Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Non-adiabatic photodissociation dynamics of vinyl iodide from $n\sigma*$ and $n\pi*$ transitions

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VUV spectroscopy analysis of C_2H_3I

Vinyl iodide is a C_S symmetry molecule in the electronic ground state with its 8 outermost electrons yielding an electronic configuration according to Sze et al.[1] of $(1a'')^2$ $(6a')^2$ $(7a')^2$ $(2a'')^2$: $\tilde{X}^1A'$. The high-resolution vacuum ultraviolet (VUV) photoabsorption spectrum of vinyl iodide, C_2H_3I, measured at room temperature in the photon energy range 5.0−10.7 eV, is shown in Figure S1 (and expanded views in Figures S2-S7) and the fine structure much better resolved than in the previous collected by Boschi and Salahub [1] and the pseudo-optical conditions of Sze et al. [2]. The main absorption bands relevant to the present data can be classified as valence, ($\pi^* \leftarrow n_I$), and members of Rydberg series of the type ($ns \leftarrow n_I$) and ($nd \leftarrow n_I$) (Table I) [1]. The absorption features are rich in vibrational progressions. The normal mode description has been assigned according to the information in the vibrational spectrum of Torkington and Thompson [3] and involves mainly C=C stretching, υ_4, C–I stretching, υ_5, C–I deformation, υ_6, CH_2 deformation, υ_7, and deformation, υ_8 modes, with energies in the ground state 0.198 eV (1593 cm^{-1}), 0.066 eV (535 cm^{-1}), 0.038 eV (309 cm^{-1}), 0.171 eV (1376 cm^{-1}) and 0.123 eV (990 cm^{-1}), respectively [3]. Relevant to note that Sze et al. [2] have reported for the lowest-lying ionic state vibrational energy values of 0.156 eV (υ_4), 0.037 eV (υ_5), 0.144 eV (υ_7), which are relevant for identifying vibrational series present in the different Rydberg series assigned below.

The photoabsorption structure observed in the 5.4–6.2 eV band is shown in detail in Figure S2 with its origin 0_0^0 at 5.58(5) eV followed by a weak progression of broad features assigned to the C=C stretching mode, υ_4; also visible in this energy region, a second absorption feature at 6.03(8) eV accommodating υ_4 and also the C–I stretching mode, υ_5 (see Table II). Boschi and Salahub [1] have speculated about the assignment of the later as either being part of the former band separated by 3600 cm^{-1} (0.446 eV) from its origin and assigned to a C–H stretching quantum or just simply due to another electronic transition. Yet, a close inspection of this photoabsorption feature at 6.03(8) eV, shows a different slope from the feature at 5.58(5) eV and so we believe that the former may belong to a different electronic transition. Nonetheless, the theoretical calculations should provide an answer for this ansatz.

The 6.0–6.8 eV energy range with its vibrational assignments is depicted in Figure S3 and Tables IIIa and IIIb. Electronic excitations discussed in this region are solely due to promotion from the highest occupied molecular orbitals (HOMO) and (HOMO-1), iodine lone pairs n_I ($5p_\perp$) and n_I ($5p_\parallel$), to valence (σ_{CI}*, π_{CC}*) (see Table I). The 0^0_0 photoabsorption feature at 6.03(8) eV is assigned to the (σ_{CI}* ← $n_{I(\parallel)}$) transition, and in good agreement with the experimental data reported by Boschi and Salahub, [1] and Sze et al. [2] at 6.050 and 6.060 eV, respectively (Table I). The potential energy curves for the low-lying excited singlet states of vinyl iodide plotted as a function of the C–I coordinate depicted in the manuscript are consistent with the relevant σ_{CI}* antibonding character resulting from the adiabatic description of the transition at ~ 6 eV. This electronic transition is accompanied by a weak feature at 6.106 eV and is here tentatively assigned for the first time to excitation of one quantum C–I stretching mode, υ_5, with an energy of 0.068 eV (see Table IIa). Such feature can be related to the predissociative character of the accessed electronic state in the diabatic description at ~ 2.5 Å, 30 fs after the C–I bond is stretched. This can only be possible if in the electronic transition, as the reaction coordinate evolves, the nuclear wavepacket survives long enough for the system to change its π* to σ* character.

The next 0^0_0 band is tentatively assigned at 6.166 eV with a maximum at 6.291 eV and a local cross-section value of 50.7 Mb (Table I). Although this could be due to a (6s ← n_I) Rydberg transition, the present results, experiments and calculations, predict a (π_{CC}* ←n) character. Within this absorption band vibrational assignments (Tables IIa) together with progressions involving the C=C stretching mode, υ_4, (4^n) coupled with the C–I stretching mode, υ_5 (Table IIb) are reported. A careful inspection of the absorption band reveals that the feature at 6.452 eV, assigned to the excitation of C–I stretching mode, υ_5 coupled with a progression of the C=C stretching mode, υ_4 (see Table IIb), has been assigned in the pseudo-optical experiment of Sze et al. [2] to a (π_{CC}* ← $n_{I(\parallel)}$) transition at 6.467 eV. The π_{CC}* character is consistent with the electron spin densities calculated here and assigned to state 13.

The next absorption band in the 6.8–7.5 eV energy region may accommodate three electronic transitions as per in Boschi and Salahub's data analyses [1] and our assignments are presented in Table IV. The first transition is tentatively assigned at 6.849 eV and accommodates fine structure due to C–I deformation, υ_6, and deformation, υ_8, modes [3]. Two weak features to the left of the transition are proposed to be hot-bands involving υ_6 and υ_8, modes. The other two transitions have been assigned at 6.99(1) and 7.228 eV, the former more difficult to determine due to the considerable contribution of several modes being active in this region, the later mainly involving a Rydberg excitation coupled with C–I deformation mode, υ_6.

The next absorption region 7.4–8.2 eV is assigned in detail in Table V where a rich vibrational pattern involves mainly C=C stretching, υ_4, C–I stretching, υ_5, C–I deformation, υ_6, and CH_2 deformation, υ_7, modes. Also present in this energy region progression bands involving mainly CH_2 deformation, υ_7, mode.

The next set of Tables VI–VII reports the vibrational assignments and progressions in the 8.1–10.3 eV photon energy region mainly coupled with Rydberg series converging to the three lowest ionisation energies ($2a''^{-1}$), ($7a'^{-1}$) and ($1a''^{-1}$).

