

Photochemistry of Fe:H₂O Adducts in Argon Matrixes: A Combined Experimental and Theoretical Study in the Mid-IR and UV–Visible Regions

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Vincent Deguin,[†] Joëlle Mascetti,[†] Aude Simon,[‡] Nadia Ben Amor,[‡] Christian Aupetit,[†] Sandra Latournerie,[†] and Jennifer A. Noble^{*,§,¶}

[†]Institut des Sciences Moléculaires (ISM), Université de Bordeaux and CNRS, 351 Cours de la Libération, F-33405 Talence, France

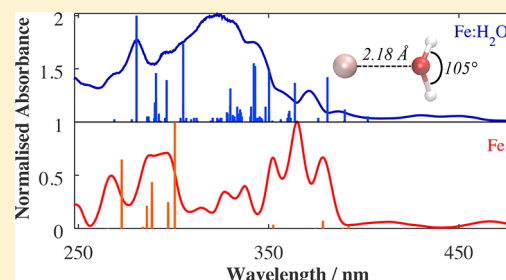
[‡]Université Toulouse UPS CNRS, Laboratoire de Chimie et Physique Quantiques, LCPQ IRSAMC, 118 Route Narbonne, F-31062 Toulouse, France

[¶]Université Lille 1, Laboratoire Physique Lasers Atomes et Molécules, CNRS, UMR 8523, F-59655 Villeneuve D’Ascq, France

[§]Institut des Sciences Moléculaires (ISM), Université de 806 Bordeaux and CNRS, 351 Cours de la Libération, F-33405 Talence, France

Supporting Information

ABSTRACT: The photochemistry of Fe:H₂O adducts is of interest in fields as diverse as catalysis and astrochemistry. Industrially, iron can be used as a catalyst to convert H₂O to H₂, whereas in the interstellar medium it may be an important component of dust grains, influencing the chemistry on their icy surfaces. This study consisted of the deposition and spectral characterization of binary systems of atomic iron with H₂O in cryogenic argon matrixes. In this way, we were able to obtain information about the interaction of the two species; we observed the formation of adducts of iron monomers and dimers with water molecules in the mid-IR and UV–visible spectral domains. Upon irradiation with a UV radiation source, the iron species were inserted into the water molecules to form HFeOH and HFe₂OH, leading in some cases to the formation of FeO possibly accompanied by the production of H₂. DFT and correlated multireference wave function calculations confirmed our attributions. This combination of IR and UV–visible spectroscopy with theoretical calculations allowed us to determine, for the first time, the spectral characteristics of iron adducts and their photoproducts in the UV–visible and in the OH stretching region of the mid-IR domain.



INTRODUCTION

Iron atoms can form adducts with water, which rearrange upon UV irradiation to form insertion molecules. Such Fe_n:H₂O_m adducts and their photoproducts are of interest in diverse fields of research, including catalysis, atmospheric chemistry, corrosion, and astrochemistry. The use of transition metals as catalysts has been an active area of research since the energy crisis of the 1960s, with the production of H₂ from H₂O of particular interest.¹ Iron:water adducts are also important in the Earth’s upper atmosphere, where a layer of iron atoms is present in the mesosphere due to meteoritic ablation. Fe is efficiently scavenged from the metallic layer by water-ice particles upon the formation of polar mesospheric clouds, and thus Fe interaction with water is key to the reactivity in these clouds.² The astrophysical relevance of Fe:H₂O interactions is due to the depletion of gas phase Fe in dense interstellar regions at rates higher than 90%, which is believed to be predominantly due to the presence of Fe in its metallic form in the solid phase.³ Where this iron is incorporated into icy dust

grains, energetic processing by cosmic rays or photons could give rise to oxygenated iron species.

Such a wide range of applications has led to much fundamental experimental and theoretical investigation of the activation of water by iron clusters. Many studies are performed on cationic species, due to the ease of implementation (both experimentally and theoretically).^{4–10} In particular, groups have studied IR signatures,^{7,9,10} photofragmentation,⁶ or mass spectra^{4,5,8,10} and performed density functional theory (DFT) calculations^{9,10} on Fe⁺:H₂O_n complexes. Water dissociation was observed in a few cases.¹⁰ Investigations of the reactivity of neutral iron atoms/clusters with water molecules are scarcer.^{11,12} Water dissociation has also been observed on neutral iron clusters,^{1,13} as well as on iron surfaces.^{14–17} To mimic the cold, low pressure conditions of the Earth’s upper atmosphere or astrophysical environments, experiments must

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be carried out in a cryogenic setup, using spectroscopic diagnostics to observe the iron:water adducts and their reaction products. Vibrational spectroscopy has previously been used to study Fe:H₂O adducts and their photoproducts in argon matrixes¹¹ in the context of a wider study of the interaction of transition metals with water. The subject was more recently revisited in a joint theoretical and experimental study using DFT to explore the potential energy surface (PES) of the observed photoreactions.¹² Although both previous studies were carried out on neutral Fe in argon matrixes, the more recent work by Zhang et al.¹² produced Fe atoms using laser evaporation, rather than the heating resistance method employed by Kauffman et al.¹¹ Laser evaporation often produces metal atoms in electronically excited states, rather than the ground state, which could impact the subsequent UV-induced photolysis studies. Importantly, neither of the previous photochemical studies addressed the ν_1/ν_3 OH stretching bands in the mid-IR or considered the UV-visible spectra of these complexes.

Quantum calculations on unsaturated clusters including transition metals are challenging due to both the complexity of the PES for such clusters, and to their open shell character. Pure theoretical work on the structures and energetics of Fe_nH₂O^{+0/-} ($n = 1-4$) clusters, computed at the DFT level with the BPW91 functional,^{18,19} was published by Gutsev et al.²⁰ For a given stoichiometry, several isomers were optimized, and for each isomeric structure, several spin states were considered. The authors then focused on the most stable structure for a given stoichiometry and computed its harmonic vibrational frequencies. Zhang et al.¹² also computed the harmonic spectra of the Fe:H₂O adducts and their (presumed) photoproducts. This was done with the B3LYP functional, which considerably overestimates the energy of the stretching water modes. Regarding the reaction paths, the mechanism for the reaction of Fe with H₂O was investigated by means of DFT and wave function correlated methods.²¹ This study by Karlicky and Otyepka²¹ demonstrates that DFT approaches fail to accurately reproduce the PES, making the use of correlated wave function approaches such as coupled cluster single, double, and perturbative triple CCSD(T) mandatory for Fe:H₂O systems. DFT studies have also been performed with the B3LYP functional to investigate the energetics of the reaction of metal dimers, among them Fe₂, with water.¹

To the best of our knowledge, no UV-visible spectroscopy of Fe:H₂O and its HFeOH photoproduct has been published. This is likely due in part to the time-consuming and challenging nature of the calculations required to allow the identification of the experimental bands. Owing to the multireference character of the states, multireference methods are required to obtain the most accurate electronic spectra, as previously shown for [Fe(C₆H₆)]⁺.²² In addition, very large basis sets and a large active space must be used. Due to the degeneracies, the calculations have been done for a very large number of states. In this study we could not have performed the same type of calculation for complexes containing two iron atoms with equivalent active space.

We present a joint experimental and theoretical study of Fe:H₂O adducts and their UV photoproducts, extending previous experimental and theoretical studies to cover the ν_1/ν_3 OH stretching bands in the mid-IR and the UV-visible spectra of these species. To the best of our knowledge this represents the first joint UV-visible spectroscopic study of Fe:H₂O and its photoproducts. The ν_1/ν_3 OH stretching

region and the UV-visible region are of particular interest in astrophysical studies, where these spectral regions are important probes of the chemical and physical nature of interstellar environments including star forming regions.

EXPERIMENTAL AND THEORETICAL METHODS

Experiments were performed in a high vacuum experimental setup consisting of a stainless steel chamber (base pressure 10⁻⁷ mbar) containing a CsBr substrate cooled to 10 K by a closed-cycle He cryostat. Deionized water was subjected to multiple freeze-pump-thaw cycles under vacuum to remove dissolved gases. Argon and water were mixed in a dosing line (at varying concentrations) and dosed into the chamber at a rate of 2 mL min⁻¹. Simultaneously, iron atoms were sublimated from an iron filament (38 mm × 10 mm × 0.5 mm, Goodfellow, 99.99%) by application of a voltage of ~1.3 V. Depositions lasted approximately 2 h. Additional experiments were performed using deuterated water (Eurisotop 99.9%) to aid attributions. Infrared spectra were obtained in transmission mode using a Bruker 70 V Fourier Transform InfraRed (FTIR) spectrometer with a DTGS mid-IR detector. Spectra were recorded from 4000–400 cm⁻¹ at a resolution of 0.5 cm⁻¹ and an average of ~100 scans. UV-visible spectra were obtained in transmission mode using a Shimadzu UV 2600 UV-visible spectrometer. Spectra were recorded from 200–600 nm at a resolution of 0.2 nm. The deposited Fe:H₂O:Ar matrixes were annealed to 20–25 K, recooled to 10 K, and then irradiated with a mercury lamp for 3 min ($\lambda < 235$ nm, average power ~150 mW). All spectra were measured at 10 K.

