cross sections was done with an in-house program. At each of the sampled geometries, the MS-CASPT2 computations of ΔE 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 $N_{fs}=10$ 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 $\delta=0.05$ 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 frequen-

cies and tested. In addition, absorption spectra were also computed, using samplings 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 Def2QZVP 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 S.II of the ESI†.

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 structure 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 absorption cross sections 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 S.I and S.II (see ESI†). In this section, we will focus only on the main trends. For the HgX₂ molecules, experimental measurements using electron diffraction technique and compiled by Hargittai⁶³ 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 up to 0.04 Å.⁶³ In contrast, for the mixed HgXY halides, no experimental geometry data is available. Regarding the theoretical studies, two main group of works can be highlighted in which the DFT method and CCSD with perturbative triplet excitations [CCSD(T)] are used. Kim *et al.* carried out benchmark computations with several DFT functionals and analyzed the effect of including SOC.²⁰ The authors conclude that PBE0 functional produces good estimations of the equilibrium structure. On the other hand, Balabanov and Peterson reported high-level *ab initio* CCSD(T) data with aug-cc-pVXZ-PP basis sets and analyzed the effects of basis sets, SOC, scalar relativity (SR) effects, and core-valence correlation (CV).¹⁹ Corrections for the CV electron correlation were found to produce the strongest changes although with small differences of up to 0.009 Å.¹⁹ Meanwhile, SR and SOC yielded non-significant contributions, which agrees with the almost pure singlet nature of the $1^1\Sigma_g^+$ ground electronic state as determined in our previous work.^{16,19}

The CASPT2 results were computed in the present study by using the all-electron ANO-RCC-VQZP basis set which was shown to be more accurate for the determination of the geometrical and electronic-structure properties of the HgBr₂ molecule as compared to the Def2QZVP and aug-cc-pVQZ-PP basis sets containing ECPs.¹⁶ SOC was not considered for the geometry determina-

tion 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) 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 Σ_u^+ and Π_u electronic states, which become A₁/B₁ and B₂ states in C_{2v} symmetry, respectively, with bond angles around 90°.^{15,16}

From the comparison of the different bond distances compiled in Tables S.I and S.II, heavy atom effects can be quantified. The Hg–X bond length in the symmetric compounds (HgX₂) increases 0.13 Å from X = Cl to Br and 0.17 Å from X = Br to I. For the mixed molecules (HgXY), the change in 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 corresponds to UV, Raman, and IR measurements.^{65–76} The symmetric stretching (ν_{sym}), asymmetric stretching (ν_{asym}), and bending (ν_{bend}) normal modes frequencies are compiled in Tables S.I and S.II together with the corresponding theoretical values from the literature (selected DFT^{19,20} and CC¹⁹ methods) and those computed in this study with the CASPT2 method. In general, CASPT2/ANO-RCC-VQZP values of ν_{sym} , ν_{asym} , and ν_{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 ν_{bend} normal mode is much less affected than ν_{sym} and ν_{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 by I. This trend is also observed in the case of the mixed HgXY halides for the ν_{bend} normal mode, whereas it is not found for ν_{sym} and ν_{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 ESI† (see Tables S.III–S.VI). In the corresponding calculations, the highest Abelian symmetry point-group of the HgX₂/HgXY molecules was used, D_{2h}/C_{2v} point group (in SA-CASSCF procedures 8 roots per IrRep were used). The point group was later translated by using correlation tables to the full

$D_{\infty h}/C_{\infty v}$ group. The first five columns show the orbital nature and spectroscopic properties of the SF states, while the remaining columns compile the information for the SO states, with SF contributions and SO-based spectroscopic properties. Only symmetry allowed and relevant electronic transitions are included in such tables for both the pure HgX_2 and mixed $HgXY$ halides. Triplet states which mix with singlet SF states or which give rise to important SO states for the absorption spectra are also added. Data corresponding to other secondary and non-allowed electronic transitions can be found in Tables S.VII–S.XVI in the ESI†. To facilitate comparisons between non-mixed and mixed halides, Tables II and S.V–S.VI also show the relationships between SF of the mixed halides and those of the HgX_2 molecules (which are established taking into account the nature (orbital excitations) of the main configuration state function of each SF state). Note that the gerade-like electronic transitions are not symmetry forbidden in the C_{2v} compounds. For the representation of the SO states, two types of notations are used, one in which the information about the main SF state contributing in the SO state is indicated and other in which the focus is only on the Ω number and the energetic order of the states (for example, $1^1\Pi_{u1}$ and $(2)1_u$, respectively; see more details in the previous work).¹⁶

