



Spectroscopic characterisation of radical polyinterhalogen molecules†

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 Cite this: *Phys. Chem. Chem. Phys.*, 2020, 22, 8284

 Received 8th March 2020,
Accepted 3rd April 2020

DOI: 10.1039/d0cp01311k

rsc.li/pccp

Spectroscopic characterisations of the radical polyinterhalogen molecules IF₂ and I₂F are reported using anion photoelectron spectroscopy. The corresponding parent anions, IF₂[−] and I₂F[−], are common products formed in hard Ar–CF₃I plasmas and are relevant in the semiconductor manufacture industry. The I₂F[−] species, which is present as the [I–I–F][−] isomer, is a “non-classical” polyinterhalogen.

The propensity for halide anions to combine and form polyhalogen anions, such as I₃[−], has been known for around 200 years.¹ However, examples and spectroscopic characterisation of polyinterhalogen molecules, particularly open-shell species, have proven to be elusive.² To date, most spectroscopic characterisations of polyinterhalogen anions are as crystallised solids or have been performed in matrix isolation with a counter cation.^{2–4} There are no known vibrationally-resolved spectroscopic determinations of radical (open-shell) polyinterhalogen molecules. On the other hand, closed-shell polyinterhalogen molecules such as IF₃, IF₅, IF₇ and I₂F₄ are relatively stable compounds. Polyinterhalogen anions and their corresponding radical neutrals are appealing targets for gas-phase spectroscopy due to being textbook examples for valence-shell electron pair repulsion (VSEPR) theory and the Rundle–Pimentel scheme for hypervalency.^{5,6} They are also desirable systems to benchmark high-level quantum chemical calculations due to challenges associated with describing heavy atoms.^{7,8}

This paper reports a combined photoelectron spectroscopy and electronic structure theory study on the IF₂[−], I₂F[−], IF₂ and I₂F species. There have been several reports of synthesis, crystallography and spectroscopic characterisation of IF₂[−] embedded in a solid state matrix,^{9,10} and computational studies on IF₂[−] and I₂F[−] and related species,^{7,10–14} however, a recent

review by Riedel and co-workers² noted “Thus far, ... [I₂F][−] have not been detected experimentally.” While this statement might be true for condensed phases, I₂F[−] appears to be a common product formed in hard Ar–CF₃I plasmas.

There are only a handful of examples of gas-phase spectroscopic studies on polyhalogen species, mostly targeting I₃[−]. A series of pioneering investigations by Neumark and co-workers^{15–18} applied anion photoelectron spectroscopy with different laser sources to characterise vibronic properties of the radical neutral I₃, and photodissociation dynamics of the parent anion. Several other studies have focussed on photodissociation dynamics.^{19–22} There have been two investigations on I₂Br[−] probing the dissociation dynamics, with one of these studies providing a single-colour photoelectron spectrum at 267 nm.^{23,24} In the present work, we have coupled a jet-cooled plasma discharge source with time-of-flight mass spectrometry and anion photoelectron spectroscopy. This strategy allows for generation and mass selection of IF₂[−] and I₂F[−], and determination of spectroscopic properties of the radical neutral IF₂ and I₂F species.

Intriguingly, radical polyinterhalogen molecules may have a significant bearing in industrial plasma processes. In particular, in the present study we produced the IF₂[−] and I₂F[−] species through plasmatisation of an Ar–CF₃I mixture; this mixture and process is relevant in the semiconductor manufacture industry. In this industry, dry-etching plasma processes utilise the reaction between silicon wafers, which are the substrate for semiconductor and microprocessors, and fluorine atoms and CF₃ radicals to etch the substrate at specific locations on the wafer.²⁵ Conventionally, these radical species are produced in a plasma consisting of an inert carrier gas seeded with CF₄ or C₃F₈. In recent years, there has been growing interest in the use of CF₃I as an alternative to CF₄ because the use of CF₄ is restricted in many countries by the Montreal Protocol due to the molecule’s high global warming potential (GWP).^{26,27} For example, even though CF₃I is infrared active, CF₃I has an atmospheric residence life of ≈ 1 day and corresponding GWP ≈ 1.^{28,29} In contrast, CF₄ has a residence life of ≈ 50 000 years and corresponding GWP ≈ 6000.^{29,30} Furthermore, although iodine atoms formed through UV photodissociation of

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† Electronic supplementary information (ESI) available: Experimental methods, theoretical methods, calculated vertical excitation energies, further Franck–Condon simulations. See DOI: 10.1039/d0cp01311k



