ESI: Real-time dynamics of vibrational and vibronic wavepackets within Rydberg and ion-pair states of molecular iodine

Jean-Michel Mestdagh[a], Lou Barreau[b] and Lionel Poisson*[b]

S1 Detailed fit of the photoelectron spectra

Here are presented the fits that feed the Table 1 of the paper. The bands fitted are presented in Figure 8 of the main text. Here the same colours are used for consistency. The fit model used provides three time constants:

- τ^-: a decay toward the negative times
- τ_A: a decay toward the positive times
- τ_B: a decay toward the positive times

S1.1 Analytic equation model

The fit procedure uses the following analytic functions. Assuming an instrumental response function with the gaussian shape:

$$\mathrm{IRF}(t) = \frac{1}{\pi\sigma} e^{-(\frac{t}{\sigma})^2} \quad (1)$$

where σ defines the experimental width, then the expressions of the convolution of the product of a step function times an exponential decay, with the gaussian function above writes:

$$\mathrm{declf}(t,\tau,\sigma) = \frac{1}{2} e^{-(\frac{t}{\tau}-(\frac{\sigma}{2\tau})^2)} \,\mathrm{erfc}(-\frac{t-\frac{\sigma^2}{2\tau}}{\sigma}) \quad (2)$$

where erfc is the complementary error function. The fitting equations used are then:

$$Neg(t) = \mathrm{declf}(-t,\tau^-,\sigma) \quad (3)$$

$$A(t) = \mathrm{declf}(t,\tau_A,\sigma) \quad (4)$$

$$B(t) = \frac{\tau_B}{\tau_B-\tau_A}(\mathrm{declf}(t,\tau_B,\sigma) - \mathrm{declf}(t,\tau_A,\sigma)) \quad (5)$$

$$C(t) = \frac{1}{2}\mathrm{erfc}(-\frac{t}{\sigma}) - A(t) - B(t) \quad (6)$$

S1.2 Fit of the experimental data

To improve the fit, both $S_0^{elec}(E,t)$ (top figure for each band) and $S_2^{elec}(E,t)$ (bottom figure for each band) where fitted together with the same time constants.

[a]Université Paris-Saclay, CEA, CNRS, Laboratoire Interactions Dynamiques et Lasers, 91191 Gif-sur-Yvette, France.
[b]Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405 Orsay, France.
* E-mail:lionel.poisson@universite-paris-saclay.fr

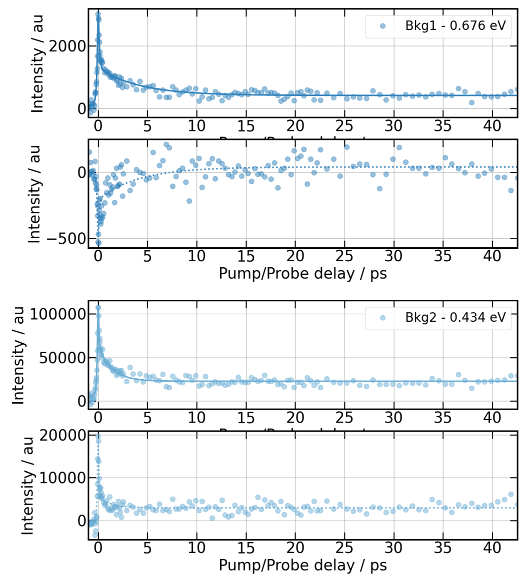


Fig. S1 Evolution of the continua Bkg1 and Bkg2, spectrally modelled as exponential decays in main text Fig. 8, and their fit. The corresponding energy constants are reported on each graph. For each figure, the top one reports for the total signal, and the bottom one is the anisotropical component of the signal issued from the pBASEX[1] inversion. Both declays are fitted together.

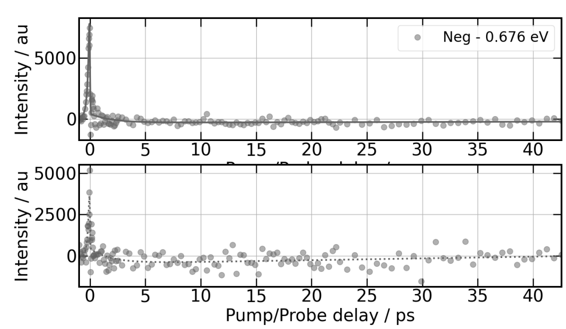


Fig. S2 Evolution of the Neg band modelling signal at negative time delays and its fit.

