

## Electronic Supplementary Information

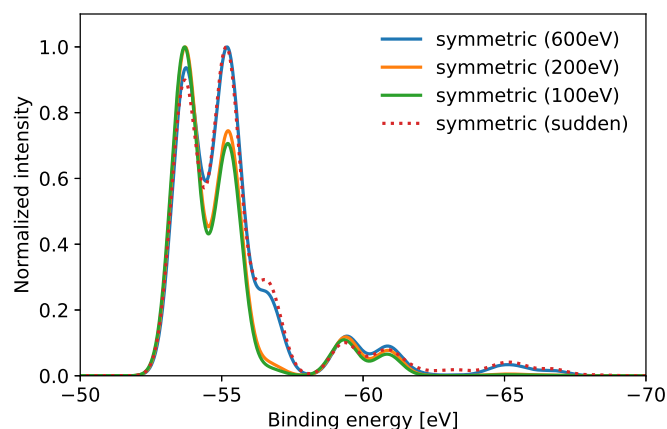
### S1 The sudden approximation

To investigate the effects of the sudden approximation on the obtained XPS intensities, numerical integration of equation 3 was carried out with the ezDyson 3.0 program<sup>1</sup>.

The spatial plane wave is expanded in a basis of spherical waves with angular momentum  $l = 0, 1, \dots, l_{max}$ . A rectangular numerical grid of 360 points from -6 to 6 Å along the molecular symmetry z-axis, and 180 points from -3 to 3 Å along the x- and y-axes was applied, with  $l_{max} = 10$ . To limit the computational cost, the integration was only performed for transitions with Dyson orbital norms  $|\phi_{fi}^{DO}| \geq 0.01$ .

Fig. S1 displays the XPS results for the symmetric geometry at RASPT2 level and photon energies 600 eV, 200 eV and 100 eV. At 600 eV the spectrum is in good agreement with the results derived from the sudden approximation, as presented in the main manuscript, and the presented experimental reference. At reduced photon energies the shape of the main features is clearly affected. The XPS intensities would typically be expected to be more sensitive to the photon energy at low photon energies (due to the increased interaction between the ejected photo-electron and the local potential of the remaining molecular system). The nearly identical spectra for 100 eV and 200 eV photon energies thereby suggests that the applied numerical integration is not sufficient to accurately describe the XPS at lowered photon energies.

While the accuracy of the ezDyson integration could likely be improved through different choice of parameters, we note that the current setup already results in a total computational cost (per spectrum) that is comparable to the expensive RASPT2 step of the simulations. Further testing is thereby not motivated in the current work, since good agreement to experiment is already obtained within the sudden approximation. The analysis is consequently, in the main manuscript, most safely and efficiently performed for comparison of the sudden approximation (theory) and 600 eV photon energies (experiment).



**Fig. S1** Photon energy effects on the  $I_3^-$  4d XPS intensities obtained from numerical integration with ezDyson. For 600 eV photon energy the results are in good agreement with the sudden approximation results presented in the main manuscript and the experimental reference. At reduced photon energy the spectral shape of the main features is clearly affected.

## S2 Occupation number analysis

### S2.1 Spin-orbit effects

Inclusion of spin-orbit coupling for  $I_3^-$  4d XPS simulations is essential to describe the 4d core-hole, as seen from e.g. the 1.7 eV splitting between features with  $4d_{3/2}$  and  $4d_{5/2}$  level ionization respectively. This could, in principle, affect the occupation number analysis in a similar way as the final state molecular orbital relaxation, as both the initial and final spin-orbit coupled states are expressed in two bases of molecular orbitals obtained from calculations of spin-free states with pure multiplicities (singlet and triplet for initial states, doublet and quartet for final states). However, the spin-free triplet state basis has no influence on the spectrum, as the initial spin-orbit coupled state (with no core-hole) is a pure singlet. Fig. S2b shows a histogram of the spin-orbit coupled final states sorted according their total weights in terms of spin-free doublet states. While essentially pure doublet spin-orbit coupled states are by far most common, it is clear that states exist in the whole range from pure doublets to pure quartets. Shown in Fig. S2a, however, is also a decomposition of the XPS spectrum into contributions from spin-free doublet and quartet states, respectively, which makes clear that the spectral influences of the spin-free quartet states is nearly negligible. Consequently, spin-orbit coupling with relevance for the spectrum is only the doublet-doublet coupling, and we need only consider the  $I_3^-$  singlet and  $I_3$  doublet molecular orbital bases for the occupation number analysis.