CF₃I are exceptionally destructive towards stratospheric ozone,³¹ the short residence time of CF₃I released at terrestrial altitudes means that these molecules do not reach the stratosphere and contribute to ozone destruction. Ultimately, modelling and tuning of the etching process allows maximisation of process efficiency and minimisation of unwanted by-products. Theoretical plasma models require a detailed qualitative and quantitative understanding of the rich ion–molecule and electron–molecule chemistry that occurs in dry-etching plasmas (particularly the chemistry associated with fluorine-containing radicals).^{32–36}

IF₂[−] & IF₂

Photoelectron spectra for IF₂[−] are shown in Fig. 1, revealing a clear vibrational progression with spacing 600 ± 50 cm^{−1}. The adiabatic detachment energy (ADE), assigned as the lowest energy discernible detaching vibration in the $h\nu = 4.13$ eV spectrum, is ADE = 4.03 ± 0.02 eV. The vertical detachment energy (VDE), determined as the most intense vibration in the $h\nu = 4.66$ eV photoelectron spectrum, is VDE = 4.23 ± 0.04 eV. These ADE and VDE values are most consistent with the calculated values (Table 1) for the [F–I–F][−] isomer shown in Fig. 2; there was no evidence for the [F–F–I][−] isomer, which was calculated to lie 2.74 eV (264 kJ mol^{−1}) higher in energy. Calculated ADE and VDE values for [F–I–F][−] at the CCSD(T)//def2-TZVPD level of theory (Table 1) are both ≈ 4% larger than the experimental values (similar to the result for I[−] given in the ESI[†]). Increasing the basis set to def2-QZVPD gave calculated values that were ≈ 6% larger than the experimental values (Table 1). The better agreement with the smaller basis set is presumably a fortuitous cancellation of errors with some fraction of this associated with heavy atom/relativistic effects.



Fig. 1 Photoelectron spectra for IF₂[−] at $h\nu = 4.66$ eV and 4.13 eV (inset) and Franck–Condon simulation (red sticks) of the D₀ ← S₀ detaching transition for the [F–I–F][−] isomer. Electron binding energy (eBE) and electron kinetic energy (eKE) are related by $eBE = h\nu - eKE$, where $h\nu$ is the photon energy.

Table 1 Experimental (subscript e) and calculated (subscript c) electron detachment energies for IF₂[−] and I₂F[−]. Calculations are at the CCSD(T)/def2-TZVPD level of theory (CCSD(T)/def2-QZVPD in parentheses). Experimental uncertainties account for velocity-map imaging calibration using I[−] and pixel-to-energy conversion in image reconstruction

	[F–I–F] [−]	[F–F–I] [−]	[I–I–F] [−]	[I–F–I] [−]
ADE _e	4.03 ± 0.02	—	4.04 ± 0.06	—
VDE _e	4.23 ± 0.04	—	4.23 ± 0.04	—
ADE _c	4.14 (4.15)	3.17	4.22 (4.28)	3.19 (3.38)
VDE _c	4.40 (4.50)	3.88	4.40 (4.55)	3.96 (4.08)



Fig. 2 Calculated equilibrium geometries at the CCSD(T)//def2-TZVPD level of theory for: (a) [F–I–F][−] and [F–I–F], and (b) [F–F–I][−] and [F–F–I]. NBO charges (red and blue font) are given for the anions. The lowest energy isomer, [F–I–F][−] has D_{∞h} symmetry, and [F–I–F] has C_{2v} symmetry.

A Franck–Condon simulation of the photoelectron spectrum for the [F–I–F][−] configuration is shown in Fig. 1 and has good agreement with the experimental spectrum. The simulation suggests that the vibrational progression is dominated by detaching transitions to the ν_2 (asymmetric stretch) and ν_3 (symmetric stretch) vibrations of the [F–I–F] radical neutral species; calculated frequencies suggest that these two vibrations are nearly degenerate – see Table 2. We can therefore assign the experimental value of ν_2/ν_3 at 600 ± 50 cm^{−1} for the [F–I–F] species. The small feature denoted by * in the inset in Fig. 1 is probably a hot band from vibrationally-excited ions produced in the plasma (see ESI[†]). The ADE assignment to the 0–0 transition should be robust based on alignment of the VDE with the Franck–Condon simulation. It is worth noting that a Franck–Condon simulation of the photoelectron spectrum for the [F–F–I][−] isomer (see vibrational frequencies for [F–F–I] in Table 2) is inconsistent with the experimental spectra, lending support to the above isomer assignment.

Calculated vertical excitation energies for the [F–I–F][−] isomer are given in Table S1 in the ESI[†]. These data show that although an excited state resonance is energetically accessible with a $h\nu = 4.66$ eV photon, oscillator strengths are zero and therefore the photoelectron spectra in Fig. 1 should be described by direct photodetachment to the ground electronic state of the neutral.