3.2.1 HgX_2

Within the Hartree-Fock picture, the combination of the Hg and X atoms in the linear HgX_2 molecules ($X=Cl, Br, \text{ and } I$) gives rise to the following relevant highly-occupied and lowly-occupied molecular orbitals which are ordered here by their energies: $a_g(\sigma_g^+) < b_{1u}(\sigma_u^{nb+}) < b_{2u}(\pi_u^{nb})/b_{3u}(\pi_u^{nb}) < b_{2g}(\pi_g^{nb})/b_{3g}(\pi_g^{nb}) < a_g(\sigma_g^{*+}) < b_{2u}(\pi_u)/b_{3u}(\pi_u) < b_{1u}(\sigma_u^+)$. In the ground-state Hartree-Fock wavefunction, the first 6 MOs are occupied while the others are empty. As can be seen in Fig. 1, σ_u and $\pi_{u/g}$ -type orbitals are more localized than σ_g -type ones either in the Hg atom or in the X halogen atoms. Based on the orbital energy order, the predicted lowest-energy electronic transitions are $\pi_g^{nb} \rightarrow \sigma_g^{*+}$, which gives rise to the $1^1\Pi_g$ state. Next, $\pi_u^{nb} \rightarrow \sigma_g^{*+}$ gives rise to $1^1\Pi_u$. $\pi_g^{nb} \rightarrow \pi_u$ produces a set of three electronic states Σ_u^+ , Δ_u , and Σ_u^- . Similarly, $\pi_u^{nb} \rightarrow \pi_u$ generates Σ_g^+ , Δ_g , and Σ_g^- states. At higher energies, $2^1\Sigma_u^+$, which mainly corresponds now to the $\sigma_u^{nb+} \rightarrow \sigma_g^{*+}$ excitation plus some contribution from the $\pi_g^{nb} \rightarrow \pi_u$ one, is the most probable transition. The $1^1\Sigma_u^+$ and $1^1\Pi_u$ states follow, with a decrease of the f of one order of magnitude each. Taking into account now the distinct multiplicities, it can be readily seen that for equivalent states, singlet-triplet energy splitting is not larger than 0.1 eV in Π_u , Δ_u , and Σ_u^- . This is not the case of Σ_u^+ , where the configuration state functions represented by the $\sigma_u \rightarrow \sigma_g^*$ and $\pi_g \rightarrow \pi_u^*$ excitations are strongly mixed. While the latter dominates the low-energy $1^1\Sigma_u^+$ state, the former has a higher weight in the low-energy triplet $1^3\Sigma_u^+$. The opposite behaviour is found for the high energy $2^1\Sigma_u^+$ and $2^3\Sigma_u^+$ states. In general, this qualitative description is maintained for the three HgX_2 molecules (see Table I and Tables S.III–S.IV in the ESI†). The only difference observed is an average decrease of 0.6 eV for the ΔE upon increasing the atomic number of the halogen atom, which is ascribed to the lower electronegativity of the X atom and the corresponding energetic increase of the $p_{x/y/z}$

atomic orbital ($3p_{x/y/z} (Cl) < 4p_{x/y/z} (Br) < 5p_{x/y/z} (I)$).