To rationalize the experimental results, quantum chemical calculations were performed using two levels of theory, based on (i) DFT for structure determination and the production of IR spectra and (ii) multireference wave function approaches for the determination of electronic spectra. The geometries of Fe_xH_yO_z complexes (with x , y , and z values between 0 and 2) likely to be formed in our matrix experiments were optimized with the gradient corrected BPW91 functional and a combination of Becke's exchange¹⁸ and Perdew-Wang's correlation functional,¹⁹ in conjunction with the triple- ζ cc-pVTZ basis set. In the discussion below, we will occasionally refer to the BPW91/cc-pVTZ level as "DFT" for the sake of simplicity. For Fe_xH_yO_z and their deuterated counterparts, the harmonic IR spectra were obtained after full diagonalization of the weighted Hessian matrix. It is worth noting that the vibrational frequencies reported here are not scaled. The BPW91 functional was chosen as it was shown to provide the best results when harmonic frequencies of Fe₂CO (and Co₂CO) complexes were compared with those measured in matrix (10–60 cm⁻¹ discrepancies).^{23,24} In these papers, unscaled DFT harmonic spectra of isolated complexes are compared to rare gas matrix results and the agreement is very satisfactory. We therefore decided to use the same approach, and in particular not to take into account some anharmonic effect using scaling factors. In this way, we do not bias the calculations. Indeed, scaling factors are very likely to be mode dependent, and anharmonic effects are expected to be different for hydrogenated and deuterated species. Besides, we do not describe matrix effects in the calculations, and these may also be important to take into account if we want to compute accurate IR spectra. This functional was also used by Gutsev et al.²⁰ to perform an exhaustive exploration of the PES of Fe₁₋₄(H₂O)^{1/0/+} complexes. As mentioned above, the authors of that study only focused on the most stable isomers for a

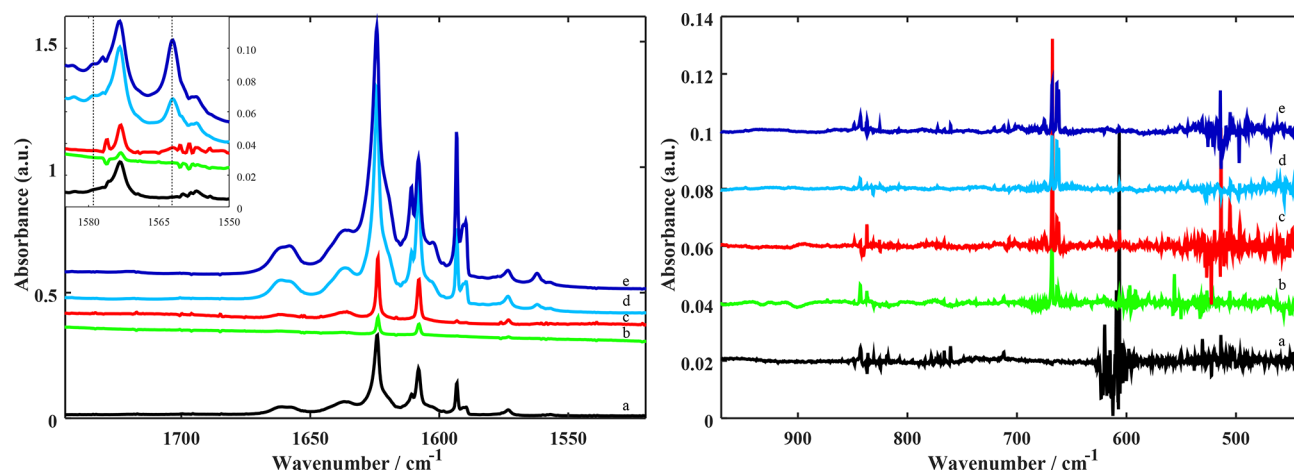


Figure 1. Depositions of Fe:H₂O:Ar with increasing H₂O concentrations in the spectral regions 1745–1520 cm⁻¹ (left-hand panel) and 970–400 cm⁻¹ (right-hand panel). Individual spectra are as follows: (a) H₂O:Ar (reference) from a gas phase mixture of ~1:200; (b)–(e) depositions of Fe:H₂O:Ar with increasing concentrations of H₂O. In the 1745–1520 cm⁻¹ (left-hand panel) spectral region, water aggregates give rise to a series of absorption features, as observed in spectrum a, including the peaks at 1573 and 1557 cm⁻¹ in the inset, which are attributed to ν_2 bending vibrations.⁵⁸ The inset highlights the presence of bands attributed to Fe:H₂O (1562 cm⁻¹) and Fe₂:H₂O (1579 cm⁻¹). The latter is only visible for higher H₂O concentrations. In the 970–400 cm⁻¹ spectral region (right-hand panel), as expected, there are very few bands, all of which are attributable to the presence of trace amounts of contaminants in the matrix (for example, CO₂ at ~670 cm⁻¹) or detector noise.

given stoichiometry, and some of these were found to be irrelevant to our study, i.e., impossible to form under the experimental conditions used here. However, some species that were deemed by Gutsev et al.²⁰ to be likely to form in the present experiments were not identified in our matrixes. We also specify that we used some of their results as starting point calculations in the appropriate cases. Indeed, their work was very useful in helping determine some of the most stable structures and spin states in the present work. The BPW91 functional has, however, proven to provide a poor description of the energetics for several intermediates of the reaction of water with Fe in CCSD(T) calculations,²¹ showing an overall overestimation of Fe–O binding energies. Therefore, to obtain energetic data on water:iron adducts, single point CCSD(T)/cc-pVTZ//BPW91/cc-pVTZ calculations, occasionally referred to as “CCSD(T)//DFT” below, for the sake of simplicity, were also performed. For iron:water molecular complexes, with noncovalent (weak) metal–ligand interactions, the role of dispersion interactions may be non-negligible, and these are not taken into account in the BPW91 potential. Therefore, we investigated the influence of dispersion by adding the D2 version of Grimme’s dispersion²⁵ to the BPW91 potential. The geometries of the molecular complexes were then reoptimized and the harmonic IR spectrum recomputed using this BPW91-D2 potential.⁴ Such an approach has been recently used to study vanadium-water complexes.²⁶ The BPW91-D2 approach will be labeled “DFT-D” for the sake of simplicity. The Gaussian09 suite of programs²⁷ was used for both DFT and CCSD(T) calculations. Regarding convergence criteria, a tight convergence criterion was used for SCF cycles, i.e., 10⁻⁸ for the root-mean-square (RMS) change, in conjunction with a maximum change of 10⁻⁶ in the density matrix. In the case of SCF convergence problems, a Fermi temperature and (sometimes) a quadratic convergence algorithm were required. A very tight convergence criterion was used for geometry optimization, i.e., 10⁻⁶ for the RMS force, in conjunction with an ultrafine integration grid.

Concerning the electronic spectra, the calculations of the different states were carried out with the 7.8 MOLCAS

package^{28–30} and were based on relativistic correlation consistent atomic natural orbitals (ANO-RCC)^{31,32} basis sets. For Fe, a (21s15p10d6f4g2h) basis set was contracted to [7s6p4d3f2g1h]; for O a (14s9p4d3f2g) set was contracted to [5s4p3d2f1g] and for H a (8s4p3d1f) set was contracted to [6s4p3d1f]. Scalar relativistic effects were taken into account by using the second-order Douglas–Kroll–Hess Hamiltonian.^{33,34} C₁ spatial symmetry was used for Fe, Fe:OH₂, and HFeOH calculations. The zeroth-order description was obtained by means of complete active space self-consistent field (CASSCF) calculations.³⁵ For the iron atom and the Fe:OH₂ complex, the active space consists of the 3d, 4s, 4p and five correlating 3d’ orbitals, leading to eight electrons in 14 orbitals and is denoted CAS(8,14). This active space allows the description of the ground state [⁵D₄(3d⁶4s²) for the iron atom; ⁵A’ for Fe:OH₂ (3d⁶4s²)] as well as of all the quintet excited states until 240 nm, corresponding to the lowest wavenumbers observed in the experimental study. The number of calculated quintet states takes into account the number of degenerate components of the considered states. In the case of the iron atom, to get all these states, it was necessary to calculate 103 quintet states corresponding to the ⁵D (3d⁶4s²), ⁵F, ⁵P (3d⁷4s¹), ⁵D, ⁵F, ⁵P, ⁵S, ⁵G, ⁵I, ⁵H (3d⁶4s¹4p¹), ⁵D, ⁵F, and ⁵G (3d⁷4p¹) configurations. For the Fe:OH₂ complex, 70 quintet states have been calculated. Concerning the HFeOH complex, the active space consists of the 3d, 4s, one 4p (in-plane 4p_x, perpendicular to the y axis of the molecule), and five correlating 3d’ orbitals for the iron, of one occupied orbital involving the oxygen atom and its two neighbors, i.e., the hydrogen and the iron, and of one orbital for the terminal hydrogen atom, leading to 10 electrons in 14 orbitals, and is denoted CAS(10,14). To reach the upper part of the spectrum (200 nm), 30 quintet states were calculated. The ground state for the HFeOH complex is ⁵A’ H⁻Fe²⁺(3d⁶)O⁻H with a NBO (natural bond orbital) population of H(1s^{1.59})-Fe(4s^{0.37}3d^{6.07}4p^{0.18})-O-(2s^{1.79}2p^{5.46})-H(1s^{1.59}).