Table 2 Calculated harmonic vibrational frequencies for IF₂[−] and IF₂ at the CCSD(T)//def2-TZVPD level of theory in units of cm^{−1}

Mode	[F–I–F] [−]	[F–I–F]	[F–F–I] [−]	[F–F–I]
ν_1	193 ^a	96 ^a	137 ^a	18 ^a
ν_2	193 ^a	547 ^c	137 ^a	18 ^a
ν_3	401 ^c	548 ^b	230 ^c	38 ^b
ν_4	437 ^b	—	247 ^b	614 ^c

^a Bend. ^b Symmetric stretch. ^c Asymmetric stretch. [F–F–I] has C_{∞h} symmetry. Note the symmetric vs. asymmetric stretch mode ordering.



Calculated vertical excitation energies for neutral [F–I–F], *i.e.* electronic excited states of [F–I–F] at the [F–I–F][−] equilibrium geometry, suggested that only the ground electronic state is accessible using the photon energies in Fig. 1, consistent with a single vibrational progression.

I₂F[−] & I₂F

Photoelectron spectra for I₂F[−] at three photon energies are shown in Fig. 3a, revealing two detachment bands. The lower binding energy band has ADE = 4.04 ± 0.06 eV and VDE = 4.23 ± 0.04 eV. There is no clear vibrational structure. The higher binding energy band has ADE2 = 4.60 ± 0.04 eV and VDE2 = 4.68 ± 0.04 eV, and vibrational spacing of 550 ± 100 cm^{−1}.

The ADE and VDE parameters for the lower energy band are consistent with the calculated values for the [I–I–F][−] isomer (Table 1), again with a small overestimation by theory. The two bands in Fig. 3a are thus assigned to detaching transitions to the ground and excited electronic states of the [I–I–F] radical neutral. Equilibrium geometries for the I₂F[−] and I₂F isomers are shown in Fig. 4; the [I–I–F][−] isomer is more stable by 1.35 eV (130 kJ mol^{−1}), consistent with it being the predominant isomer formed in the plasma. There was no evidence for the [I–F–I][−]

isomer when photoelectron spectra were recorded at photon energies below the ADE for the [I–I–F][−] isomer. A Franck–Condon simulation of the photoelectron spectrum to give the ground electronic state of the neutral (red in Fig. 3b) shows no clear vibrational structure, consistent with experimental spectrum. Calculated vibrational frequencies are given in Table 3.

The second, higher binding energy photodetachment band in Fig. 3a was assigned to direct photodetachment to the A₁ state of the [I–I–F] species. Geometry optimisation of this state at the EOM-CCSD//def2-TZVPD level of theory produced a linear (C_{∞h} symmetry) structure with r_{II} = 3.02 Å and r_{IF} = 1.96 Å. Using this structure, ADE2 was calculated at 4.79 eV (term energy, T_e, of 0.57 eV which is close to the experimental value of T_e = 0.56 ± 0.08 eV), which is again ≈ 4% larger than experiment. Calculated vibrational frequencies for the A₁ state are ν₁ = 109 cm^{−1} (bend), ν₂ = 157 cm^{−1} (symmetric stretch) and ν₃ = 530 cm^{−1} (asymmetric stretch). A Franck–Condon simulation of the photoelectron spectrum associated with formation of the A₁ state of the neutral is shown in green in Fig. 3b, and predicts that the vibrational structure is predominantly from the ν₃ = 530 cm^{−1} mode. The feature denoted by * in Fig. 3a at eBE = 4.56 eV is assigned to hot band signal (see ESI†).

Calculated vertical excitation energies for the I₂F[−] isomers are given in Table S1 in the ESI.† For the [I–I–F][−] isomer, the first few electronic states have very low oscillator strengths and the photoelectron spectra for photon energies < 5 eV should be dominated by direct photodetachment. There is, however, a bright A₁-symmetry resonance with a calculated vertical excitation energy in the 5.1–5.2 eV range (see ESI†). Fortunately, the photoelectron spectra for both of these species are at lower binding energies and should not interfere with the spectra shown in Fig. 3. It is worth noting that the issue of bright excited state resonances in the detachment continuum is more serious for I₃[−] (ref. 15–18) and larger polyinterhalogen anions due to an increased density of electronic states.