Rydberg transitions

Vynil iodide electronic excitation in the photon energy range studied in this work displays Rydberg character where a summary of the experimental energies, assignments and quantum defects can be found in Tables VIIIa-c. The peak positions have been tested using the Rydberg formula: $E_n = E_I - R/(n-\delta)^2$, where E_I is the ionisation energy, n is the principal quantum number of the Rydberg orbital of energy E_n, R is the Rydberg constant (13.61 eV), and δ is the quantum defect resulting from the penetration of the Rydberg orbital into the core. Yet, with quantum defect calculations as our only guide, we cannot propose assignments for these bands with confidence, so values for higher n Rydberg states in Table VIIIa-c are tentative assignments. The lowest-lying ionisation energies relevant to this work 9.26, 10.01 and 11.50 eV were taken from the He(I) photoelectron spectroscopy data of Sze et al. [2] and assigned to the removal of an electron from ($n_{I(\perp)}$)($2a''^{-1}$), ($n_{I(\parallel)}$)($7a'^{-1}$) and (π_{CC})($1a''^{-1}$), respectively.

Figure S1. High-resolution VUV photoabsorption spectrum of vynil iodide, C_2H_3I in the 5.9−10.7 eV photon energy range.

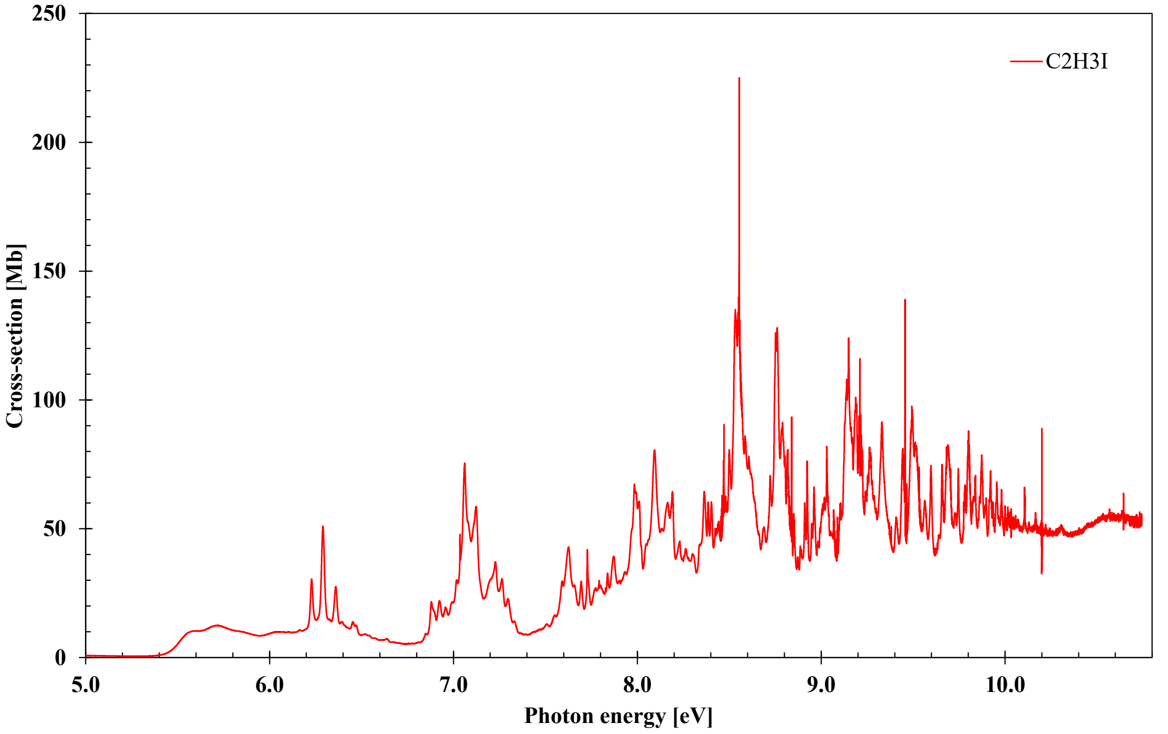

Figure S2. VUV photoabsorption spectrum of vinyl iodide, C_2H_3I in the 5.4−6.2 eV photon energy range together with assignments of the main absorption features.

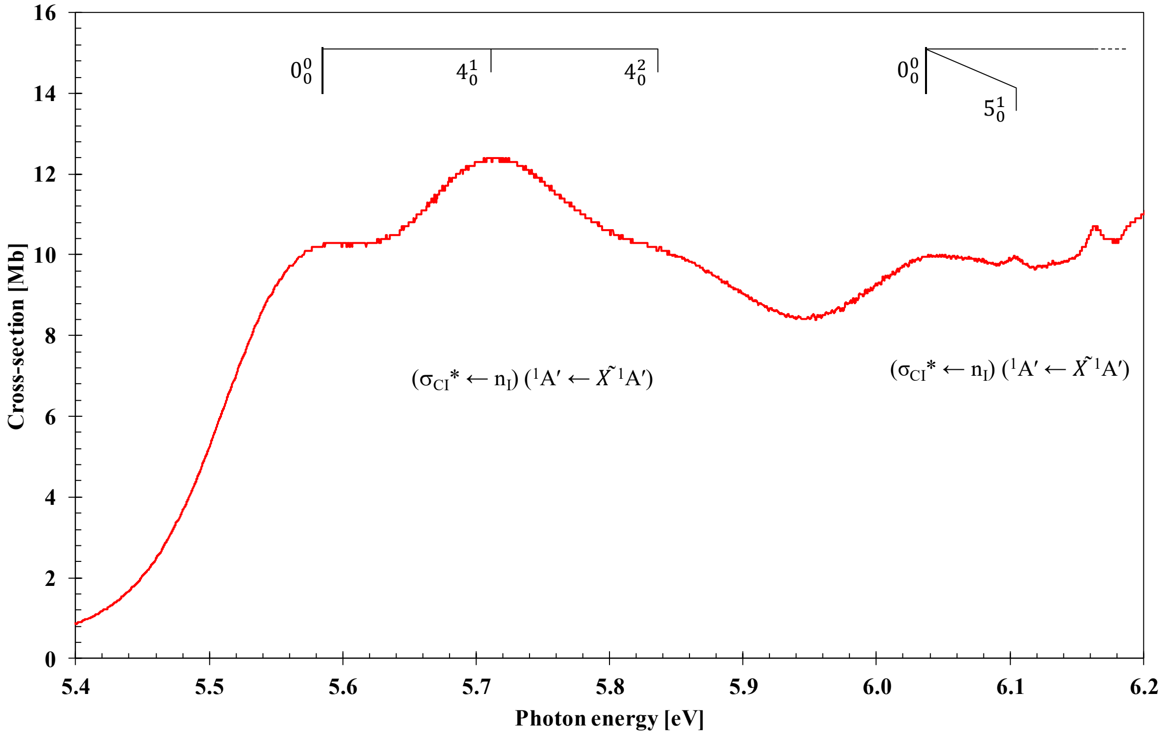

Figure S3. VUV photoabsorption spectrum of vinyl iodide, C_2H_3I in the 6.0−6.8 eV photon energy range together with assignments of the main absorption features.