In addition to the CASSCF wave function, dynamical polarization and correlation effects were then included following the complete active space with perturbation at the

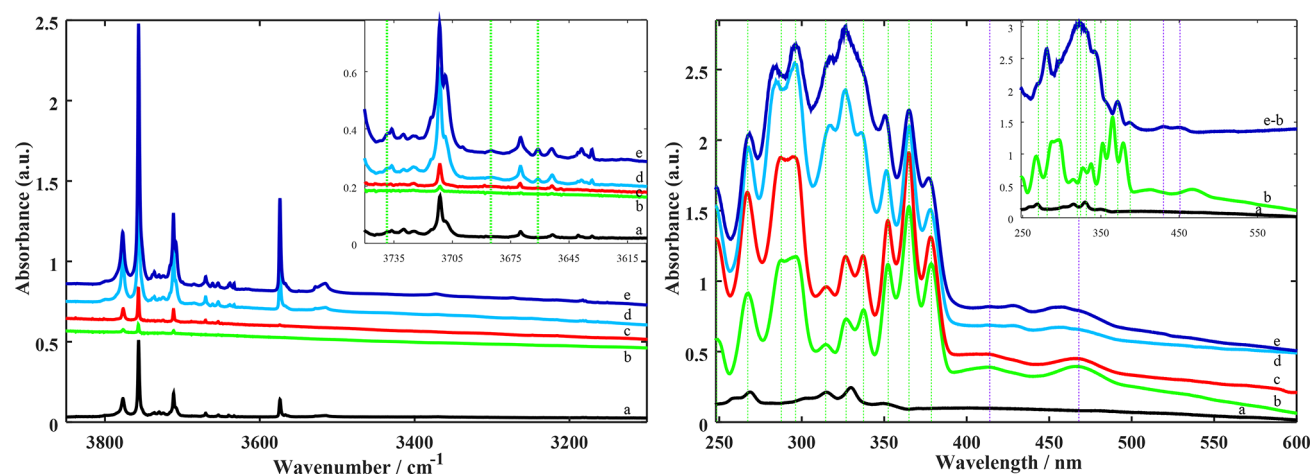


Figure 2. Depositions of Fe:H₂O:Ar with increasing H₂O concentrations in the spectral regions 3850–3100 cm⁻¹ (left-hand panel) and 245–600 nm (right-hand panel). Individual spectra are as follows: (a) H₂O:Ar (reference) from a gas phase mixture of ~1:200; (b)–(e) depositions of Fe:H₂O:Ar with increasing concentrations of H₂O. In the left-hand panel inset, bands attributed to Fe:H₂O and Fe₂:H₂O adducts are highlighted with dotted lines at 3661 (Fe:H₂O), 3685 (Fe₂:H₂O), and 3739 (Fe₂:H₂O) cm⁻¹. In the right-hand panel, peaks attributed to Fe are highlighted with green dotted lines (249–378 nm) and those attributed to Fe₂ are identified in purple (414 and 468 nm). The inset replots spectra a and b and compares them to the difference spectrum e – b, i.e., the difference between the spectrum of Fe:H₂O:Ar and that of Fe:Ar, to highlight the bands attributed to the Fe:H₂O adduct. Overplotted in green are peaks attributed to Fe:H₂O adducts (270–387 nm) and in purple to Fe₂:H₂O (430, 451 nm).

Table 1. Attribution of IR Spectral Bands to Iron-Containing Adducts and Molecules Observed in This Work

species	symmetry	wavenumber/cm ⁻¹				assignment
		experimental		calculated		
		this work	literature	this work DFT (DFT-D)	literature	
Species Observed upon Deposition						
Fe:H ₂ O	⁵ A''	3661		3649 (3660)	3802, ^a 3778 ^b	ν_{aOH}
				3547 (3554)	3691, ^a 3656 ^b	ν_{sOH}
Fe ₂ :H ₂ O	⁷ A'	1562	1563, ^c 1562 ^a	1565 (1567)	1592, ^a 1614 ^b	δ_{OH_2}
		3739		3726 (3731)		ν_{aOH}
		3685		3632 (3634)		ν_{sOH}
		1576	1576 ^c	1585 (1586)		δ_{OH_2}
Species Observed after UV Irradiation						
HFeOH	⁵ A''	3742		3787	3972, ^a 3963, ^b 3831 ^d	ν_{OH}
		1733	1732, ^c 1731 ^a	1777	1801, ^a 1871, ^b 1806 ^d	ν_{FeH}
		682	682, ^c 680 ^a	684	708, ^a 788, ^b 683 ^d	ν_{FeO}
		458	458 ^c	475	287, ^a 406, ^b 411 ^d	$\delta_{\text{FeOH}}/\delta_{\text{HFeO}}$
HFeOFeH	⁹ A ₁	1725 ^e /1712	1724/1708, ^c 1708 ^a	1778/1767	1771/1447 ^d	ν_{FeH}
		914	915/912, ^c 912 ^a	849	780/692 ^d	ν_{FeO}
Fe(OH) ₂	⁵ A	3728		3774/3773	3939/3938 ^a	ν_{OH}
		737	736 ^c ; 737 ^a	745	761 ^a	ν_{aFeO}
		631		622	631 ^a	ν_{sFeO}
FeO	⁵ Δ	513		544/520	439 ^a	$\delta_{\text{OFeO}}/\delta_{\text{FeOH}}$
		873	873 ^{a,f}	923	1008 ^b	

^aFrom Zhang et al.¹² matrix isolation FTIR (Fe atoms produced by laser ablation) and DFT (B3LYP functional) study. ^bFrom Mebel et al.⁵² DFT (B3LYP functional) study. ^cFrom Kauffman et al.¹¹ matrix isolation FTIR study (Fe atoms produced by sublimation). ^dFrom Gutsev et al.²⁰ DFT study on Fe_nH₂O clusters (BPW91 functional). ^eVery weak band. ^fFrom Green et al.⁵³ and Chang et al.⁵⁴ matrix isolation FTIR studies of FeO.

second order (CASPT2)³⁶ or multistate CASPT2 (MS-CASPT2).³⁷ All the electrons are correlated. The Cholesky decomposition technique,^{38,39} which allows a drastic reduction of the number of bielectronic integrals, was used with a 10⁻⁸ au threshold. Spin-orbit coupling was calculated as the state interaction between the spin-orbit free states by the restricted active space state interaction approach (SO-RASSI).⁴⁰ Concerning the iron atom, a small splitting (the mean value for the 103 roots is about 60 cm⁻¹) of the degenerate states appears at

the CASPT2 level. The degeneracy is re-established by averaging the 2J + 1 CASPT2 energies of the components of a given J. These energies and CASSCF wave functions are considered in the SO-RASSI calculations.⁴¹ This procedure only leads to tiny differences in the final energy levels compared to the MS-CASPT2 SO-RASSI results but allows an accurate assignment of the SO states. However, for the Fe:OH₂ and HFeOH complexes, both wave functions and energies are those of the MS-CASPT2 calculations. In none of the electronic

Table 2. Attribution of UV Spectral Bands to Iron and Iron-Containing Adducts (Band Positions in nm and Intensities Reported as in the Literature)

species	free atom exp ^a position (I ²)	calc SO-CASPT2 ^b position (rel osc str)	argon matrix	
			1:1000 (present work) ^c position (rel I)	1:2000 (literature) ^d position (osc str (or I))
Fe	248.4(4.6) x ⁵ F ₅	232.1(0.59) 3d ⁶ 4s4p x ⁵ F ₅		236.4(52) 237.8(88)
	250.2 x ⁵ D ₃	241.9(0.11) 3d ⁶ 4s4p x ⁵ D ₃		241.4(72)
	252.4(4.1) x ⁵ D ₄	243.7(0.51) 3d ⁶ 4s4p x ⁵ D ₄	248.5(0.44)	243.9(0.0033) 246.0(57)
	272.0(4.0) y ⁵ P ₃	272.8(0.65) 3d ⁶ 4s4p y ⁵ P ₃	267.1(0.63)	248.2(59) 263.9(0.0033) 267.4(15)
	293.8(5.0) y ⁵ F ₄	286.0(0.21) 3d ⁷ 4p y ⁵ F ₄	287.2(0.77)	269.6(0.0029) 271.4(0.0003) 279.0(0.0008) 286.0(0.0017)
	296.8 y ⁵ F ₅	288.7(0.43) 3d ⁷ 4p y ⁵ F ₅		291.1(0.0012)
	298.4 y ⁵ D ₃	297.2(0.25) 3d ⁷ 4p/3d ⁶ 4s4p y ⁵ D ₃		294.5(0.0042)
	302.1 y ⁵ D ₄	300.7(1.00) 3d ⁷ 4p/3d ⁶ 4s4p y ⁵ D ₄		295.5(15) 297.7(23)
	344.1(6.1) z ⁵ P ₃	352.4(0.04) 3d ⁶ 4s4p z ⁵ P ₃	296.2(0.79)	299.2(0.0059) 299.8(38)
			314.3(0.42)	301.0(0.0005) 306.9(4)
			326.6(0.52)	325.8 (0.0006)
			337.4(0.56)	337.1(0.0003)
	372.1 z ⁵ F ₅	378.5(0.07) 3d ⁶ 4s4p z ⁵ F ₅	352.1(0.75)	351.9(0.0008)
	382.6(6.0) z ⁵ D ₃	389.0(0.01) 3d ⁶ 4s4p z ⁵ D ₃	364.8(1.00)	363.9(0.0004)
	386.1 z ⁵ D ₄	392.1(0.03) 3d ⁶ 4s4p z ⁵ D ₄	378.4(0.76)	378.0(0.0007)
	Fe ₂			414 468
Fe:H ₂ O			387(0.08) 372(0.28) 356(0.27) 342(0.74)	
	380.9(0.42) 3d ⁶ 4s4p(0.51)/3d ⁷ 4p(0.32)			
	363.8(0.37) 3d ⁶ 4s4p(0.17)/3d ⁷ 4p(0.62)			
	350.2(0.49) 3d ⁶ 4s4p(0.17)/3d ⁷ 4p(0.62)			
	348.4(0.14) 3d ⁶ 4s4p(0.17)/3d ⁷ 4p(0.62)			
	342.9(0.53) 3d ⁶ 4s4p(0.14)/3d ⁷ 4p(0.59)			
	342.2(0.55) 3d ⁶ 4s4p(0.10)/3d ⁷ 4p(0.67)			
	340.8(0.14) 3d ⁶ 4s4p(0.10)/3d ⁷ 4p(0.58)	331(0.94)		
	333.5(0.14) 3d ⁶ 4s4p(0.17)/3d ⁷ 4p(0.53)	324(1.00)		
	329.9(0.32) 3d ⁶ 4s4p(0.26)/3d ⁷ 4p(0.48)	320(0.99)		
	329.8(0.16) 3d ⁶ 4s4p(0.28)/3d ⁷ 4p(0.45)			
	305.1(0.74) 3d ⁶ 4s4p(0.26)/3d ⁷ 4p(0.48)	297(0.65)		
	305.1(0.17) 3d ⁶ 4s4p(0.26)/3d ⁷ 4p(0.49)			
	296.4(0.38) 3d ⁶ 4s4p(0.56)/3d ⁷ 4p(0.14)	281(0.76)		
	296.4(0.39) 3d ⁶ 4s4p(0.56)/3d ⁷ 4p(0.14)			
	290.8(0.46) 3d ⁶ 4s4p(0.57)/3d ⁷ 4p(0.09)			
	290.8(0.24) 3d ⁶ 4s4p(0.57)/3d ⁷ 4p(0.09)			
	290.2(0.18) 3d ⁶ 4s4p(0.56)/3d ⁷ 4p(0.09)			
	280.6(0.97) 3d ⁶ 4s4p(0.59)/3d ⁷ 4p(0.08)	270(0.45)		
	280.6(1.00) 3d ⁶ 4s4p(0.59)/3d ⁷ 4p(0.08)			
Fe ₂ :H ₂ O			430 451	