In terms of SO electronic states, it can be seen in Table I and Tables S.III–S.IV that $1^1\Pi_u$, $1^1\Sigma_u^+$, and $2^1\Sigma_u^+$ contribute predominantly to $(2)1_u$, $(2)0_u^+$, and $(4)0_u^+$, respectively. While $(2)0_u^+$ and $(4)0_u^+$ arise mainly from the respective singlet SF states, $(2)1_u$ present a large participation of triplet states, in particular, $1^3\Sigma_u^+$ and $1^3\Pi_u$. 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 $(1)1_u$, $(1)0_u^+$, $(3)1_u$, and $(3)0_u^+$, with f values of 0.004–0.007. The comparison of the SO data for the distinct halogen compounds allows to analyze the heavy-atom effect, which contribute by increasing the SOC or singlet-triplet mixing. This can be easily seen by analyzing the contributions of singlet and triplet SF states in the SO states. Thus, higher mixings appear in HgI_2 as compared to $HgBr_2$ and $HgCl_2$, 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 $(1)0_u^+$ state, with $f = 0.00001$, 0.00645, and 0.04102 for $HgCl_2$, $HgBr_2$, and HgI_2 , respectively. The $(3)1_u$ SO state also has higher f values for HgI_2 and $HgBr_2$ than for $HgCl_2$. Meanwhile, transition to the $(5)1_u$ SO state with a pure triplet character is also more probable for the HgI_2 compound than for $HgBr_2$ and very small in $HgCl_2$.

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 HgX_2 – $HgXY$ comparison.¹³ Firstly, transitions to the $2^1\Pi$ state, which correspond to $\pi_1^{nb} \rightarrow \sigma^{*+}$ orbital excitations, are close in energy to the corresponding $1^1\Pi_u$ state ($\pi_u^{nb} \rightarrow \sigma_g^{*+}$) of the parent halide with the highest electronegative halogen atom (similarly for the gerade-like $1^1\Pi$ state, which involves $\pi_2^{nb} \rightarrow \sigma^{*+}$ excitations and is related to the $1^1\Pi_g$ state of the parent compounds mainly formed by the $\pi_g^{nb} \rightarrow \sigma_g^{*+}$ excitations). Secondly, electronic transitions to $4^1\Sigma^+$ ($\sigma_{g/u} \rightarrow \sigma_g^*$) related to $3^1\Sigma_g^+$ ($\sigma_u^+ \rightarrow \sigma_g^{*+}$) show the opposite behaviour and they appear closer to the corresponding states of the non-mixed halide with the lowest electronegative halogen atom (higher atomic number). Meanwhile, transitions to the set of $2^1\Sigma^+$, $1^1\Delta$, and $1^1\Sigma^-$ states, which corresponds to $\pi_2^{nb} \rightarrow \pi$ NO excitations and are related to the set of $2^1\Sigma_u^+$, $1^1\Delta_u$, and $1^1\Sigma_u^-$ states, respectively, with $\pi_g^{nb} \rightarrow \pi_u$ dominant excitations, appear in between the corresponding transitions of the parent halides, (similarly for the gerade-like states $3^1\Sigma^+$, $2^1\Delta$, and $2^1\Sigma^-$ ($\pi_1^{nb} \rightarrow \pi$) related to the $2^1\Sigma_g^+$, $1^1\Delta_g$, and $1^1\Sigma_g^-$ ($\pi_u^{nb} \rightarrow \pi_u$) states of HgX_2).

In general, there are five relevant vertical electronic transitions in the SF description of the mixed halides, ascribed to the energetically ordered $1^1\Pi$, $2^1\Pi$, $2^1\Sigma^+$, $3^1\Sigma^+$, and $4^1\Sigma^+$ 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 the $3^1\Sigma^+$ is more intense than $2^1\Sigma^+$ in $HgClI$, their relative intensity decreases in $HgBrI$, and the opposite trend is found for $HgBrCl$.