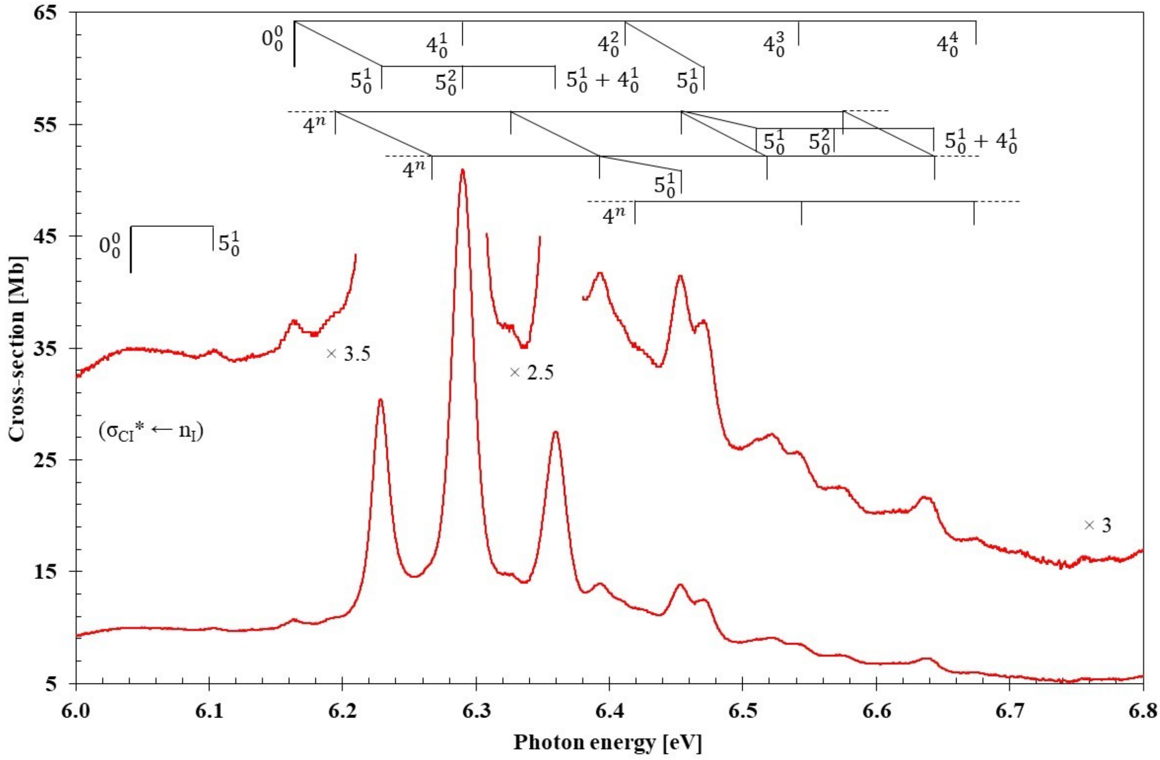

Figure S4. VUV photoabsorption spectrum of vinyl iodide, C_2H_3I in the 6.7−7.5 eV photon energy range together with assignments of the main absorption features.

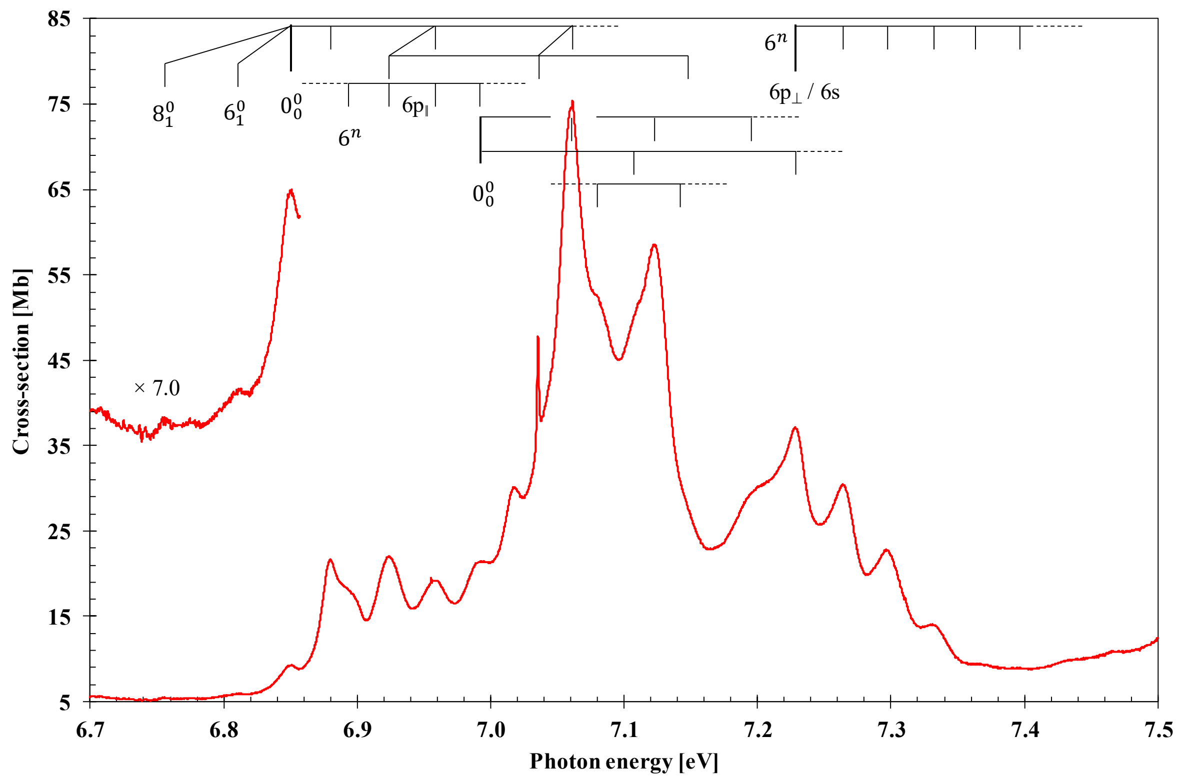

Figure S5. VUV photoabsorption spectrum of vynil iodide, C_2H_3I in the 7.4−8.2 eV photon energy range together with assignments of the main absorption features.