^aExperimental reference data for free Fe atom from Nave et al.⁵⁵ ^bSO-CASPT2 energy levels for free iron atoms and SO-MS-CASPT2 energy levels for Fe:H₂O adducts, with relative oscillator strengths in parentheses. ^cPositions of absorption bands in experimental spectra presented in this work (Fe:Ar ~ 1:1000), with relative abundance in parentheses. ^dExperimental reference data for Fe in an argon matrix (Fe:Ar 1:2000) from Mann and Broida,⁵⁶ with oscillator strengths in parentheses and poorly resolved bands in italics (with intensities rather than oscillator strengths). Experimental reference data for Fe₂ in an argon matrix from de Vore et al.⁵⁷

spectra calculated here was the argon matrix included. To avoid intruder states, the real level shift was applied in all the

CASPT2 calculations, with a value of 0.4 au. The ionization potential-electron affinity (IPEA) shift⁴² was not used here as

Table 3. Attribution of IR Spectral Bands to Iron-Containing Adducts and Molecules Observed for Deuterated Water

species	wavenumber/cm ⁻¹			
	experimental		calculated	
	this work ^a	literature	this work DFT (DFT-D)	literature
		Species Observed upon Deposition		
D ₂ O	2772, 2658, 1176	2772, 2658, 1176 ^b	2789, 2671, 1180	2875, 2754, 1200 ^f
Fe:D ₂ O (2681, 2560, 1146)	2675, –, 1159	–, –, 1158 ^{c,d}	2673, 2555, 1145	
Fe ₂ :D ₂ O	2716, –, 1169	–, –, 1169 ^d	2729, 2617, 1160 (⁷ A')	
			(2736, 2619, 1161)	
			2728, 2601, 1151, 1158 (⁹ A)	
		Species Observed after UV Irradiation		
DFeOD	–, 1246, 675/670, –	–, 1246/1245, 660/661, – ^{c,d}	2758, 1267, 668, 362	
FeO	873	873 ^c	923	1008 ^e

^aWhere no value is given, the experimental band either was too weak to be observed under our experimental conditions or, in the case of DFeOD, was too close to the ν_2 of CO₂ to be extracted ^bFrom Bentwood et al.⁶⁰ matrix isolation FTIR study ^cFrom Zhang et al.¹² matrix isolation FTIR and DFT (B3LYP functional) study ^dFrom Kauffman et al.¹¹ matrix isolation FTIR study ^eFrom Mebel et al.⁵² ^fFrom Coussan et al.⁶¹

there is some controversy in the literature concerning its application.^{43–51} The validation of the different CASPT2 parameters was performed by determining the ⁵D₄–⁵F₅ energy splitting of the iron atom with different IPEA and level shifts. For this, 12 states were calculated, corresponding to the ⁵D (3d⁶4s²) and ⁵F (3d⁷4s¹) configurations. A full discussion is presented in the Supporting Information, including Table S1.

RESULTS AND DISCUSSION

Fe and Fe Adducts with H₂O. Four experimental depositions of Fe:H₂O:Ar were made with varying H₂O concentrations. The spectra of these matrixes are presented in Figures 1 and 2. In both of these figures, trace a is a H₂O:Ar reference spectrum, and traces b–e are Fe:H₂O:Ar matrixes of increasing H₂O concentration. The attribution of experimental IR and UV–visible absorption bands is presented in Tables 1 and 2, respectively, on the basis of comparison with quantum calculations.

In the Fe:H₂O:Ar matrix with the lowest H₂O concentration (trace b, Figures 1 and 2), only a small trace amount of H₂O is present, due to the low level contamination of the experimental chamber with H₂O. When the iron filament is heated, water molecules adsorbed to nearby metal surfaces desorb into the gas phase and are deposited along with the iron in the matrix. As the concentration of H₂O in the matrix increases, by mixing of water with the matricial gas, argon, the water molecules are present in aggregates of larger sizes. The characterization of water aggregates in our experimental setup has been done previously in a combined experimental and theoretical study.⁵⁸ In the present study, we observe only water monomers and dimers in trace c (Figures 1 and 2), with larger aggregates (up to the hexamer) observed for traces d and e (Figures 1 and 2).

In all four Fe:H₂O:Ar matrixes, iron has approximately a constant concentration and is present in both monomeric and dimeric forms. This is confirmed by the presence of multiple bands corresponding to Fe and Fe₂ in the UV–visible spectrum (Figure 2, right-hand panel, and Table 2). In the present work, we produce Fe atoms using resistive heating, as in the study of Kauffman et al.,¹¹ to ensure that all Fe atoms are in the ground electronic state. This would not necessarily be the case for Fe atoms produced by laser ablation methods, as in the study of Zhang et al.¹² Attribution of Fe bands in the UV spectra was made by comparison with literature values for free Fe atoms⁵⁵

and Fe in an argon matrix at 4.2 K,⁵⁶ as well as by comparison with the calculated electronic spectrum.

For the electronic spectrum of atomic iron, the 103 calculated quintet states were identified in the following order: a⁵D a⁵F a⁵P z⁵D z⁵F z⁵P γ⁵D γ⁵F γ⁵P z⁵G γ⁵G z⁵S x⁵D x⁵P z⁵H z⁵I x⁵F. Including the spin–orbit coupling gives rise to 515 spin–orbit states. Spin–orbit states with an oscillator strength higher than 0.01 (relative value, defined with respect to the maximum of 0.041) are presented in Table 2, with the corresponding energies and oscillator strengths.

The most intense band corresponds to a transition to the γ⁵D₄ state. Compared to experimental results⁵⁵ the agreement is rather good, in the range from –9 to +9 nm (–1540 to 690 cm⁻¹), except for the highest x⁵F₅ state for which the error is 16 nm (2830 cm⁻¹), which is the largest one. All the calculated states are presented in Table S2 in the Supporting Information. The theoretical work proposes three missing values in the experimental data, corresponding to the three quintet states z⁵I₈, z⁵I₇, and z⁵H₇. The oscillator strengths are not comparable to the experimental intensities and cannot be used for the assignment. The ⁵D₄–⁵F₅ energy splitting of 1.16 eV (9320 cm⁻¹) is shifted by 0.16 eV compared to the value obtained for 12 roots (Tables S1 and S2 in the Supporting Information). Averaging the orbitals on 103 roots introduces a bias that is quite unavoidable. However, this calibration gives some hints on the accuracy expected for the two complexes for which smallest number of states are investigated (70 for Fe:OH₂ and 30 for HFeOH). Better agreement is found for the energy splitting of the ⁵D₄–⁵F₅ states of the iron atom with the multireference configuration interaction method (MRCI),⁵⁹ with the minimal eight electrons in six orbitals active space necessary to describe the 3d⁶4s² and 3d⁷4s¹ configurations. To also describe the 3d⁶4s¹4p¹ and 3d⁷4p¹ states, a larger active space that includes the 4p orbitals is necessary and the MRCI method is no longer adapted. The CASPT2/MS-CASPT2 method used in this study is a good compromise between the feasibility of the calculation and the accuracy of the results. Finally, the presence of the argon matrix gives rise to a slight blue shift compared to the free atom and it is expected that the same shift occurs in the two complexes.