### S2.2 Molecular orbitals

The full set of molecular orbitals obtained for both initial (singlet) and final (doublet) states are, as an extension of Fig. 1 from the main manuscript, shown in Fig. S3.

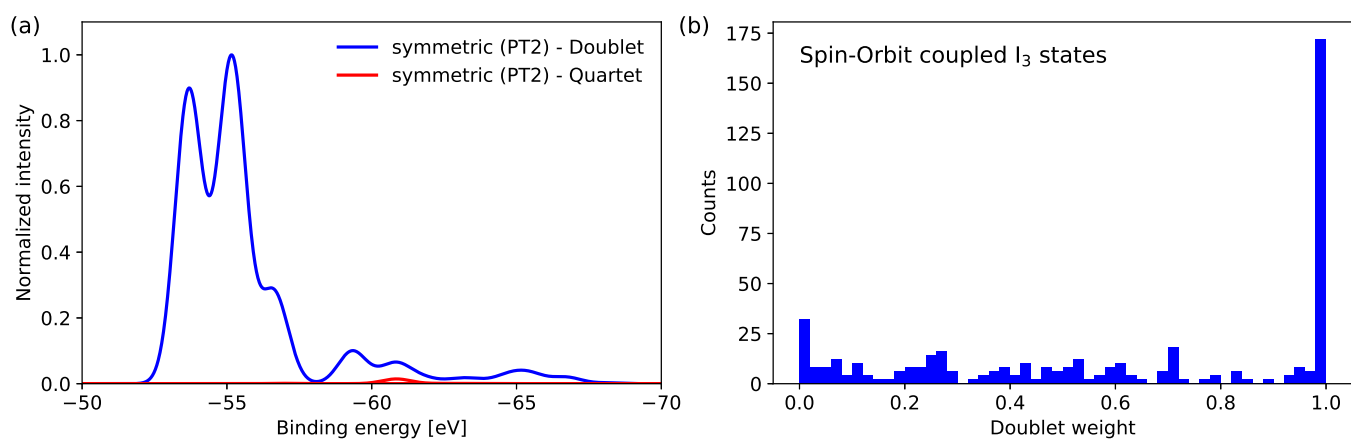
### S2.3 Assignment of the additional weak central site ionization feature for the asymmetric geometry

While the orbital relaxation upon photo-ejection prohibits definitive molecular orbital assignments, the residual occupations in Fig. 3c indicates that the low intensity feature near -51.6 eV associated with central site ionization can be tentatively rationalized as charge-transfer excitation from  $I^-$  to  $I_2^+$  in the final state, as compared to direct ionization. This explains both the lower energy (as the charge-transfer counteracts the charge imbalance caused by photo-ionization from the neutral  $I_2$ ) and the low intensity (low orbital overlap between  $I^-$  and  $I_2^+$ ) as compared to the strong feature at 54.9 eV. As the active orbitals 19 and 20 are both fully occupied (1.98 and 1.95 occupation respectively)