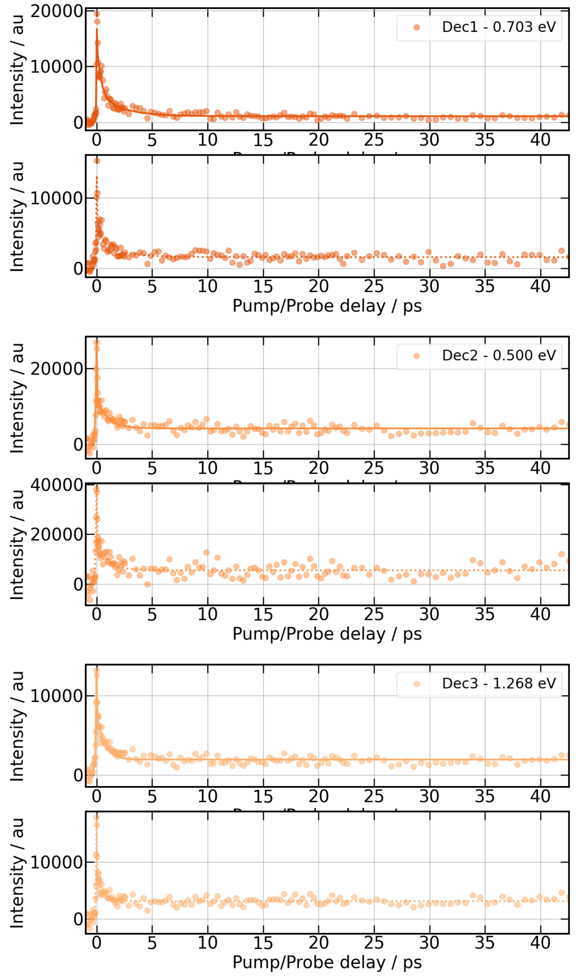


Fig. S3 Evolution of the three decaying bands Dec1, Dec2 and Dec3 and their fit.

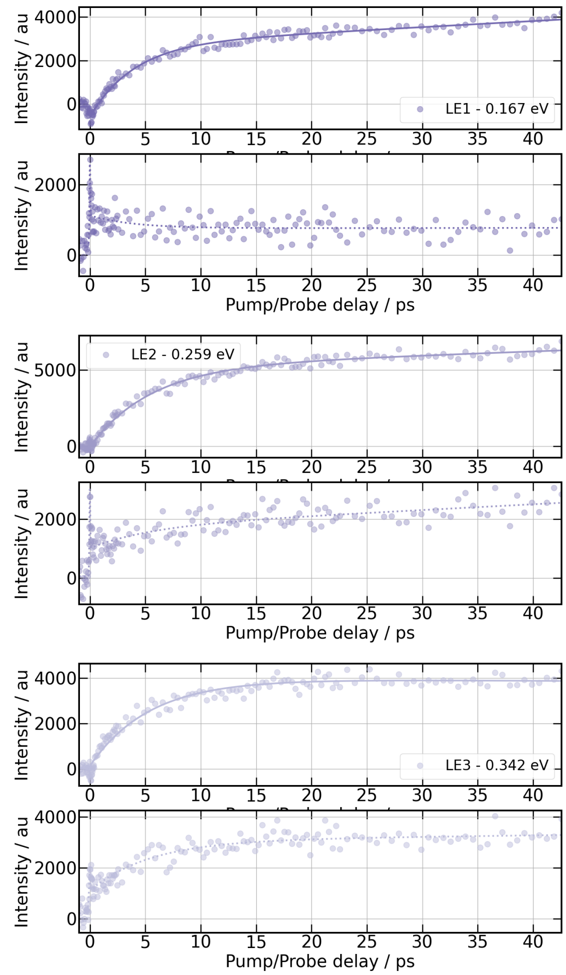
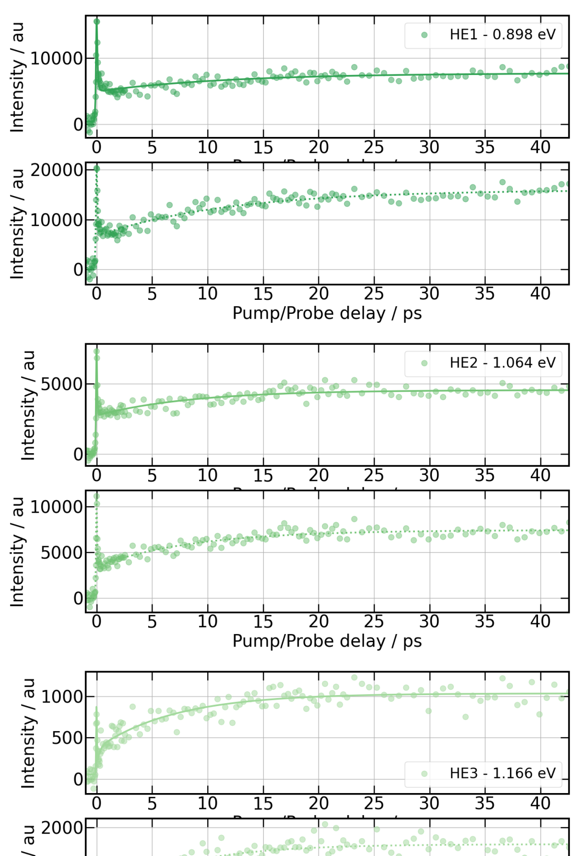


Fig. S5 Evolution of the three low energy rising bands LE1, LE2 and LE3 and their fit.