Regarding the energy splitting between related singlet and

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 excitations 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 S.VIII), and the main SF states contributing to the SO states (columns 8 and 9, only weights larger than 2% are provided)

SF state	Weight [%]	Excitation	ΔE [eV]	f [au]	SO state/ Ω state	Weight [%]	SF state	ΔE [eV]	f [au]
$1^1\Sigma_g^+$	93		0.00		$1^1\Sigma_{g0}^+$ (1) 0_g^+	100	$1^1\Sigma_g^+$	0.00	
$1^3\Pi_u$	85	$\pi_u^{nb} \rightarrow \sigma_g^{+*}$	5.17		$1^3\Pi_{u1}$ (1) 1_u	72	$1^3\Pi_u$	5.09	0.00663
						28	$1^1\Pi_u$		
$1^1\Pi_u$	86	$\pi_u^{nb} \rightarrow \sigma_g^{+*}$	5.29	0.02444	$1^3\Pi_{u0}^+$ (1) 0_u^+	100	$1^3\Pi_u$	5.34	0.00645
					$1^1\Pi_{u1}$ (2) 1_u	53	$1^1\Pi_u$	5.32	0.01296
						30	$1^3\Sigma_u^+$		
$1^3\Sigma_u^+$	88	$\sigma_u^{+nb} \rightarrow \sigma_g^{+*}$	5.50		$1^3\Sigma_{u1}^+$ (3) 1_u	16	$1^3\Pi_u$		
						69	$1^3\Sigma_u^+$	5.62	0.00474
						19	$1^1\Pi_u$		
$1^1\Sigma_u^+$	65	$\pi_g^{nb} \rightarrow \pi_u$	6.36	0.09646	$1^1\Sigma_{u0}^+$ (2) 0_u^+	12	$1^3\Pi_u$		
	23	$\sigma_u^{+nb} \rightarrow \sigma_g^{+*}$				99	$1^1\Sigma_u^+$	6.39	0.09004
$2^3\Sigma_u^+$	87	$\pi_g^{nb} \rightarrow \pi_u$	6.45			1	$1^3\Sigma_u^-$		
					$2^3\Sigma_{u1}^+$ (4) 1_u	68	$2^3\Sigma_u^+$	6.21	1.9E-06
						32	$1^3\Sigma_u^-$		
$1^3\Delta_u$	89	$\pi_g^{nb} \rightarrow \pi_u$	6.59		$1^3\Delta_{u1}$ (5) 1_u	100	$1^3\Delta_u$	6.53	0.00053
$1^3\Sigma_u^-$	88	$\pi_g^{nb} \rightarrow \pi_u$	6.74		$1^3\Sigma_{u0}^-$ (3) 0_u^+	99	$1^3\Sigma_u^-$	6.77	0.00389
					$1^3\Sigma_{u1}^-$ (6) 1_u	68	$1^3\Sigma_u^-$	7.03	0.00084
						32	$2^3\Sigma_u^+$		
$2^1\Sigma_u^+$	70	$\sigma_u^{+nb} \rightarrow \sigma_g^{+*}$	8.08	2.52704	$2^1\Sigma_{u0}^+$ (4) 0_u^+	97	$2^1\Sigma_u^+$	8.10	2.40671
	26	$\pi_g^{nb} \rightarrow \pi_u$				3	$3^3\Pi_u$		

triplet states, gaps are higher than those obtained in the non-mixed halides. Singlet–triplet energy splittings are around 0.1 eV for the Δ and Σ^- states and 0.3 eV for the Π states. As can be seen in Tables II and Tables S.V–S.VI (see ESI†), Σ^+ states show a strong mixture of the $\pi_{1/2}^{nb} \rightarrow \pi$ and $\sigma_1^+/\sigma^{+nb} \rightarrow \sigma^{+*}$ 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 the ΔE , with an average difference of 0.3 eV between HgBrCl and HgClI, of 0.3 eV between HgClI and HgBrI, and of 0.6 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 becomes 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 Tables II and S.V–S.VI, this mixing is more pronounced in HgBrI due to the heavy-atom effect. The brightest transition computed corresponds to the $(9)0^+$ SO state which is mainly generated by the singlet $4^1\Sigma^+$ SF state. The other singlet SF states $1^1\Pi$, $2^1\Pi$, $2^1\Sigma^+$, and $3^1\Sigma^+$ gives rise mainly to the $(2)1$, $(5)1$, $(4)0^+$, and $(6)0^+$ SO 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” $(2)1$ state, the relevant transitions to SO states with dominant triplet character are $(2)0^+$ for HgBrCl, $(2)0^+$, $(3)0^+$, $(6)1$ for HgClI and $(2)0^+$, $(3)1$, $(3)0^+$, and $(4)1$ for HgBrI. The SO states $(2)0^+$ and $(3)0^+$ are basically pure triplet $1^3\Pi$ and $2^3\Pi$ SF states, respectively. Meanwhile, at higher energies, significant transitions characterized with the strong triplet components are $(7)0^+$ 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 Equation 1). An extended analysis of such benchmarks can be found in Section S.II of the ESI†. In summary, negligible changes are obtained by comparing the cross sections obtained by using DFT/PBE0, CCSD, or CASPT2 starting geometries and frequencies (see Fig. S.1). For the second test, since the studied molecular systems have a small number of degrees of freedom, 100 configurations is clearly enough to produce a converged absorption spectrum (see Fig. S.2 which compares the spectra generated by sampling 25, 50, 75, and 100 geometries). On the other hand, the δ value which 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 δ values is not reliable because the exact vibronic couplings are not computed here with the semi-classical approximation.