Deposition of Fe with H₂O produced Fe:H₂O and Fe₂:H₂O adducts in the argon matrixes. In the ν_2 OH bending mode region, absorption bands are observed at 1562 and 1579 cm⁻¹, corresponding to Fe:H₂O and Fe₂:H₂O, respectively (Figure 1,

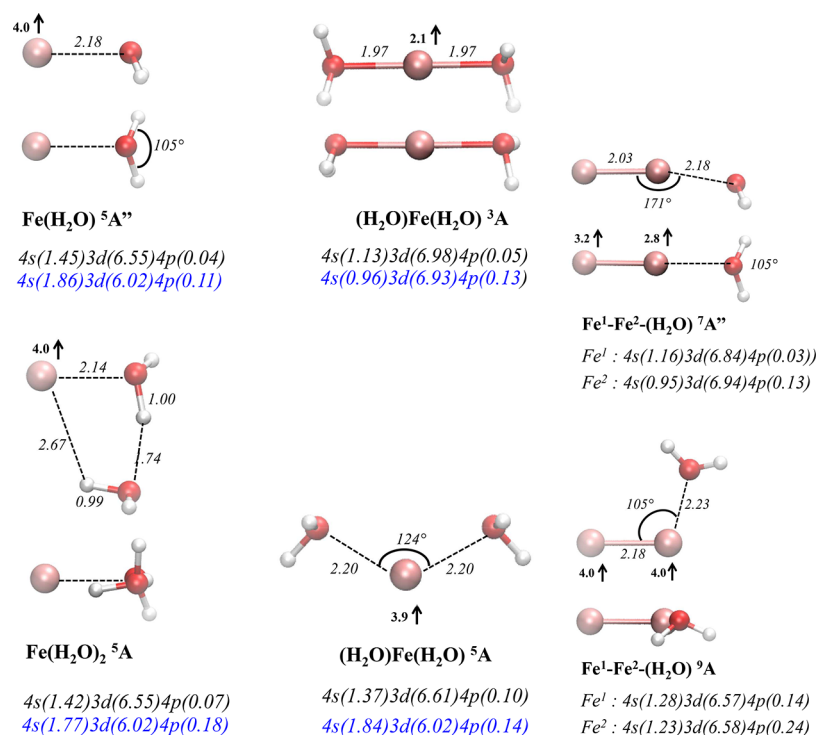


Figure 3. BPW91/cc-pVTZ optimized geometries of iron–water complexes (two views are shown when necessary for clarity). The stoichiometries and electronic states are specified in bold characters, along with the natural population on the valence orbitals of the Fe atoms (in black italics, DFT; in blue italics, CCSD(T)//DFT). When larger than 0.1, the spin densities are mentioned. Relevant bond/intermolecular distances (in angstroms) and angles (in degrees) are also reported.

left-hand panel, and Table 1). These modes were shifted to 1159 and 1169 cm^{-1} , respectively, in experiments with deuterated water (Table 3). This is in agreement with the previous experimental studies of Kauffman et al.¹¹ and Zhang et al.¹² The attributions of the complexes (including those with D₂O) are confirmed by our DFT calculations (Table 1), as discussed in detail below. At low frequencies we see no absorption bands corresponding to Fe-related adducts or molecules upon deposition (Figure 1, right-hand panel). This is in agreement with the study of Kauffman et al.,¹¹ where Fe was deposited thermally, as in our current work. There is no evidence of the deposition of FeO, unlike the study of Zhang et al.,¹² where Fe was deposited by laser ablation.

The spectral properties of the adducts Fe:H₂O and Fe₂:H₂O have not previously been published in the ν_3/ν_1 OH stretching region or in the UV–visible region. In the ν_3/ν_1 OH stretching region, we observe absorption bands at 3661, 3685, and 3739 cm^{-1} in the deposition spectra, which we attribute to Fe:H₂O and Fe₂:H₂O by comparison with their calculated IR spectra (Figure 2, left-hand panel inset, and Table 1). In our experiments with D₂O, the ν_3 at 3661 and 3739 cm^{-1} are shifted to 2675 and 2716 cm^{-1} , respectively (Table 3). In the UV–visible, we observe known bands of Fe and Fe₂ in the pure argon matrix.^{56,57} As the concentration of water in the matrix increases, we observe the presence of other bands that we attribute to Fe:H₂O, as highlighted in Figure 2, right-hand panel inset. These bands are attributed on the basis of our calculation of the electronic spectrum (Table 2 and the discussion below) as no literature data was available. It should be noted that we did not calculate the electronic spectrum of Fe₂:H₂O (which gives rise to the observed bands at 414 and 468 nm) because of the number of active electrons and orbitals (16, 24) that must be taken into account, leading to an

inaccessible active space for the CASSCF/CASPT2 method. The intensity of the experimental IR and UV–visible absorption bands increases with H₂O concentration in the matrixes, indicating the presence of a larger number of adducts upon deposition. Annealing of the matrixes had only a minimal impact on the water aggregates, largely some accelerated conversion between the ortho and para forms of H₂O, and no apparent effect on the concentration of Fe:H₂O and Fe₂:H₂O adducts.

The BPW91/cc-pVTZ optimized geometries of the various iron:water adducts that were initially considered as being potentially formed in the experiments, and for which the harmonic IR spectra were computed, are presented in Figure 3 along with the natural electronic population on the Fe atom within the complexes. All computed geometries and harmonic spectra for hydrogenated and deuterated complexes are reported in Table S3 in the Supporting Information. The energetics of the reactions forming adducts from iron atoms/dimers and water molecules are reported in Table 4. We identified a ⁵A'' state to be the most stable one for the Fe:H₂O complex. The geometrical parameters are slightly different from those determined—using the B3LYP functional—by Zhang et al.,¹² who found a ⁵A' ground state. Concerning energetics, we found a complexation energy of -39 kJ mol^{-1} at the DFT level, which diminishes to -16 kJ mol^{-1} at the CCSD(T)//DFT level. The former value is in agreement with that computed by Karlicky and Otyepka at the same level of theory (Table 5 in ref 21). These authors also found a decrease of the complexation energy using a CCSD(T) Hamiltonian, amounting to -7.5 kJ mol^{-1} using a large basis set (CCSD(T)/cc-pwCVnZ-DK). It is interesting to note that Zhang et al. calculated an exothermicity of -56 kJ mol^{-1} with the B3LYP functional¹² whereas Karlicky and Otyepka determined a value of -38 kJ mol^{-1} at the B3LYP

Table 4. Energetics for the Formation of Fe:H₂O Adducts and Photoproducts Determined at the BPW91/cc-pVTZ (DFT) and at the CCSD(T)/cc-pVTZ//DFT Levels of Theory^a

reactants	products	$\Delta H(0K)/\text{kJ mol}^{-1}$	
		DFT (DFT-D)	CCSD(T)//DFT (/DFT-D)
Fe + H ₂ O	Fe(H ₂ O) (⁵ A ^o)	-39 (-44)	-16 (-13)
	HFeOH (⁵ A ^o)	-159	-129
	FeO ($\Delta 5$) + H ₂	-29	+113
Fe + 2 H ₂ O	(H ₂ O)Fe(H ₂ O) (³ A)	-62 (-70)	+27 (+32)
	(H ₂ O)Fe(H ₂ O) (⁵ A)	-55 (-65)	-3.5 (-9)
	Fe(H ₂ O) ₂ (⁵ A)	-74 (-89)	-52 (-44)
	HOFeOH (⁵ A) + H ₂	-266	-225
Fe ₂ + H ₂ O	Fe ₂ (H ₂ O) (⁷ A)	-47 (-54)	+14 (+18)
	Fe ₂ (H ₂ O) (⁹ A)	+12 (+3)	-26 (-0.1)
	HFe ₂ OH (⁷ A)	-155	-101
	HFe ₂ OH (⁹ A)	-104	-133
	HFeOFeH (⁹ A ₁)	-333	-288

^aZPEs are computed at the DFT level. Regarding the complexes with the Fe dimer, the energetics were determined with respect to the ground states of Fe₂ at the DFT and CCSD(T) level, that is, ⁷ Δ_u and ⁹ Σ_g^- , respectively (see text).

level of theory using a cc-pVTZ basis set (Table 5 in ref 21). Regarding the formation of the complex, as there is no spin change between reactants and product, no barrier is expected to be present.

As can be seen in Table 1, the wavenumber associated with the ν_{aOH} mode for the ⁵A^o Fe:H₂O complex is particularly low in energy (even slightly lower, by 11 cm⁻¹, than the experimental value) and much lower than B3LYP values mentioned in the literature. This may be due to a questionable description of long-range interactions in the BPW91 potential. Indeed, harmonic frequencies of water were determined to be 1613, 3705, and 3807 cm⁻¹ at the BPW91/cc-pVTZ level, whereas experimental gas phase values are 1594, 3657, and 3756 cm⁻¹.⁶² We may note that the agreement between both is obtained with scaling factors of 0.988, 0.987, and 0.986 respectively. Upon coordination to the Fe atom, the ν_{sOH} and ν_{aOH} values appear red-shifted by 157 and 160 cm⁻¹ at the BPW91/cc-pVTZ level, respectively, which is surely overestimated. This means that, upon interaction with Fe, the OH bond are overly weakened, and this has a larger effect on stretching than bending modes. Adding empirical dispersion corrections leads to an increase by 11 cm⁻¹ of the ν_{aOH} mode, 7 cm⁻¹ of the ν_{sOH} mode, and 2 cm⁻¹ of the δ_{OH_2} mode. The inclusion of dispersion interactions thus improves the calculated positions of the IR bands, especially those of the stretching OH bands, with respect to experimental data. It should be noted that the geometry changes induced by dispersion are small, the Fe–O bond being increased by 0.01 Å and the Fe–OH angle by 2° (from 104° to 106°). Dispersion effects stabilize the complex by 5 kJ mol⁻¹ at the DFT level, but single-point CCSD(T) calculations for the DFT-D geometry lead to a destabilization of 3 kJ mol⁻¹ with respect to the initial CCSD(T)/DFT value (first line of Table 4). The inclusion of dispersion interactions thus increases the discrepancies between DFT and CCSD(T)//DFT values in terms of the energetics.