S2 Complementary data

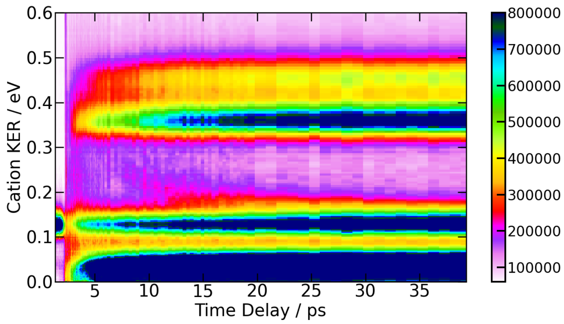


Fig. S6 Similar to Fig. 5 - top panel, with another colour map to enhance the feature shifting in KER.

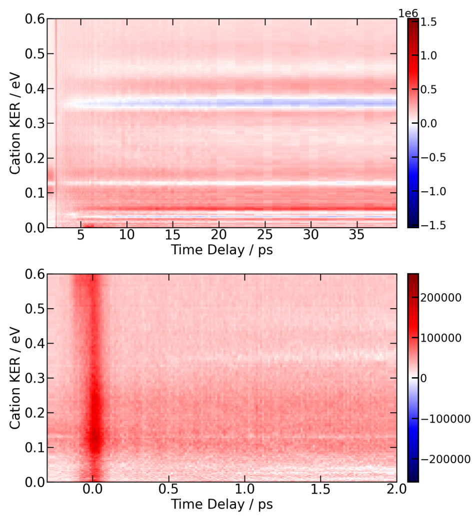


Fig. S7 269/807 nm experiment *top panel:* 3D-plot of the fs-TRKERS signal S_2^{cation}(KER,τ) up to 40 ps time delay. *Bottom panel:* zoom on the first 2 ps with a different intensity scale. Colour map is provided on the right.

S3 Energetics of the dissociation channels

Dissociation or ionization as	Excess energy 266/334 nm (eV)	Excess energy 269/807 nm (eV)
2× pump + 2 × probe photons		
$I^+(^1S_0)$ + $I^-(^1S_0)$	4.15	-0.31
$I^+(^1D_2)$ + $I^-(^1S_0)$	6.11	1.64
$I^+(^3P_1)$ + $I^-(^1S_0)$	6.93	2.47
$I^+(^3P_0)$ + $I^-(^1S_0)$	7.01	2.55
$I^+(^3P_2)$ + $I^-(^1S_0)$	7.81	3.35
$I^+(^3P_2)$ + $I(^2P_{\frac{1}{2}})$ + e^-	3.81	-0.66
$I^+(^3P_1)$ + $I(^2P_{\frac{3}{2}})$ + e^-	3.87	-0.59
$I^+(^3P_0)$ + $I(^2P_{\frac{3}{2}})$ + e^-	3.95	-0.51
$I^+(^3P_2)$ + $I(^2P_{\frac{3}{2}})$ + e^-	4.75	0.29
$I_2^+(A^2\Pi_{\frac{1}{2}u})+e^-$	4.95	0.48
$I_2^+(A^2\Pi_{\frac{3}{2}u})+e^-$	6.05	1.59
$I_2^+(X^2\Pi_{\frac{1}{2}g})+e^-$	6.81	2.34
$I_2^+(X^2\Pi_{\frac{3}{2}g})+e^-$	7.45	2.99
2× pump + 1 × probe photons		
$I^+(^1S_0)$ + $I^-(^1S_0)$	0.44	-1.85
$I^+(^1D_2)$ + $I^-(^1S_0)$	2.39	0.11
$I^+(^3P_1)$ + $I^-(^1S_0)$	3.22	0.93
$I^+(^3P_0)$ + $I^-(^1S_0)$	3.30	1.01
$I^+(^3P_2)$ + $I^-(^1S_0)$	4.09	1.81
$I^+(^3P_2)$ + $I(^2P_{\frac{1}{2}})$ + e^-	0.09	-2.19
$I^+(^3P_1)$ + $I(^2P_{\frac{3}{2}})$ + e^-	0.16	-2.13
$I^+(^3P_0)$ + $I(^2P_{\frac{3}{2}})$ + e^-	0.24	-2.05
$I^+(^3P_2)$ + $I(^2P_{\frac{3}{2}})$ + e^-	1.04	-1.25
$I_2^+(A^2\Pi_{\frac{1}{2}u})+e^-$	1.23	-1.05
$I_2^+(A^2\Pi_{\frac{3}{2}u})+e^-$	2.33	0.05
$I_2^+(X^2\Pi_{\frac{1}{2}g})+e^-$	3.09	0.80
$I_2^+(X^2\Pi_{\frac{3}{2}g})+e^-$	3.74	1.45
2× pump photons		
$I^+(^3P_2)$ + $I^-(^1S_0)$	**0.38**	**0.27**
$I^+(^3P_0)$ + $I^-(^1S_0)$	-0.42	-0.53
$I^+(^3P_1)$ + $I^-(^1S_0)$	-0.50	-0.61
$I_2^+(X^2\Pi_{\frac{3}{2}g})+e^-$	0.02	-0.09
$I(^2P_{3/2})$ + $I^\star((^3P_2)6s^2[2]_{5/2})$	0.99	0.89
$I(^2P_{3/2})$ + $I^\star((^3P_2)6s^2[2]_{3/2})$	0.81	0.71
$I(^2P_{3/2})$ + $I^\star((^3P_0)6s^2[0]_{1/2})$	0.22	0.11
$I(^2P_{3/2})$ + $I^\star((^3P_1)6s^2[1]_{3/2})$	0.10	0.002