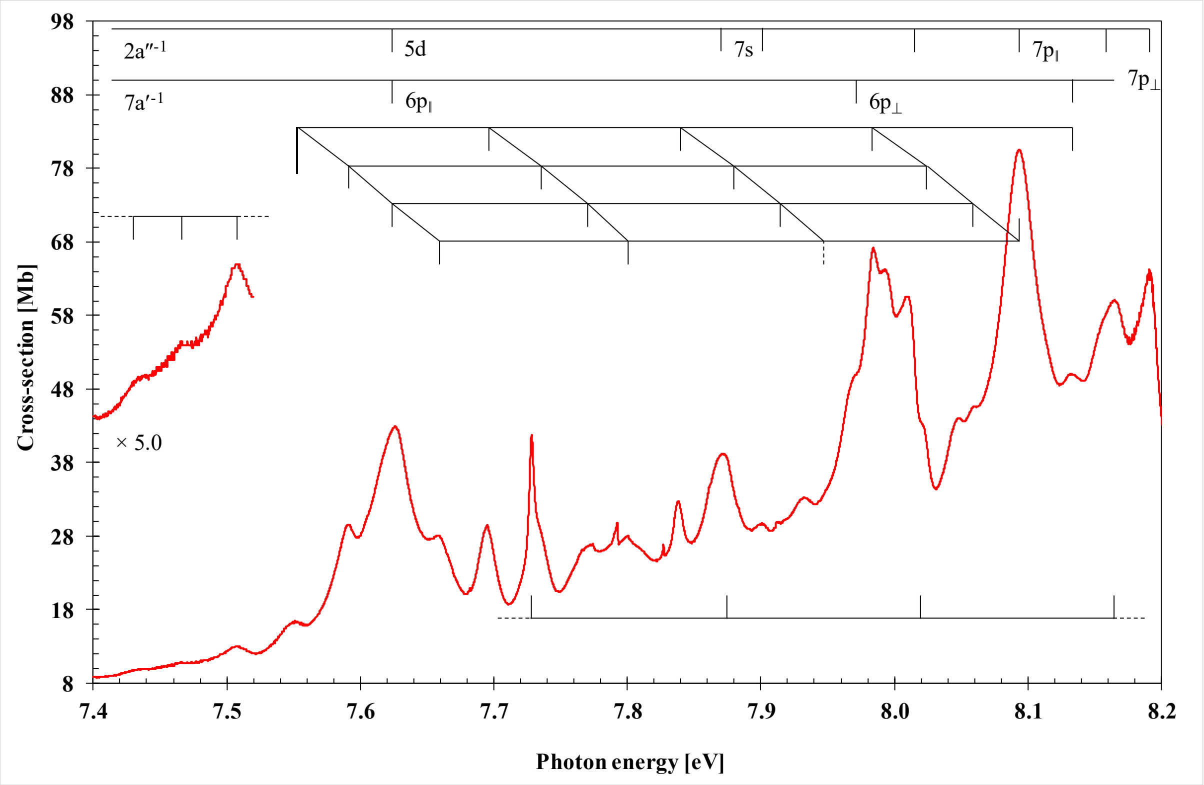

Figure S6. VUV photoabsorption spectrum of vynil iodide, C_2H_3I in the 8.1−8.9 eV photon energy range together with assignments of the main absorption features.

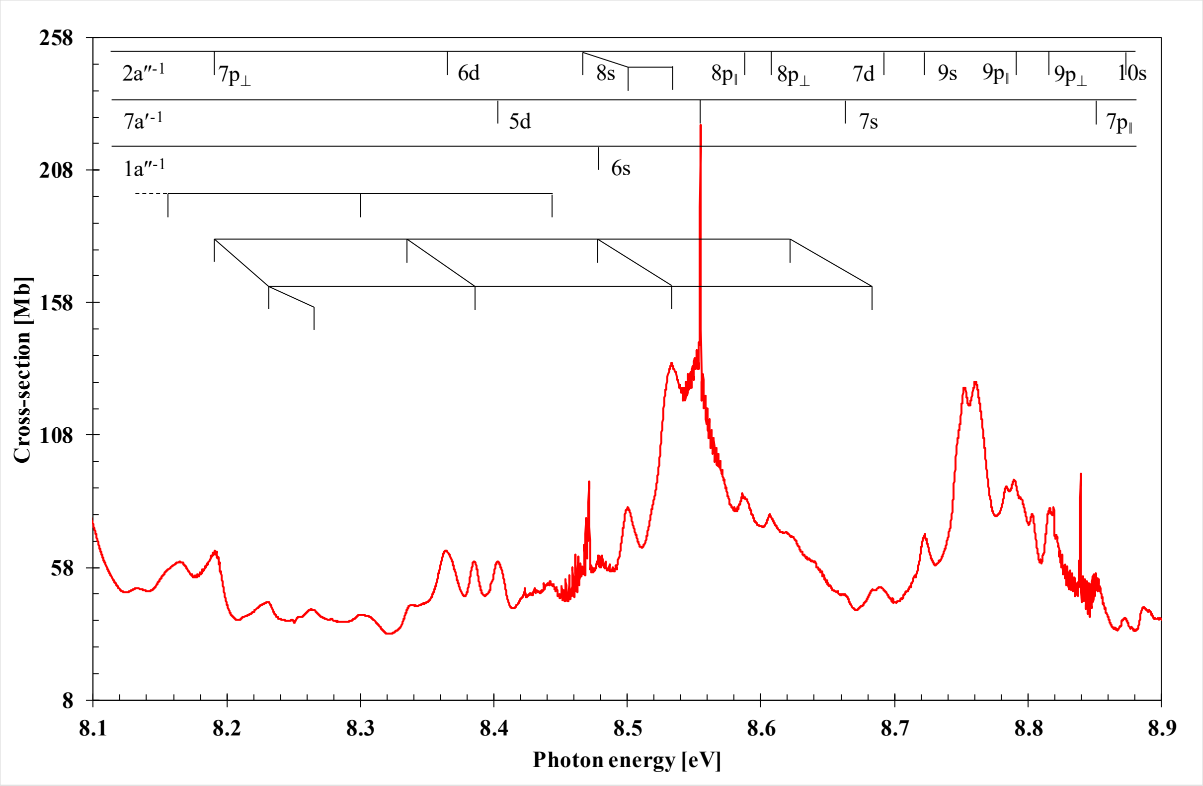

Figure S7. VUV photoabsorption spectrum of vynil iodide, C_2H_3I in the 8.9−10.3 eV photon energy range together with assignments of the main absorption features.