Polyinterhalogen molecules can be divided into two categories, classical and non-classical.³ The former is defined as containing an electropositive central atom surrounded by electronegative halogen atoms, *e.g.* [F–I–F][−]. In contrast, for a non-classical polyinterhalogen molecule, the central halide is more electronegative than the coordinating dihalogen or interhalogen molecules, *e.g.* Cl(I₂)₄[−] in which four I₂ molecules coordinate a Cl[−].^{3,37} Interestingly, the [I–I–F][−] species satisfies the non-classical criterion, possessing covalent-like bond lengths and a



Fig. 3 (a) Photoelectron spectra for I₂F[−] at $h\nu = 4.43, 4.66$ and 5.17 eV. Electron binding energy (eBE) and electron kinetic energy (eKE) are related by $eBE = h\nu - eKE$, where $h\nu$ is the photon energy. (b) Franck–Condon simulation of direct photodetachment to the D₀ and A₁-symmetry neutral electronic states. The simulations suggest that the D₀ ← S₀ detaching transition is dominated by low frequency modes and combination bands. See ESI† for Franck–Condon simulations at higher temperatures which assign the feature denoted by * to a hot band.



Fig. 4 Calculated equilibrium geometries at the CCSD(T)//def2-TZVPD level of theory for: (a) [I–I–F][−] and [I–I–F], and (b) [I–F–I][−] and [I–F–I]. NBO charges (red and blue font) are given for the anions. The lowest energy isomer, [I–I–F][−] has C_{∞h} symmetry, and [I–I–F] has C_s symmetry.



Table 3 Calculated harmonic vibrational frequencies for I_2F^- and I_2F at the CCSD(T)//def2-TZVPD level of theory in units of cm^{-1}

Mode	[I–I–F] [–]	[I–I–F]	[I–F–I] [–]	[I–F–I]
ν_1	124 ^a	102 ^a	99 ^a	20 ^a
ν_2	124 ^a	158 ^b	99 ^a	72 ^b
ν_3	136 ^b	502 ^c	120 ^b	606 ^c
ν_4	402 ^c	—	229 ^c	—

^a Bend. ^b Symmetric stretch. ^c Asymmetric stretch.

terminal F^- coordinated to an I_2 molecule (see NBO charges in Fig. 4). Similar arguments have been made about the [I–I–Cl][–] species in the solid state.^{3,38} Finally, it is worth noting that Mabbs *et al.*²³ reported a 267 nm photoelectron spectrum of I_2Br^- , which presumably exists as the [I–I–Br][–] isomer and also is an example of a non-classical polyinterhalogen, however, their photoelectron spectrum showed no vibrational structure.

Our experiments suggest that IF_2^- , I_2F^- and most likely the corresponding neutrals are amongst the major products formed in a hard Ar–CF₃I plasma. In the semiconductor manufacture industry, radical neutrals including IF_2 and I_2F formed in the etching plasma may collide and react with etchant substrates. In this context, the bond dissociation energy (BDE) to produce a fluorine atom is related to etching efficiency – a lower BDE gives enhanced etching capacity. For the [F–I–F] and [I–I–F] isomers, BDEs for fluorine atoms were calculated at 1.74 eV and 1.35 eV, respectively, using the CCSD(T)//def2-TZVPD level of theory. For comparison, the calculated BDE for a fluorine atom from the CF₃ radical is 3.51 eV, which is substantially larger than that for the [F–I–F] and [I–I–F] isomers and suggests that polyinterhalogen radicals formed in hard Ar–CF₃I plasmas are important etching species.

In summary, this paper has reported a combined photoelectron spectroscopy and electronic structure theory study on the IF_2^- , IF_2 , IF_2^- and I_2F species, determining the gas-phase structures and electron detachment parameters for the anions and vibrational structure of the neutrals. This determination provides the first vibrationally-resolved spectroscopic characterisation of isolated polyinterhalogen radicals. Whereas IF_2^- as the [F–I–F][–] isomer is a classical polyinterhalogen molecule, IF_2^- as the [I–I–F][–] isomer is a non-classical polyinterhalogen molecule. Theoretical modelling of these species has shown that the CCSD(T)//def2-TZVPD level of theory, on average, predicts ADE and VDE parameters to within $\approx 4\%$ of experiment, however, this level of theory suffers from some degree of Pauling-point agreement. The IF_2 and I_2F radicals may play an important role in plasma etching processes due to having low bond dissociation energies to give fluorine atoms.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Funding was provided by a University of East Anglia start-up allowance (to JNB) and the European Research Council (Starting

Grant 306536 to JRRV). Electronic structure calculations were carried out on the High Performance Computing Cluster supported by the Research and Specialist Computing Support service at the University of East Anglia. Prof. Dr Sebastian Riedel, Freie Universität Berlin, is thanked for insightful discussions.

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