Figure 2 displays the cross sections 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 Figs. 3 and

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 $D_{\infty h}$ symmetry, 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 S.X), and the main SF states contributing to the SO states (columns 9 and 10, only weights larger than 2% are provided)

SF state	($D_{\infty h}$)	Weight [%]	Excitation	ΔE [eV]	f [au]	SO state/ Ω state	Weight [%]	SF state	ΔE [eV]	f [au]
$1^1\Sigma^+$	($1^1\Sigma_g^+$)	95		0.00		$1^1\Sigma_{0+}^+$ (1) 0_+	100	$1^1\Sigma^+$	0.00	
$1^3\Pi$	($1^3\Pi_g$)	86	$\pi_2^{nb} \rightarrow \sigma^{++}$	4.86		$1^3\Pi_1$ (1) 1	88	$1^3\Pi$	4.83	0.00053
							12	$1^1\Pi$		
						$1^3\Pi_{0+}$ (2) 0_+	100	$1^3\Pi$	5.01	0.00118
$1^1\Pi$	($1^1\Pi_g$)	84	$\pi_2^{nb} \rightarrow \sigma^{++}$	5.15	0.00318	$1^1\Pi_1$ (2) 1	86	$1^1\Pi$	5.21	0.00267
							11	$1^3\Pi$		
							2	$1^3\Sigma^+$		
$2^3\Pi$	($1^3\Pi_u$)	83	$\pi_1^{nb} \rightarrow \sigma^{++}$	5.70		$2^3\Pi_1$ (3) 1	93	$2^3\Pi$	5.70	0.00053
							4	$2^1\Pi$		
						$2^3\Pi_{0+}$ (3) 0_+	100	$2^3\Pi$	5.79	0.00073
$1^3\Sigma^+$	($1^3\Sigma_u^+$)	85	$\sigma^{+nb} \rightarrow \sigma^{++}$	5.84		$1^3\Sigma_1^+$ (4) 1	94	$1^3\Sigma^+$	5.88	0.00019
							2	$2^1\Pi$		
							2	$1^1\Pi$		
$2^1\Pi$	($1^1\Pi_u$)	83	$\pi_1^{nb} \rightarrow \sigma^{++}$	6.00	0.01676	$2^1\Pi_1$ (5) 1	92	$2^1\Pi$	6.04	0.01579
							5	$2^3\Pi$		
							2	$1^3\Sigma^+$		
$2^1\Sigma^+$	($1^1\Sigma_u^+$)	63	$\pi_2^{nb} \rightarrow \pi$	6.66	0.05102	$2^1\Sigma_{0+}^+$ (4) 0_+	94	$2^1\Sigma^+$	6.66	0.04221
		23	$\sigma^{+nb} \rightarrow \sigma^{++}$				5	$1^3\Sigma^+$		
$2^3\Sigma^+$	($2^3\Sigma_u^+$)	72	$\pi_2^{nb} \rightarrow \pi$	6.66		$2^3\Sigma_1^+$ (6) 1	70	$2^3\Sigma^+$	6.44	0.00007
		11	$\pi_1^{nb} \rightarrow \pi$				29	$1^3\Sigma^-$		
$1^3\Delta$	($1^3\Delta_u$)	80	$\pi_2^{nb} \rightarrow \pi$	6.80		$1^3\Delta_1$ (7) 1	100	$1^3\Delta$	6.73	0.00064
		10	$\pi_1^{nb} \rightarrow \pi$							
$3^3\Sigma^+$	($1^3\Sigma_g^+$)	38	$\pi_1^{nb} \rightarrow \pi$	6.95		$3^3\Sigma_1^+$ (8) 1	88	$3^3\Sigma^+$	6.95	0.00003
		38	$\sigma_1^+ \rightarrow \sigma^{++}$				6	$1^3\Delta$		
		13	$\pi_2^{nb} \rightarrow \pi$							
$1^3\Sigma^-$	($1^3\Sigma_u^-$)	80	$\pi_2^{nb} \rightarrow \pi$	6.99		$1^3\Sigma_{0+}^-$ (5) 0_+	94	$1^3\Sigma^-$	7.02	0.01252