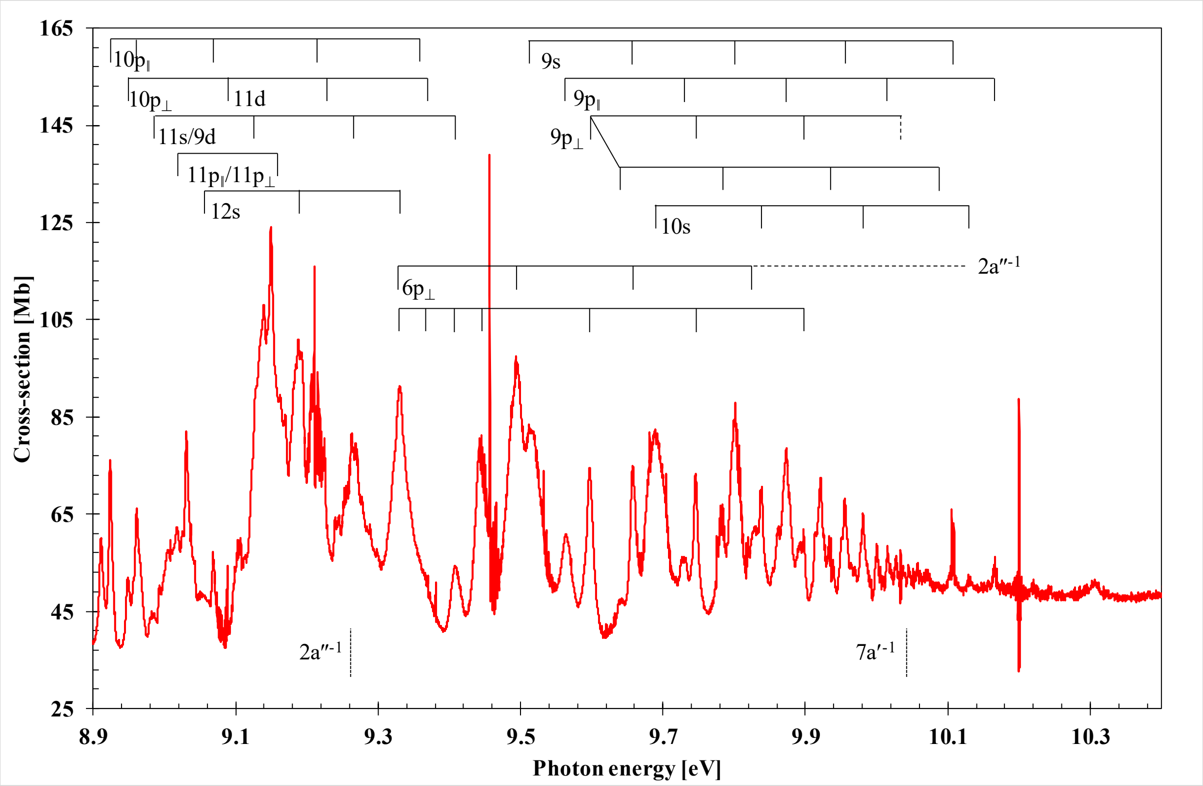

Table I – Experimental vertical excitation energies (in eV) of vinyl iodide, C_2H_3I, compared with data in the literature.

this work			previous work	
energy[#]	cross-section (Mb)	assignment	Ref. [1]	Ref. [2]
–	–	$(\sigma_{CI}^* \leftarrow n_{I(\perp)})$	4.959	4.919
5.58(5)	12.3	$(\sigma_{CI}^* \leftarrow n_{I(\parallel)})$	5.579	5.700
6.03(8)	9.9	$(\sigma_{CI}^* \leftarrow n_{I(\perp)})$	6.050	6.060
6.230	50.7	$(\pi_{CC}^* \leftarrow n_{I(\parallel)})$	~6.296	6.232
6.291				6.279
6.361				6.342

[#] The last decimal of the energy is given in brackets for these less resolved features.

Table II – Proposed vibrational assignments in the 5.4−6.2 eV absorption band of C_2H_3I compared with previous work [1].

This work				Ref. [1]	
energy[#]	assignment	ΔE, ν_4 (eV)	ΔE, ν_5 (eV)	energy	assignment*
5.58(5)(b)	0_0^0	–	–	5.598	0_0^0
5.71(3)(b)	4_0^1	0.128	–	5.727	1_0^1
5.83(6)(b,s)	4_0^2	0.123	–	5.862	1_0^2
6.03(8)(b)	0_0^0	–	–	6.048	–
6.106	5_0^1	–	0.068	–	–
6.166	4_0^1	0.128	–	–	–

[#] (b) broad structure, (s) shoulder structure (the last decimal of the energy value is given in brackets for these less-resolved features);

* note that in Ref. [1] authors assign the excitation of three modes C=C stretching to υ_1, C–I stretching to υ_2, and C–C–I bending to υ_3.

Table IIa – Proposed vibrational assignments in the 6.0–6.8 eV absorption band of C_2H_3I compared to previous work.[2]

This work				Boschi and Salahub[2]		Sze *et al.* [1]
energy[#]	assignment	ΔE, v_4 (eV)	ΔE, v_5 (eV)	energy	assignment*	energy
6.03(8)(b)	0_0^0	–	–	6.050	–	6.060
6.106	5_0^1	–	0.068	–	–	–
6.166	0_0^0	–	–	6.221	0_0^0	–
6.230	5_0^1	–	0.064	6.281	2_0^1	–
6.291	4_0^1 / 5_0^2	0.125	0.061	6.338	2_0^2	–
6.361	$5_0^1 + 4_0^1$	–	–	–	–	–
6.41(2)(s)	4_0^2	0.121	–	–	–	–
6.468	4_0^2 / 5_0^2	–	0.056	–	–	–
6.538	4_0^3	0.126	–	–	–	–
6.67(5)(w,b)	4_0^4	0.137	–	–	–	–

[#] (b) broad structure, (s) shoulder structure and (w) weak feature (the last decimal of the energy value is given in brackets for these less-resolved features);

* note that in Ref.[2] authors assign the excitation of modes C=C stretching to υ_1, C–I stretching to υ_2, and C–C–I bending to υ_3.

Table IIb – Proposed vibrational assignments for progressions in the 6.0–6.8 eV absorption band of C_2H_3I.

This work				Boschi and Salahub[2]	
energy[#]	assignment	ΔE, ν_4 (eV)	ΔE, ν_5 (eV)	energy	assignment*
6.19(7)(s)	4^{n}	–	–	–	–
6.32(5)(s)	4^{n+1}	0.128	–	6.392	1_0^1
6.452	4^{n+2}	0.127	–	6.450	$1_0^1 + 2_0^1$
6.50(8)(s,w)	$4^{n+2} + 5_0^1$	–	0.056	6.506	$1_0^1 + 2_0^2$
6.56(6)(b,w)	$4^{n+2} + 5_0^2$	–	0.058	6.560	1_0^2
6.64(2)(b)	$4^{n+2} + 5_0^1 + 4_0^1$	–	–	–	–
6.57(8)(b)	4^{n+3}	0.126	–	–	–
6.26(7)(s)	4^{n}	–	–	–	–
6.396	4^{n+1}	0.129	–	–	–
6.452	$4^{n+1} + 5_0^1$	–	0.056	–	–
6.51(9)(b)	4^{n+2}	0.123	–	–	–
6.64(2)(b)	4^{n+3}	0.123	–	6.617	$1_0^2 + 2_0^1$
6.42(1)(s)	4^{n}	–	–	–	–
6.544	4^{n+1}	0.123	–	–	–
6.67(5)(w,b)	4^{n+2}	0.130	–	6.672	$1_0^2 + 2_0^2$

[#] (s) shoulder structure, (b) broad structure, (w) weak feature (the last decimal of the energy value is given in brackets for these less-resolved features);

* note that in Ref. [2] authors assign the excitation of three modes C=C stretching to υ_1, C–I stretching to υ_2, and C–C–I bending to υ_3.