On the basis of MS-CASPT2 calculations, the 15 first quintet electronic states of the Fe:H₂O adduct can be identified as the slightly mixed 3d⁶4s² and 3d⁷4s configurations of the iron and beyond these, the presence of the water molecule gives rise to strong mixing between the 3d⁶4s4p and the 3d⁷4p configurations. The spin–orbit coupling of the 70 electronic states leads to 350 spin–orbit states. Spin–orbit states as well as energies and oscillator strengths, with relative oscillator strengths (compared to the maximal 0.076 value) higher than 0.013, are given in Table 2. The oscillator strengths are overall larger than those of the atomic iron and more spin–orbit states absorb. The most intense band, corresponding to a 3d⁶4s4p electronic configuration, is found 20 nm lower than for the iron atom (280.6 nm instead of 300.7 nm).

Returning to the DFT geometries, for complexes of Fe with two water molecules, we considered two types of isomers: one with a water dimer interacting with Fe (Figure 3, lower left), hereafter designated Fe(H₂O)₂, and a second with two individual water molecules coordinated to the Fe atom via their oxygen atoms (Figure 3, lower middle), hereafter designated (H₂O)Fe(H₂O). We considered only a quintet spin state for Fe(H₂O)₂, analogous to Fe(H₂O). In the optimized geometry, one water molecule is coordinated to the Fe atom via its oxygen and the second molecule interacts with Fe through the H atom not involved in the hydrogen bond with the first water molecule. Such a structure resembles the “filament” isomer found for [Fe(H₂O)₂]⁺ by Garza-Galindo and co-workers,⁶³ although in this cationic species the second water molecule does not interact at all with Fe⁺. Regarding energetics, the formation of Fe(H₂O)₂ is thermodynamically favorable from one Fe atom and two water molecules, as it would be exothermic by -52 kJ mol⁻¹ at the CCSD(T)//DFT level of theory. As in the case of Fe(H₂O), no spin change occurs during the complexation and therefore no energetic barrier is expected. For the (H₂O)Fe(H₂O) isomer, we found two low energy spin states: a quintet and a triplet. The latter was found to be the most stable at the DFT level, whereas the former was lower in energy at the CCSD(T)//DFT level (Table 4). In the final optimized geometry of the triplet spin state, the Fe atom is aligned with the O atoms, as found for (H₂O)Fe(H₂O)⁺,⁶³ whereas the O–Fe–O angle in the quintet is 124°. Contrary to the results for the cation, the Fe, O, and two H atoms for a given water ligand are not in the same plane. This was expected, as such a difference has already been observed between the Fe(H₂O) and Fe(H₂O)⁺ complexes. In terms of energetics, DFT calculations indicate that the formation of the two isomers is exothermic, although single-point CCSD(T) calculations indicate an endothermic process for the triplet (+27 kJ mol⁻¹), and a slightly exothermic process for the quintet (-3.5 kJ mol⁻¹). We note here that the two isomers present different stretching OH features: the combination of symmetric OH stretching modes are found at 3502/3507 cm⁻¹ for the quintet and 3403/3417 cm⁻¹ for the triplet, while the combination of antisymmetric ones are found at 3606/3607 cm⁻¹ for the quintet and at 3476/3493 cm⁻¹ for the triplet. None of these positions are in agreement with experimental data. Taking into account dispersion effects for such complexes induces very small changes in the harmonic IR mode positions (maximum shift of +11 cm⁻¹ observed for the ν_{aOH} of (H₂O)Fe(H₂O) ⁵A). This is associated with tiny geometrical changes (Table S3 in the Supporting Information) and stabilization (respectively destabilization) at the DFT (respectively CCSD(T)) levels of theory. We only observe that

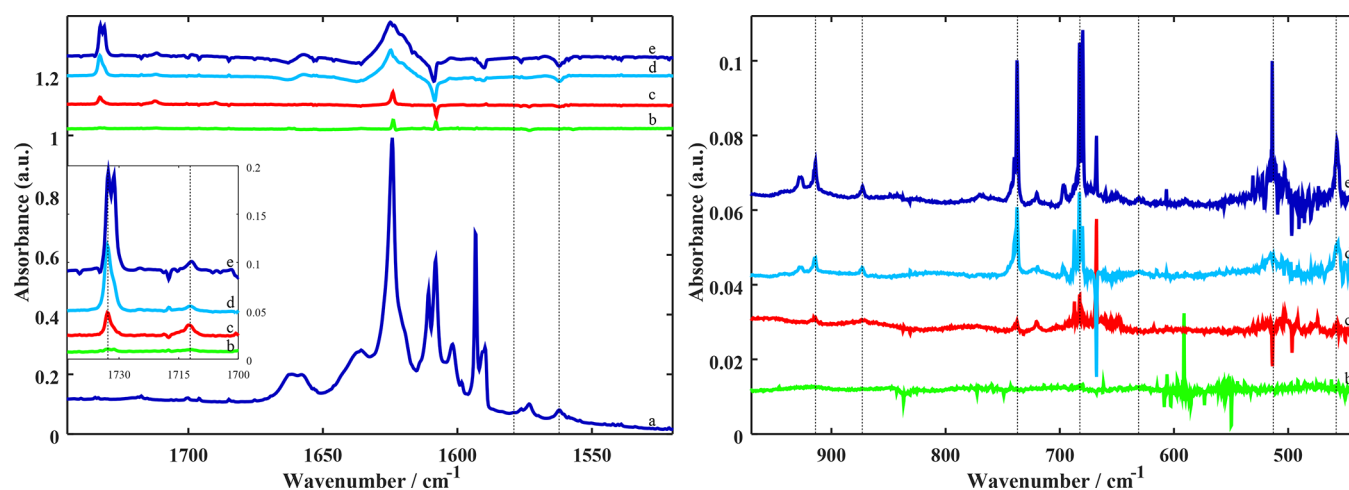


Figure 4. Processing of Fe:H₂O:Ar matrixes with UV radiation ($\lambda < 235$ nm), presented in the spectral regions 1745–1520 cm⁻¹ (left-hand panel) and 970–400 cm⁻¹ (right-hand panel). In the left-hand panel, spectrum a is an unprocessed Fe:H₂O:Ar matrix (spectrum e in Figure 1), presented for comparison to the processed spectra. Spectra b–e are presented as difference spectra (irradiated minus nonirradiated samples) for increasing concentrations of H₂O. Dotted lines represent the position of Fe:H₂O and Fe₂:H₂O complexes (1562 and 1579 cm⁻¹), which decrease upon irradiation. The inset presents a zoom of the 1700–1740 cm⁻¹ region, where, upon irradiation, new bands are formed at 1733 and 1712 cm⁻¹. These are attributed to the insertion of Fe and Fe₂ into H₂O, as has previously been reported in the literature. In the right-hand panel, four spectra (traces b–e) are presented. These spectra, corresponding to the difference spectra of the four Fe:H₂O:Ar matrixes after processing with UV radiation, have the same labels as those in the left-hand panel and in Figure 1. Various photoproduct absorption bands appear upon irradiation, and their attributions are detailed in Table 1 and in the text.