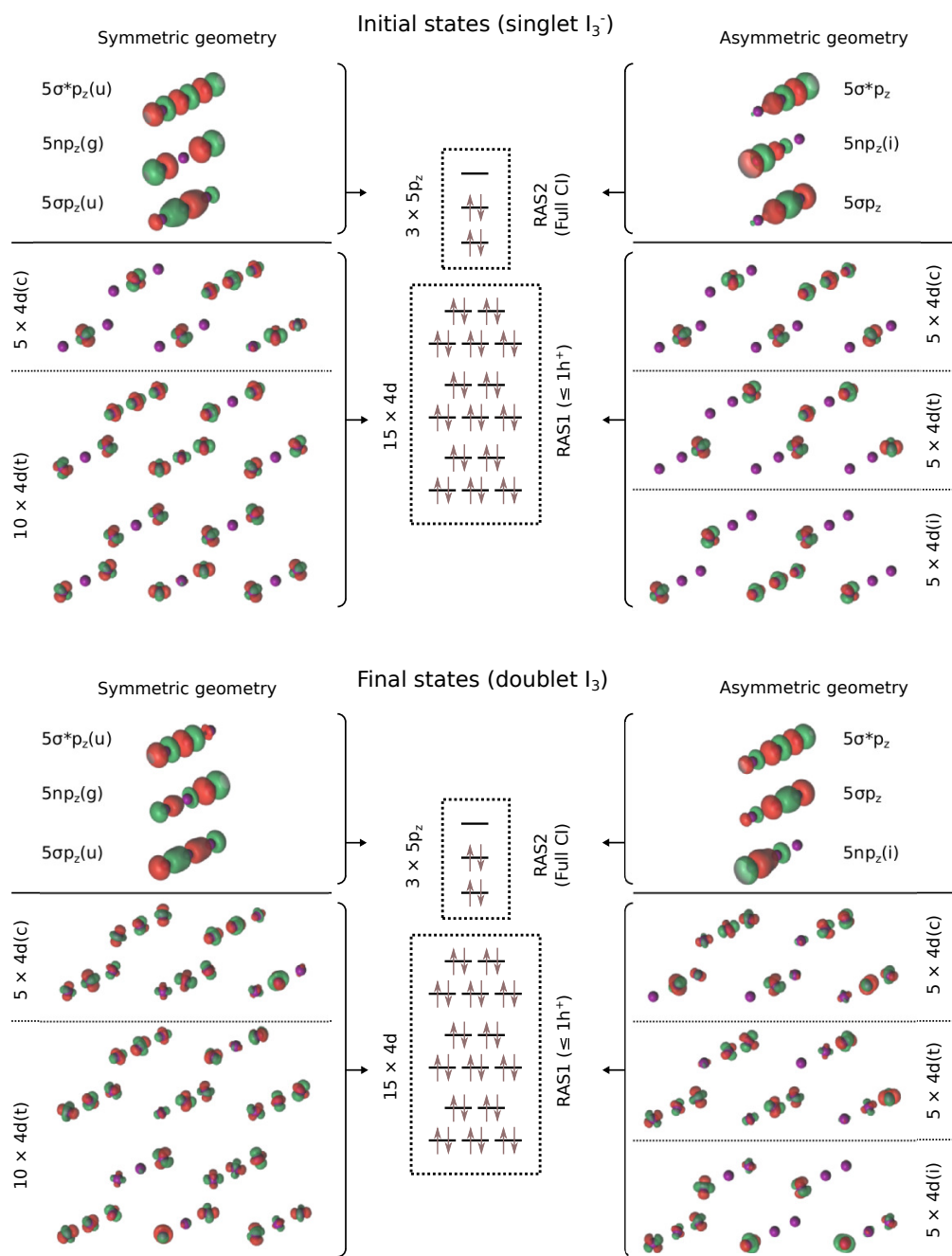
in the initial state, we ascribe the residual occupation of the feature to CI excitation in the final state  $I_3$  from orbital 19 to 20 in its orbitals basis, which as shown in Fig. S3 indeed constitutes a charge-transfer excitation from the  $I^-$  to the  $I_2^+$  site.

## References

- 1 C. Melania Oana and A. I. Krylov, *The Journal of chemical physics*, 2007, **127**, 234106.



**Fig. S2** Spin-orbit effects in the  $I_3$  final states. **(a)** The RASPT2 level sudden spectrum obtained from the spin-orbit coupled states, decomposed into contributions from spin-free states with doublet and quartet multiplicities. **(b)** Histogram of the spin-orbit coupled neutral  $I_3$  final states sorted according to their total weights of spin-free doublet states.



**Fig. S3** Extended version of Fig. 1 from the main manuscript: Active space of the RAS(15, 3; 34 e<sup>-</sup>, 1 h<sup>+</sup>) calculations and multi-state RASPT2 natural orbitals obtained for the initial state singlet I<sub>3</sub><sup>-</sup> species (above) and final state doublet I<sub>3</sub> species (below) for the spectrum simulations.