Table IV – Proposed vibrational assignments in the 6.7−7.5 eV absorption band of C_2H_3I.

This work					Ref. [1]	
energy[#]	assignment	ΔE, ν_5 (eV)	ΔE, ν_6 (eV)	ΔE, ν_8 (eV)	energy	assignment*
6.754	8^0_1	–	–	–	–	–
6.81(1)(w)	6^0_1	–	–	–	–	–
6.849	0^0_0 (?)	–	–	–	6.877	0^0_0
6.879	6^1_0	–	0.030	–	6.920	3^1_0
6.89(1)(s)	6^n	–	–	–	–	–
6.923	6p$_\parallel$	–	–	–	–	–
6.957	8^1_0 / 6p$_\parallel$ + 6^{n+1}	–	0.034	0.108	6.963	3^2_0
6.99(1)(b)	6p$_\parallel$ + 6^{n+2}	–	0.034	–	–	–
7.035	6p$_\parallel$ + 8^1_0	–	–	0.112	–	–
7.061	8^2_0	–	–	0.104	7.005	3^3_0
7.148	6p$_\parallel$ + 8^2_0	–	–	0.113	7.045	3^4_0
6.99(1)(b)	0^0_0 (?)	–	–	–	–	–
7.016	6^1_0	–	0.025	–	–	–
7.04(8)(s)	6^2_0	–	0.032	–	7.053	0^0_0
7.061	5^1_0	0.070	–	–	–	–
7.07(8)(s)	5^n	–	0.030	–	7.115	2^1_0
7.10(8)(s)	8^1_0	–	–	0.117	–	–
7.121	5^2_0	0.060	–	–	–	–
7.14(1)(w,s)	5^{n+1}	0.063	–	–	7.178	2^2_0
7.19(7)(b,s)	5^3_0	0.076	–	–	–	–
7.228	8^2_0	–	–	0.120	–	–
7.228	0^0_0 / 6p$_\perp$ / 6s	–	–	–	7.217	0^0_0
7.263	6^1_0	–	0.035	–	7.253	3^1_0
7.296	6^2_0	–	0.033	–	7.288	3^2_0
7.330	6^3_0 / 8^1_0	–	0.034	0.100	7.323	3^3_0
7.36(5)(s,w)	6^4_0	–	0.035	–	7.357	3^4_0
7.39(6)(s,w)	6^5_0	–	0.031	–	–	–

[#] (w) weak feature, (s) shoulder structure, (b) broad structure (the last decimal of the energy value is given in brackets for these less-resolved features);

* note that in Ref. [1] authors assign the excitation of three modes C=C stretching to υ_1, C–I stretching to υ_2, and C–C–I bending to υ_3.

Table V – Proposed vibrational assignments in the 7.4−8.2 eV absorption band of C_2H_3I.

energy$^{\#}$	assignment	ΔE, v_4 (eV)	ΔE, v_5 (eV)	ΔE, v_6 (eV)	ΔE, v_7 (eV)
7.42(9)(s)	?	–	–	–	–
7.46(2)(s)	?	–	–	–	–
7.506	?	–	–	–	–
7.549	0_0^0 (?)	–	–	–	–
7.589	5_0^1	–	0.040	–	–
7.628	5d ($2a''^{-1}$) / 6p$_{\parallel}$ ($7a'^{-1}$)	–	–	–	–
7.658	5d ($2a''^{-1}$) / 6p$_{\parallel}$ ($7a'^{-1}$) + 6_0^1	–	–	0.030	–
7.693	7_0^1	–	–	–	0.144
7.728	7^n	–	–	–	–
7.73(6)(s)	$5_0^1 + 7_0^1$	–	–	–	0.147
7.76(8)(b)	5d ($2a''^{-1}$) / 6p$_{\parallel}$ ($7a'^{-1}$) + 7_0^1	–	–	–	0.140
7.800	5d ($2a''^{-1}$) / 6p$_{\parallel}$ ($7a'^{-1}$) + $6_0^1 + 7_0^1$	–	–	–	0.142
7.837	7_0^2	–	–	–	0.144
7.86(9)(b)	7s + 7^{n+1}	–	–	–	0.141
7.87(9)(s,w)	$5_0^1 + 7_0^2$	–	–	–	0.143
7.900	7s + 6_0^1	–	–	0.031	–
7.91(3)(b)	5d ($2a''^{-1}$) / 6p$_{\parallel}$ ($7a'^{-1}$) + 7_0^2	–	–	–	0.145
7.95(0)(w,s)	5d ($2a''^{-1}$) / 6p$_{\parallel}$ ($7a'^{-1}$) + $6_0^1 + 7_0^2$	–	–	–	0.150
7.97(0)(s)	6p$_{\perp}$	–	–	–	–
7.984	7_0^3	–	–	–	0.147
8.02(0)(s)	$5_0^1 + 7_0^3$ / 7^{n+2}	–	–	–	0.141
8.05(7)(w)	5d ($2a''^{-1}$) / 6p$_{\parallel}$ ($7a'^{-1}$) + 7_0^3	–	–	–	0.144
8.01(9)(s)	7s ($2a''^{-1}$) + 7_0^1	–	–	–	0.150
8.095	7p$_{\parallel}$ ($2a''^{-1}$) / 5d ($2a''^{-1}$) / 6p$_{\parallel}$ ($7a'^{-1}$) + 7_0^4	–	–	–	–
8.13(0)(b)	6p$_{\perp}$ ($7a'^{-1}$) + 4_0^1 / 7_0^4	0.160	–	–	0.146
8.16(2)(b)	7s ($2a''^{-1}$) + 7_0^2 / 7^{n+3}	–	–	–	0.143
8.191	7p$_{\perp}$ ($2a''^{-1}$)	–	–	–	–

$^{\#}$ (s) shoulder structure, (b) broad structure, (w) weak feature (the last decimal of the energy value is given in brackets for these less-resolved features); (?) unassigned feature.