		10	$\pi_1^{nb} \rightarrow \pi$				6	$2^1\Sigma^+$		
						$1^3\Sigma_1^-$ (9) 1	67	$1^3\Sigma^-$	7.25	0.00051
							28	$2^3\Sigma^+$		
							3	$3^3\Sigma^+$		
$3^1\Sigma^+$	($2^1\Sigma_g^+$)	55	$\pi_2^{nb} \rightarrow \pi$	7.51	0.00683	$3^1\Sigma_{0+}^+$ (6) 0_+	91	$3^1\Sigma^+$	7.50	0.00499
		28	$\sigma_1^+ \rightarrow \sigma^{++}$				9	$2^3\Sigma^-$		
$2^3\Delta$	($1^3\Delta_g$)	77	$\pi_1^{nb} \rightarrow \pi$	7.62		$2^3\Delta_1$ (11) 1	100	$2^3\Delta$	7.48	0.00024
		10	$\pi_2^{nb} \rightarrow \pi$							
$4^3\Sigma^+$	($2^3\Sigma_g^+$)	49	$\sigma_1^+ \rightarrow \sigma^{++}$	7.64		$4^3\Sigma_1^+$ (10) 1	64	$4^3\Sigma^+$	7.45	1.1E-06
		38	$\pi_1^{nb} \rightarrow \pi$				34	$2^3\Sigma^-$		
$2^3\Sigma^-$	($1^3\Sigma_g^-$)	76	$\pi_1^{nb} \rightarrow \pi$	7.81		$2^3\Sigma_1^-$ (7) 0_+	88	$2^3\Sigma^-$	7.85	0.00259
		11	$\pi_2^{nb} \rightarrow \pi$							
$4^1\Sigma^+$	($3^1\Sigma_g^+$)	50	$\sigma_1^+ \rightarrow \sigma^{++}$	8.14	1.54965	$4^1\Sigma_{0+}^+$ (9) 0_+	98	$4^1\Sigma^+$	8.16	1.58677
		26	$\pi_2^{nb} \rightarrow \pi$							
$3^3\Pi$	($2^3\Pi_u$)	63	$\sigma_1^+ \rightarrow \pi$	8.19		$3^3\Pi_1$ (12) 1	49	$3^3\Pi$	8.03	0.00601
		29	$\sigma^{+nb} \rightarrow \pi$				31	$3^1\Pi$		
							14	$2^3\Sigma^-$		
							5	$4^3\Sigma^+$		
						$3^3\Pi_{0+}$ (8) 0_+	99	$3^3\Pi$	8.00	0.00001

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† (see Figs. S.3–S.6) for the sake of a more appropriate organization of the work. Note that for the symmetric HgX₂ molecules, experimental spectra corresponds to gas-phase data,^{9–12} whereas, for the mixed halides they are obtained from measurements in methanol solution.¹³ 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 S. XVI 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 in 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 $1^3\Sigma_{u0+}^-$ and $1^3\Sigma_{0+}^-$ states for HgX₂ and HgXY, respectively. It corresponds to the bands *a*, *b*, and *c* of HgX₂ discussed in section 3.2.1. At higher energies, Rydberg states are present according to the experimental observations.⁷⁷ Those 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 func-

tions 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.