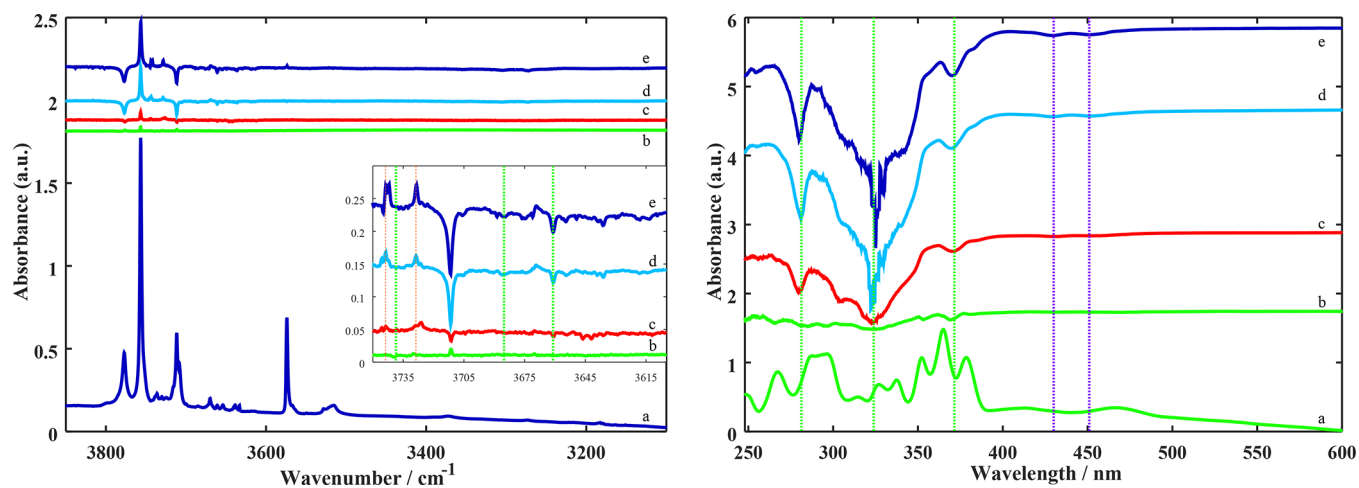


Figure 5. Processing of Fe:H₂O:Ar matrixes with UV radiation ($\lambda < 235$ nm), presented in the spectral regions 3850–3100 cm⁻¹ (left-hand panel) and 245–600 nm (right-hand panel). In the left-hand panel, spectrum a is an unprocessed Fe:H₂O:Ar matrix (spectrum e in Figure 1), presented for comparison to the processed spectra. The spectra b–e are presented as difference spectra (irradiated minus nonirradiated samples) for increasing concentrations of H₂O. The inset presents a zoom of the 3750–3610 cm⁻¹ region, where, upon irradiation, bands attributed to Fe:H₂O and Fe₂:H₂O decrease while new bands appear at 3742 and 3728 cm⁻¹. By comparison with calculations, these are attributed to the insertion of Fe into H₂O and to the formation of Fe(OH)₂. In the right-hand panel, spectrum a is an unprocessed Fe:H₂O:Ar matrix with only a trace of H₂O (spectrum b in the right-hand panel of Figure 2) for comparison with the processed spectra b–e. Bands corresponding to Fe:H₂O and Fe₂:H₂O adducts disappear with irradiation (the three most intense for Fe:H₂O (281, 324, 372 nm) and the two bands for Fe₂:H₂O (430, 451 nm) are plotted here to guide the eye).

the Fe(H₂O)₂ complex is more stabilized than the others when dispersion is included (Table 4), which is probably due to the presence of the weakly bound water dimer.

We also considered the complex formed between the Fe dimer and one water molecule. For Fe₂:H₂O, we found a ⁷A' ground state at the DFT level, with Fe–Fe–O slightly deviating from linearity (Figure 3, top right). Both spin state and geometry are similar to those found by Zeinalipour-Yazdi and van Santen,¹ with a maximum difference in the geometrical parameters of 0.02 Å (in the Fe₂–O bond length). We found a Fe₂–H₂O interaction energy of –47 kJ mol⁻¹ at the DFT level

of theory whereas those authors found –10 kcal mol⁻¹ (about –42 kJ mol⁻¹). At the CCSD(T)//DFT level, the formation of this complex in its ⁷A' state becomes endothermic (+14 kJ mol⁻¹). In fact, in contrast to the results of Zeinalipour-Yazdi and van Santen,¹ we found a nonuplet spin state for Fe₂:H₂O with a different geometry from that of the ⁷A' state, and lying +59 kJ mol⁻¹ above it at the DFT level (Figure 3 and Table 4). This nonuplet complex is, however, found to be stable at the CCSD(T)//DFT level, leading to a Fe₂–H₂O complexation energy of –26 kJ mol⁻¹ (Table 4). This was expected, as the ground state of Fe₂ was found to be ⁷Δ_u at the DFT level (ΔE

= 55 kJ mol⁻¹) and ${}^9\Sigma_g^-$ at the CCSD(T)//DFT level ($\Delta E = 95$ kJ mol⁻¹). This type of calculation illustrates the limitation of DFT treatment for complexes involving transition metal clusters. The formation of Fe₂:H₂O from the reactants Fe₂ + H₂O should be energetically favorable, and no energetic barrier is expected to be present (no spin change). We may notice that, as the differences in the vibrational frequencies of the ${}^7A'$ and 9A isomers are of the same order of magnitude as the uncertainties in the DFT mode positions, it is not possible to determine which isomer is formed in the experiment. Taking into account dispersion effects leads to the same conclusions as for the Fe:H₂O complexes: it leads to very small changes in harmonic mode positions (less than 5 cm⁻¹) and geometries, while the discrepancies between DFT and CCSD(T)//DFT energetics are increased. Overall, taking into account dispersion interactions does not modify the conclusions of the comparison between experiment and theory. For the current study, it is likely that the fact that calculations are performed on gas phase molecules and complexes, and thus the matrix effects are not taken into account, is a larger source of discrepancy than the consideration of dispersion interactions.

Photoproducts of Fe Adducts with H₂O. The experimental IR and UV–visible spectra recorded after UV irradiation of matrixes containing iron:water adducts are presented in Figures 4 and 5. The adducts Fe:H₂O and Fe₂:H₂O are removed from the argon matrixes, as evidenced by the disappearance of absorption bands attributed to these species. The loss of the bands at 3661, 3685, and 3739 cm⁻¹ in the ν_3/ν_1 OH stretching region of the mid-IR confirms their attribution to Fe adducts. Similarly, in the UV–visible spectra, the bands at 270, 281, 320, 324, 331, 342, 356, 372, 387, 430, and 451 nm are confirmed to be due to Fe adducts. The assignments of the IR bands, based on comparison with DFT calculations, are reported in Table 1. Similar data for their deuterated counterparts are reported in Table 3.

The loss of Fe adducts in the matrixes coincides with the appearance of new absorption bands due to the formation of insertion photoproducts. In the ν_2 OH bending mode region (Figure 4, left-hand panel), new absorption features are observed at 1733 and 1712 cm⁻¹. As in previous studies,^{11,12} these are attributed to the insertion products HFeOH and HFeOFeH, respectively. These species also give rise to bands at 682 and 458 cm⁻¹ and at 914 cm⁻¹, respectively (Figure 4 and Table 1). In this work, we have identified bands of photoproducts in the ν_3/ν_1 OH stretching region for the first time on the basis of our experimental spectra and quantum chemistry calculations. An absorption feature at 3742 cm⁻¹ is attributed to HFeOH.

In addition to insertion photoproducts, two further species are identified in the experimental spectra. First, Fe(OH)₂ gives rise to absorption features at 737, 631, and 513 cm⁻¹, identified in previous studies,^{11,12} and at 3728 cm⁻¹, identified here for the first time on the basis of our DFT calculations. Second, the absorption feature at 873 cm⁻¹ is attributed to FeO,^{53,54} observed in the study of Zhang et al.¹² but not that of Kauffman et al.¹¹ In the same spectral region, we observe a few minor peaks that are low intensity, but which increase with the concentration of H₂O in the matrix. These are all in the region where we expect to see absorptions due to O–Fe–O (for example, Zhang et al.¹² propose HFeOFeOH as the attribution for the band at 695 cm⁻¹), so we tentatively assign them to multiple insertion species without providing a precise attribution.

The BPW91/cc-pVTZ optimized geometries of the theoretically treated photoproducts are presented in Figure 6, and the

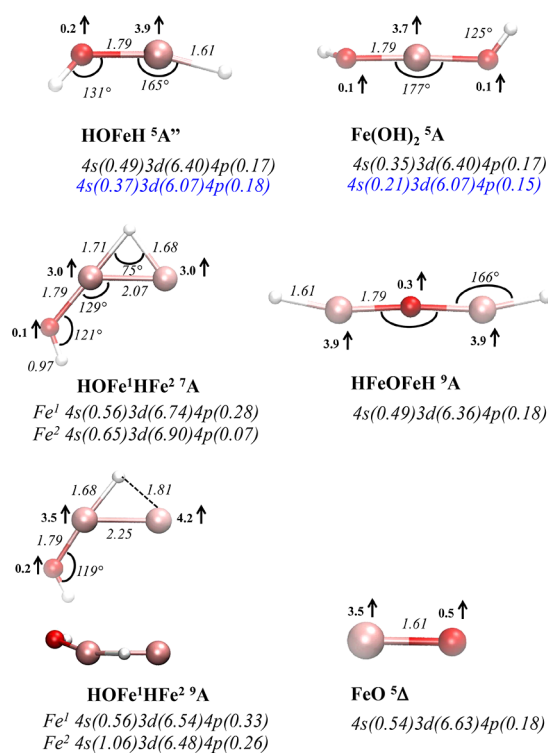


Figure 6. As for Figure 3, BPW91/cc-pVTZ optimized geometries of iron–water complex photoproducts.

thermodynamics of their formation from the Fe atom/dimer and water molecule(s) can be found in Table 4. All computed geometries and harmonic spectra for hydrogenated and deuterated complexes are reported in Table S4 in the Supporting Information. The energetics of the reactions forming adducts from iron atoms/dimers and water molecules are reported in Table 4. The ground state of the complex resulting from the insertion of the Fe atom into one O–H bond of the water molecule, HFeOH, was determined to be a ${}^5A''$ state, lying 120 kJ mol⁻¹ below the Fe:H₂O complex at the DFT level of theory. We note that Gutsev et al. determined an energy difference of 104 kJ mol⁻¹ between HFeOH (for which they found two degenerate ${}^5A'$ and ${}^5A''$ complexes as the most stable) and Fe:H₂O (${}^5A'$), using the same functional as us (BPW91) but a different basis set (6-311+G**).²⁰ We concluded that the formation of HFeOH from Fe + H₂O was exothermic by 159 kJ mol⁻¹ at the DFT level, and by 129 kJ mol⁻¹ at the CCSD(T)//DFT level. These values are consistent with those obtained by Karlicky and Otyepka.²¹ These authors also computed the reaction path leading to HFeOH from Fe + H₂O and showed that the insertion of Fe into the O–H water bond cost 99 kJ mol⁻¹ (Figure 3 in ref 21). They also determined the reaction path that leads from HFeOH to the formation of FeO and H₂, and showed that it cost 151 kJ mol⁻¹ with respect to Fe + H₂O. In agreement with this prior study,²¹ we found the relative energy of FeO + H₂ with respect to Fe + H₂O to be significantly underestimated at the BPW91/cc-pVTZ level of theory (–29 kJ mol⁻¹ vs +113 kJ mol⁻¹ at the CCSD(T)//DFT level, Table 4).