Table VI – Proposed vibrational assignments and progressions in the 8.1−8.9 eV absorption band of C_2H_3I.

energy[#]	assignment	ΔE, ν_6 (eV)	ΔE, ν_7 (eV)
8.16(2)(b)	7s (2a$''^{-1}$) + 7^2_0 / 7^{n+3}	–	–
8.191	7p$_\perp$ (2a$''^{-1}$)	–	–
8.22(9)(b)	7^n	–	–
8.26(2)(b)	7^n + 6^1_0	0.033	–
8.29(7)(b)	7s (2a$''^{-1}$) + 7^3_0 / 7^{n+4}	–	0.135
8.33(6)(s)	7p$_\perp$ (2a$''^{-1}$) + 7^1_0	–	0.145
8.384	7^{n+1}	–	0.155
8.405	5d (7a$'^{-1}$)	–	–
8.441	7s (2a$''^{-1}$) + 7^4_0 / 7^{n+5}	–	0.144
8.464	8s (2a$''^{-1}$)	–	–
8.478	6s (1a$''^{-1}$) / 7p$_\perp$ (2a$''^{-1}$) + 7^2_0	–	0.142
8.499	8s (2a$''^{-1}$) + 6^1_0	0.035	–
8.532	7^{n+2} / 8s (2a$''^{-1}$) + 6^2_0	0.033	0.148
8.555	5d (7a$'^{-1}$) + 7^1_0	–	0.150
8.608	8s (2a$''^{-1}$) + 7^1_0 / 8p$_\perp$ (2a$''^{-1}$)	–	–
8.61(9)(s)	6s (1a$''^{-1}$) + 7^1_0 / 7p$_\perp$ (2a$''^{-1}$) + 7^3_0	–	0.141
8.68(3)(s)	7^{n+3}	–	0.151
8.723	9s (2a$''^{-1}$)	–	–
8.752	8s (2a$''^{-1}$) + 7^2_0 / 8p$_\perp$ (2a$''^{-1}$) + 7^1_0	–	0.144
8.760	9s (2a$''^{-1}$) + 6^1_0	0.037	–
8.839	7d (2a$''^{-1}$) + 7^1_0	–	–
8.885	9s (2a$''^{-1}$) + 7^1_0 / 10s (2a$''^{-1}$)	–	0.162

[#] (s) shoulder structure, (w) weak feature, (b) broad structure, (the last decimal of the energy value is given in brackets for these less-resolved features);

Table VIIa – Proposed vibrational assignments in the 8.9−10.3 eV absorption band of C_2H_3I converging to the ionic electronic ground state (2a″$^{-1}$).

energy$^{\#}$	assignment	ΔE, ν_6 (eV)	ΔE, ν_7 (eV)
8.924	10p$_{\parallel}$ (2a″$^{-1}$)	–	–
8.950	10p$_{\perp}$ (2a″$^{-1}$)	–	–
8.960	10p$_{\parallel}$ (2a″$^{-1}$) + 6^1_0	0.036	–
8.982	11s (2a″$^{-1}$) / 9d (2a″$^{-1}$)	–	–
9.01(7)(s)	11p$_{\parallel}$ (2a″$^{-1}$) / 11p$_{\perp}$ (2a″$^{-1}$)	–	–
9.05(9)(b)	12s (2a″$^{-1}$)	–	–
9.068	10p$_{\parallel}$ (2a″$^{-1}$) + 7^1_0	–	0.144
9.088	11d (2a″$^{-1}$) / 10p$_{\perp}$ (2a″$^{-1}$) + 7^1_0	–	0.138
9.123	11s (2a″$^{-1}$) / 9d (2a″$^{-1}$) + 7^1_0	–	0.141
9.15(9)(s)	11p$_{\parallel}$ (2a″$^{-1}$) / 11p$_{\perp}$ (2a″$^{-1}$) + 7^1_0	–	0.142
9.188	12s (2a″$^{-1}$) + 7^1_0	–	0.129
9.211	10p$_{\parallel}$ (2a″$^{-1}$) + 7^2_0	–	0.143
9.22(8)(s,w)	11d (2a″$^{-1}$) + 7^1_0 / 10p$_{\perp}$ (2a″$^{-1}$) + 7^2_0	–	0.140
9.262	11s (2a″$^{-1}$) / 9d (2a″$^{-1}$) + 7^2_0	–	0.139
9.330	12s (2a″$^{-1}$) + 7^2_0	–	0.142
9.35(7)(s,w)	10p$_{\parallel}$ (2a″$^{-1}$) + 7^3_0	–	0.146
9.36(4)(s)	11d (2a″$^{-1}$) + 7^2_0 / 10p$_{\perp}$ (2a″$^{-1}$) + 7^3_0	–	0.136
9.407	11s (2a″$^{-1}$) / 9d (2a″$^{-1}$) + 7^3_0	–	0.145

$^{\#}$ (s) shoulder structure, (b) broad structure, (w) weak feature (the last decimal of the energy value is given in brackets for these less-resolved features).

Table VIIb – Proposed vibrational assignments in the 8.9−10.3 eV absorption band of C_2H_3I converging to the ionic electronic first excited state ($7a'^{-1}$).

energy$^{\#}$	assignment	ΔE, ν_5 (eV)	ΔE, ν_7 (eV)
9.519	9s ($7a'^{-1}$)	–	–
9.567	$9p_{\parallel}$ ($7a'^{-1}$)	–	–
9.598	$9p_{\perp}$ ($7a'^{-1}$)	–	–
9.63(7)(s)	$9p_{\perp}$ ($7a'^{-1}$) + 5^1_0	0.039	–
9.657	9s ($7a'^{-1}$) + 7^1_0	–	0.138
9.69(0)(b)	10s	–	–
9.727	$9p_{\parallel}$ ($7a'^{-1}$) + 7^1_0	–	0.160
9.745	$9p_{\perp}$ ($7a'^{-1}$) + 7^1_0	–	0.147
9.783	$9p_{\perp}$ ($7a'^{-1}$) + 5^1_0+ 7^1_0 / $11p_{\parallel}$ ($7a'^{-1}$)	–	0.146
9.802	9s ($7a'^{-1}$) + 7^2_0	–	0.145
9.835	10s + 7^1_0 / 12s	–	0.145
9.873	$9p_{\parallel}$ ($7a'^{-1}$) + 7^2_0	–	0.146
9.897	$9p_{\perp}$ ($7a'^{-1}$) + 7^2_0	–	0.152
9.933	$9p_{\perp}$ ($7a'^{-1}$) + 5^1_0+ 7^2_0 / $11p_{\parallel}$ ($7a'^{-1}$) + 7^1_0	–	0.150
9.955	9s ($7a'^{-1}$) + 7^3_0	–	0.153
9.981	10s ($7a'^{-1}$) + 7^2_0 / 12s + 7^1_0	–	0.146
10.015	$9p_{\parallel}$ ($7a'^{-1}$) + 7^3_0	–	0.142
10.03(0)(w)	$9p_{\perp}$ ($7a'^{-1}$) + 7^3_0	–	0.133
10.08(0)(w,b)	$9p_{\perp}$ ($7a'^{-1}$) + 5^1_0+ 7^3_0 / $11p_{\parallel}$ ($7a'^{-1}$) + 7^2_0	–	0.147
10.105	9s ($7a'^{-1}$) + 7^4_0 / 7s ($1a''^{-1}$)	–	0.150
10.129	10s ($7a'^{-1}$) + 7^3_0 / 12s + 7^2_0	–	0.148
10.166	$9p_{\parallel}$ ($7a'^{-1}$) + 7^4_0	–	0.151

$^{\#}$ (s) shoulder structure, (b) broad structure, (w) weak feature (the last decimal of the energy value is given in brackets for these less-resolved features).