Fig. 2 Compilation of the simulated UV-Vis absorption cross sections of HgXY halides with DKH3–SOC–MS–CASPT2(12,10)/ANO–RCC–VQZP and statistical averaging procedure. Additionally, vertical excitation energies (and associated f values) between SO states for the optimized ground-state structure of HgXY are graphically represented with red sticks (see the discussion in Section II).

3.3.1 HgX₂

In general, the positions and shapes of the bands are reproduced well, as compared with the experimental data, specially for HgCl₂ and HgBr₂. In HgI₂, discrepancies appear between distinct reported experimental spectra (see Fig. S.4) and for this system, our simulations show a better agreement with the spectrum measured by Maya.⁹ Cross section intensities (σ) 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 σ values, as can be seen in the case of HgBr₂ in Fig. 3. The best agreement with our simulated spectra is reached for the data from Frantom.¹² In any case, both experimental and theoretical σ 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 cross sections 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 $1^3\Pi_{u1}$, $1^1\Pi_{u1}$, $1^3\Pi_{u0+}$, and $1^3\Sigma_{u1}^+$ SO states (see Table I and Tables S.III–S.IV). Therefore, band *a* involves certain degree of SOC. For HgCl₂, the most intense transition is related to the $1^1\Pi_{u1}$ state with dominant singlet character ($1^1\Pi_u$). The second most intense transition corresponds to $1^3\Pi_{u1}$ which has mainly triplet character ($1^3\Pi_u$). In HgBr₂, transition to the „singlet” $1^1\Pi_{u1}$ state is still the most intense but now three SO states with triplet dominance have similar σ values: $1^3\Pi_{u1}$, $1^3\Pi_{u0+}$, and $1^3\Sigma_{u1}^+$. Finally, in HgI₂, the „triplet” $1^3\Pi_{u0+}$ becomes the most probable transition, and the „singlet” $1^1\Pi_{u1}$ has a similar f as $1^3\Pi_{u1}$ and $1^3\Sigma_{u1}^+$. 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 Figs. S.3–S.4). 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 HgBr₂ and HgI₂.

Band *b* is much sharper and 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 $1^1\Sigma_{u0+}^+$ SO state. As can be seen in Tables I and S.III–S.IV, this state is mainly formed by the singlet $1^1\Sigma_u^+$ SF state with small contributions from states of triplet character ($1^3\Sigma_u^-$ for HgCl₂ and HgBr₂ and this state plus $1^3\Pi_u$ for HgI₂). The „singlet” nature of band *b* and the „triplet” increasing nature of band *a* in the series Cl, Br, and I, allows to interpret the distinct relative intensity of the two analyzed bands observed experimentally (large relative intensity difference in HgCl₂ and small in HgI₂). This is a clear manifestation of the higher SOC in the heavy atom.

At the high-energy part of the spectra, another even sharper band arise (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 $1^3\Sigma_{u0+}^-$ SO state, which is mainly formed by the triplet $1^3\Sigma_u^-$.¹⁶ However, subtle contributions seem to affect the band intensity. Firstly, in HgCl₂, there is an 8 % contribution of the $1^1\Sigma_u^+$ state which according to the SF properties has very large f value (see Table S.III). In HgBr₂, the small contribution of the singlet $1^1\Sigma_u^+$ state at the ground-state optimized geometry (only 1 %; see Table I) seems to underestimate the intensity of the band in the corresponding spectrum in Figure 3. For HgI₂, even though the contribution of the $1^1\Sigma_u^+$ SF state to the $1^3\Sigma_{u0+}^-$ SO state is higher (2 %; see Table S.IV), this band is almost disappearing in the absorption spectrum (see Fig. S.4). Such findings point to a higher mixing of the singlet $1^1\Sigma_u^+$ 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 SOC effect. It fully disappears in the SF simulated spectra. This confirms our predictions on the nature of this band (which is 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)1_u SO state (which is a pure triplet $1^3\Delta_u$). The peak corresponding to this transition cannot be identified in the spectra of the other symmetrical halide compounds.