The insertion of Fe₂ into a O–H bond may lead to the formation of HFe₂OH. We found that the lowest energy spin

state for this complex at the BPW91/cc-pVTZ level corresponded to a septuplet state. In the optimized geometry, the lone H atom interacts with the two Fe atoms, whereas the OH is coordinated to only one Fe atom (Figure 6, center left image). Interestingly, this spin state/geometry is similar to that found by Zeinalipour-Yazdi and van Santen (B3LYP calculations)¹ with, however, small discrepancies in the bond lengths, up to a maximum of 0.3 Å in the Fe–Fe bond, with distances in B3LYP being larger than those in BPW91. In the most stable geometry obtained for this type of isomer by Gutsev et al.,²⁰ both H atoms and the O atom interact with the two Fe atoms. We optimized the same isomer, finding it to lie 41 kJ mol⁻¹ higher in energy than our most stable one. We also optimized a nonuplet spin state starting from the ⁷A ground state geometry. The geometry was slightly distorted (Figure 6, lower left image), and the ⁹A complex was found to lie 51 kJ mol⁻¹ above the ⁷A one at the DFT level. However, when CCSD(T)//DFT calculations were performed, the ⁹A complex was found to be the ground state ($\Delta E = -32$ kJ mol⁻¹ with respect to the septuplet). The formation of both complexes was found to be exothermic. Here, we underline that Zeinalipour-Yazdi and van Santen showed that the formation of the HFe₂OH complex from Fe₂:H₂O in their septuplet spin states would require about 24 kJ mol⁻¹ at the B3LYP level (Figure 5b of ref 1), which is, interestingly, much lower than the activation energy calculated for one Fe atom. However, one has to be careful about these results because, as discussed above, DFT methods are likely to highly underestimate energetic barriers.

Finally, we optimized the geometries of other complexes whose formation paths from Fe atoms and water molecules are not trivial, namely, the complexes HOFeOH and HFeOFeH, also suggested to be formed in the experiment of Zhang et al.¹² We found quintet and nonuplet spin states for the ground states of these complexes, respectively, in agreement with the calculations of Zhang et al.¹² The final optimized geometry of HOFeOH is quite similar to that obtained by Zhang et al., except that we find a Fe–O–H angle smaller by 10°. For HFeOFeH, we found a H–Fe–O angle of 177° whereas Zhang et al. had proposed a strictly linear structure. Both HOFeOH and HFeOFeH complexes were found to be very stable with respect to the initial reactants, -225 and -288 kJ mol⁻¹ at the CCSD(T)//DFT level, respectively. We compared the energetics for the formation of HOFeOH (Fe + 2H₂O → HOFeOH + H₂) and HFeOFeH (Fe + HFeOH → HFeOFeH) computed in the present work with values obtained by Zhang et al.¹² using the B3LYP functional. For HOFeOH, we obtained -266 (respectively, -225) kJ mol⁻¹ at the DFT (respectively, CCSD(T)//DFT) level, whereas Zhang et al. obtained a value of -262 kJ mol⁻¹. For HFeOFeH, we obtained -174 (respectively, -159) kJ mol⁻¹ at the DFT (respectively, CCSD(T)//DFT) level, whereas Zhang et al. obtained a value of -192 kJ mol⁻¹. Therefore, although the calculated energetics for the formation of Fe(OH)₂ are very similar in both studies, we obtained smaller values for the formation of HFeOFeH.

There was no observation of photoproducts in the UV–visible spectrum, although the loss of Fe₁₋₂:H₂O adducts from the matrix was confirmed by the disappearance of their absorption bands (as can be verified in Figure 5, right-hand panel). The ground state obtained at the MS-CASPT2 level for the HFeOH complex is ⁵A'' H⁻Fe²⁺(3d⁶)O⁻H. It appears that the first four quintet excited states correspond to metal centered transitions d_z² → d_{xz} (41 cm⁻¹ or 242359 nm); d_z² →

d_{x²-y²} (4119 cm⁻¹ or 2428 nm); d_z² → d_{yz} (4999 cm⁻¹ or 2000 nm); d_z² → d_{xy} (6326 cm⁻¹ or 1581 nm). The following states are of different natures: excitation from the terminal hydrogen to the iron 3d or 4p orbitals, excitation centered on the iron, from a 3d orbital to the 4p orbital, and finally excitation from the oxygen lone pair to the 3d orbitals of the iron atom. However, the oscillator strengths are very weak for all the states until 245 nm (Table S5 in the Supporting Information), which could explain why no absorption bands in the experimentally accessible UV–visible region were observed for this species. States corresponding to an excitation from the oxygen lone pair to the 3d orbitals of the iron atom and local excitation on the iron atom (3d to 4p) are found lower than 245 nm with a significant oscillator strength. In Figure 7, we present the

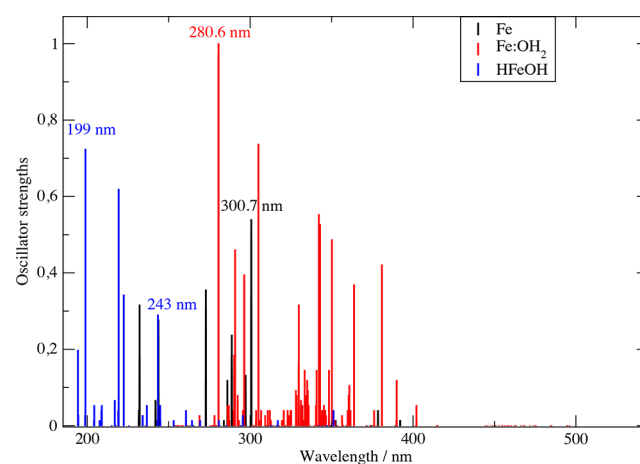


Figure 7. Calculated electronic spectra of Fe, Fe:OH₂, and HFeOH. The oscillator strengths are all relative to the maximal value obtained for the Fe:OH₂ complex.

calculated electronic spectra of Fe, Fe:H₂O, and HFeOH. It should be noted that the calculated band positions present a very good agreement with the experimental data, especially given the fact that the experimental spectra were measured in cryogenic matrixes and that the calculations did not take into account anharmonicity. It should also be noted that electronic spectra were not calculated for the other confirmed photoproducts (HFeOFeH, Fe(OH)₂, FeO), as this would represent an extensive study in itself.

Experiments and calculations using deuterated water confirm the attributions made here for Fe:H₂O, Fe₂H₂O, HFeOH, and FeO. It should be noted that our calculations were made without taking account of the anharmonicity and the effect of the argon matrix on the frequencies. However, a very good agreement was obtained, particularly for D₂O and deuterated Fe-containing compounds, for which anharmonicity effects are reduced (see Table 3 for details of attributions, or Tables S3 and S4 in the Supporting Information for a complete list of calculated deuterated species).

CONCLUSIONS

Using a combined experimental and theoretical approach, we have determined, for the first time, the UV–visible and 3800–3600 cm⁻¹ mid-IR spectra of Fe_x:H₂O_y adducts and their photoproducts (including the insertion species HFeOH, HFeOFeH, and the molecules Fe(OH)₂ and FeO). By applying the results of DFT calculations to our experimental mid-IR spectra, building upon our knowledge of the IR spectroscopy of

water clusters,⁵⁸ we were able to attribute bands to OH stretches of Fe adducts and insertion products. Using the SO-CASPT2 or SO-MS-CASPT2 method and our previous work on iron complexes,⁵¹ we were able to model the Fe, Fe:H₂O, and HFeOH UV–visible spectra. Despite the lack of matrix effects or anharmonicity (for IR spectra) in the theoretical description, both computed mid-IR and UV–visible spectra well reproduced the experimental spectra. To verify the higher energy transitions, especially for HFeOH, we intend to extend these experiments to lower wavelengths by changing the experimental setup.

The experiments presented here confirm that atomic Fe in its neutral state is highly reactive with water. We observed the production of photoproducts, even for the lowest concentrations of H₂O, despite the fact that irradiation of matrixes was only carried out for three minutes at an average power of ~150 mW. This suggests that the reaction could potentially be very important in dense astrophysical regions irradiated by UV. The identification of spectral bands in the mid-IR and UV–visible regions may also help with the identification of iron-bearing species in such interstellar environments.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b09681.

Validation of the CASPT2 parameters, accompanied by Table S1; experimental and SO-CASPT2 energy levels of neutral iron atom are given, Table S2; complete list of calculated geometries and frequencies for hydrogenated and deuterated species (without and with dispersion), Tables S3 and S4; calculated absorption energies of HFeOH, Table S5 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*J. A. Noble. E-mail: jennifer.noble@univ-lille1.fr. Phone: +33 (0) 3 20 43 49 87. Fax: +33 (0) 3 20 43 40 84.

ORCID

Joëlle Mascetti: 0000-0002-8585-9118

Aude Simon: 0000-0002-2315-9490

Jennifer A. Noble: 0000-0003-4985-8254

Notes

The authors declare no competing financial interest.

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■ ADDITIONAL NOTE

^aWe specify here that we used a value of 1.2 for s_6 in eq 11 of Grimme et al.²⁵ To be completely accurate, the value of such a

coefficient should be determined specifically for the BPW91 functional, but this is beyond the scope of the current study.

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