Table VIIc – Proposed vibrational assignments in the 8.9−10.3 eV absorption band of C_2H_3I converging to the ionic electronic second excited state ($1a''^{-1}$).

energy[#]	assignment	ΔE, ν_4 (eV)	ΔE, ν_6 (eV)	ΔE, ν_7 (eV)
9.329	$6p_{\perp}$ ($1a''^{-1}$)	–	–	–
9.36(4)(s)	$6p_{\perp}$ ($1a''^{-1}$) + 6^{1}_{0} / 11d ($2a''^{-1}$) + 7^{2}_{0} / $10p_{\perp}$ ($2a''^{-1}$) + 7^{3}_{0}	–	0.035	–
9.407	$6p_{\perp}$ ($1a''^{-1}$) + 6^{2}_{0} / 11s ($2a''^{-1}$) / 9d ($2a''^{-1}$) + 7^{3}_{0}	–	0.043	–
9.442	$6p_{\perp}$ ($1a''^{-1}$) + 6^{3}_{0}	–	0.035	–
9.493	$6p_{\perp}$ ($1a''^{-1}$) + 4^{1}_{0}	0.164	–	–
9.598	$6p_{\perp}$ ($1a''^{-1}$) + 6^{3}_{0} + 7^{1}_{0} / $9p_{\perp}$ ($7a'^{-1}$)	–	–	0.156
9.657	$6p_{\perp}$ ($1a''^{-1}$) + 4^{1}_{0} / 9s ($7a'^{-1}$) + 7^{1}_{0}	0.164	–	–
9.745	$6p_{\perp}$ ($1a''^{-1}$) + 6^{3}_{0} + 7^{2}_{0} / $9p_{\perp}$ ($7a'^{-1}$) + 7^{1}_{0}	–	–	0.147
9.82(6)(s)	$6p_{\perp}$ ($1a''^{-1}$) + 4^{2}_{0}	0.169	–	–
9.897	$6p_{\perp}$ ($1a''^{-1}$) + 6^{3}_{0} + 7^{3}_{0} / $9p_{\perp}$ ($7a'^{-1}$) + 7^{2}_{0}	–	–	0.152

[#] (s) shoulder structure (the last decimal of the energy value is given in brackets for these less-resolved features).

Table VIIIa – Energy value (eV) and effective quantum number (n^*) of the Rydberg series converging to the ionic electronic ground state of C_2H_3I.[a]

This work			Ref. [2]	
vertical energy	n^*	assignment	vertical energy	n^*
$IE_1 = 9.26$ eV[b] ($2a''^{-1}$)				
6.230	2.12	6s	6.232	2.12
6.291	2.14		6.279	2.14
6.361	2.17		6.342	2.16
7.86(9)(b)	3.13	7s	7.858	3.12
8.464	4.13	8s	8.750	4.38
8.723	5.03	9s	–	–
8.885	6.02	10s	–	–
8.982	7.00	11s	–	–
9.05(9)(b)	8.23	12s	–	–
6.921	2.41	$6p_{\parallel}$	6.920	2.41
8.095	3.42	$7p_{\parallel}$	8.093	3.41
8.585	4.49	$8p_{\parallel}$	–	–
8.791	5.39	$9p_{\parallel}$	–	–
8.924	6.36	$10p_{\parallel}$	–	–
9.01(7)(s)	7.48	$11p_{\parallel}$	–	–
7.230	2.59	$6p_{\perp}$	7.202	2.57
8.191	3.57	$7p_{\perp}$	8.171	3.53
8.608	4.57	$8p_{\perp}$	–	–
8.817	5.54	$9p_{\perp}$	–	–
8.950	6.63	$10p_{\perp}$	–	–
9.01(7)(s)	7.48	$11p_{\perp}$	–	–
7.628	2.89	5d	7.616	2.88
8.367	3.90	6d	8.546	3.95
8.694	4.90	7d	–	–
8.874	5.94	8d	–	–
8.982	7.00	9d	–	–
9.044	7.94	10d	–	–
9.088	8.90	11d	–	–

[a] (b) broad structure, (s) shoulder structure (the last decimal of the energy value is given in brackets for these less-resolved features); [b] vertical values from Ref. [2].

Table VIIIb – Energy value (eV) and effective quantum number (n*) of the Rydberg series converging to the ionic electronic first excited state of C_2H_3I.[a]

This work			Ref. [2]	
vertical energy	n*	assignment	vertical energy	n*
IE_1 = 10.04 eV[b] ($7a'^{-1}$)				
7.230	2.20	6s	7.077	2.14
8.66(5)(s)	3.15	7s	8.750	3.25
9.25(7)(s)	4.17	8s	9.313	4.32
9.519	5.11	9s	9.500	5.02
9.69(0)(b)	6.24	10s	9.672	6.06
9.783	7.28	11s	9.829	8.05
9.835	8.15	12s	–	–
9.87(9)(s,w)	9.19	13s	–	–
7.628	2.38	$6p_{\parallel}$	7.616	2.37
8.848	3.38	$7p_{\parallel}$	–	–
9.332	4.38	$8p_{\parallel}$	–	–
9.567	5.36	$9p_{\parallel}$	–	–
9.69(2)(b)	6.25	$10p_{\parallel}$	–	–
9.783	7.28	$11p_{\parallel}$	–	–
7.97(0)(s)	2.56	$6p_{\perp}$	7.984	2.57
8.982	3.59	$7p_{\perp}$	9.016	3.65
9.37(2)(s,w)	4.51	$8p_{\perp}$	–	–
9.598	5.55	$9p_{\perp}$	–	–
9.73(3)(b,w)	6.66	$10p_{\perp}$	–	–
8.405	2.89	5d	8.390	2.87
9.147	3.90	6d	–	–
9.493	4.99	7d	–	–

[a] (s) shoulder structure, (b) broad structure, (w) weak feature (the last decimal of the energy value is given in brackets for these less-resolved features).

Table VIIIc – Energy value (eV) and effective quantum number (n*) of the Rydberg series converging to the ionic electronic second excited state of C_2H_3I.[a]

This work			Ref. [2]	
vertical energy	n*	assignment	vertical energy	n*
$IE_1 = 11.50$ eV^b ($1a''^{-1}$)				
8.478	2.12	6s	8.546	2.15
10.105	3.12	7s	–	–
9.15(9)(s)	2.41	$6p_{\|}$	9.156	2.41
10.30(2)(b)	3.37	$7p_{\|}$	–	–
9.329	2.50	$6p_{\perp}$	9.313	2.49
9.82(6)(s)	2.85	5d	9.829	2.85

[a] (s) shoulder structure, (b) broad structure (the last decimal of the energy value is given in brackets for these less-resolved features).

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