Fig. 3 Simulated UV-Vis absorption cross sections ($\sigma(E)$) of HgBr₂ both without (SF, orange) and with (SOC, violet) taking into account the spin-orbit coupling between states. Shaded areas represent the statistical error for the sampled photon energies ($\delta\sigma(E)$). Experimental spectra^{9,11,12} are included for the comparison (for better comparison, the $\sigma(E)$ values of spectrum of Frantom *et al.*¹² shown on the same axis as theoretical ones). Additionally, vertical excitation energies in eV (ΔE) and associated f values between SO states for the optimized ground-state structure of HgBr₂ are graphically represented with red sticks (see the discussion in Section II).

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 that for the parent HgX₂ and HgY₂ systems. Such bands correspond to transitions to the (4)0₊ SO states with a clearly dominant singlet nature from the $2^1\Sigma^+$ SF state, which mainly involve $\pi_2^{nb} \rightarrow \pi$ orbital excitations similarly to the parent compounds ($1^1\Sigma_{u0+}^+ \equiv (2)0_{u+}^+$).

Regarding the low-energy part of the spectra, signals have in general lower intensity and are spread over the range for the low-energy band of the parent non-mixed halides. Lack of differences between the SF and SO simulated spectra clearly indicate 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 Figs. S.5 and S.6). Thus, in HgBrCl, two mainly singlet states, $1^1\Pi_1$ and $2^1\Pi_1$, contribute in the low-energy part of the spectrum, and one „triplet” state, $1^3\Pi_{0+}$, appears although with low σ values. For HgClI, two „triplet” SO states, $1^3\Pi_{0+}$ and $2^3\Pi_{0+}$, have similar

intensities as $2^1\Pi_1$. Finally, in the case of HgBrI, four „triplet” states, $1^3\Pi_{0+}$, $2^3\Pi_1$, $2^3\Pi_{0+}$, and $1^3\Sigma_1^+$, and one „singlet” state, $2^1\Pi_1$, 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 the section 3.2.2. and their nature is once more clearly understood by comparing the SF and SO spectra of Figs. 4, S.5, and S.6.

Fig. 4 Simulated UV-Vis absorption cross sections ($\sigma(E)$) of HgBrCl both without (SF, orange) and with (SOC, violet) taking into account the spin-orbit coupling between states. Shaded areas represent the statistical error for the sampled photon energies ($\delta\sigma(E)$). Experimental spectra¹³ are included for the comparison. Additionally, vertical excitation energies in eV (ΔE) and associated f values between SO states for the optimized ground-state structure of HgBrCl are graphically represented with red sticks (see the discussion in Section II).

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, 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 the simulations of the physically meaningful absorption cross sections and band shapes.

In the first part of the work, in the same manner to 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/SO-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.¹⁶ The main results of this part confirm the experimental trends observed in the HgX₂ and HgXY UV-Vis spectra^{9–11,13} 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 system-

atically decrease by 0.3 and 0.6 eV in 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 absorption cross sections of the studied mercury compounds, which were generated with the semi-classical approach based on computations of the ΔE and f for the probed set of geometries (sampled according to the Wigner distribution).^{26–28} 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 excited states, namely DKH3-SOC-MS-CASPT2/ANO-RCC-VZQP. For HgX₂, where experimental gas-phase electronic spectra are available, despite the differences in $\sigma(E)$ (within the same order of magnitude), position and shape of the electronic bands are reproduced properly. This is specially meaningful for the mixed HgXY halides, since no experimental spectra up to 170 nm have been reported (only part of the HgXY spectra is available which is estimated from the spectra of the parent molecules HgX₂ and HgY₂, measured in methanol solution).^{13,14}

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 shall be useful in future 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 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 with those of the parent HgX₂ and HgY₂ compounds. Furthermore, this work has been proved worthy in recent predictions of absorption cross sections in mercury compounds with no available experimental spectra.²⁹

Conflicts of interest

There are no conflicts to declare.

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