Table S1 Excess energy to be shared between fragments when ground state I_2 molecules absorb pump and probe photons as indicated in the table. A limited version of this table is present in the main text (Tab. 2).

S4 Spectroscopic constants

I_2 state → valence asymptote	T_e cm^{-1}	eV	D_e cm^{-1}	eV	R_e Å	ω_e cm^{-1}	Ref.
$X: 0_g^{+\,1}\Sigma_{0_g^+} \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	0.0	0.000	12547	1.556	2.666	214.52	2,3 (Exp.)
$A': 2u\,^3\Pi_u \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	10041.7	1.245	2506	0.311	3.080	108.81	4 (Exp.)
$A: 1u\,^3\Pi_u \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	10912.7	1.353	1640	0.203	3.129	88.30	5 (Exp.)
$B': 0_u^{-\,3}\Pi_u \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	12259.5	1.520	288	0.036	4.097	19.41	6 (Exp.)
$a: 1g\,^3\Pi_g \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	12141.2	1.505	406	0.050	4.311	23.62	7 (Exp.)
B”: 1u $^1\Pi_u \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	12372.5	1.534	177	0.022	4.200	19.80	Ref.12 (Exp.) de Ref. 8
$2g\,^3\Pi_g \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	12309.0	1.526	238	0.030	4.340	20.00	9 (Exp.)
$3u\,^3\Delta_u \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	12445.1	1.543	105	0.013	4.756	13.90	8 (Th.)
$a': (2)\,0_g^+ \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	12303.4	1.525	244	0.030	4.641	17.69	7 (Exp.)
$(2)\,0_u^- \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$	12501.6	1.550	48	0.006	4.803	10.90	8 (Th.)
$B: 0_u^{+\,3}\Pi_{0_u^+} \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	15769.0	1.955	4381	0.543	3.024	125.67	2 (Exp.)
$(3)\,0_g^+ \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	19295.0	2.392	855	0.106	3.665	64.78	10 (Exp.)
$1g\,^1\Pi_g \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	19685.0	2.441	465	0.058	4.050	29.60	11 (Exp.)
$0_g^{-\,3}\Pi_g \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	19905.8	2.468	468	0.058	3.851	32.70	8 (Th.)
$b': 2u\,^3\Delta_u \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	19827.0	2.458	322	0.040	4.245	25.60	12 (Exp.)
$1g\,^3\Sigma_g^- \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	20123.5	2.495	258	0.032	4.273	22.10	8 (Th.)
$(3)\,0_u^- \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	19967.0	2.476	184	0.023	4.460	18.20	9 (Exp.)
$C: 1u\,^3\Sigma_u^+ \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	19913.0	2.469	237	0.029	4.355	22.29	12 (Exp.)
$2g\,^1\Delta_g \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	19938.0	2.472	213	0.026	4.410	20.10	9 (Exp.)
$1u\,^3\Sigma_u^+ \rightarrow I(^2P_{\frac{3}{2}})+I(^2P_{\frac{1}{2}})$	20309.0	2.518	65	0.008	4.673	12.60	8 (Th.)
$0_g^{+\,1}\Sigma_g^+ \rightarrow I(^2P_{\frac{1}{2}})+I(^2P_{\frac{1}{2}})$	27761.6	3.442	436	0.054	3.928	33.80	8 (Th.)
$(4)\,0_u^- \rightarrow I(^2P_{\frac{1}{2}})+I(^2P_{\frac{1}{2}})$	27273.0	3.381	480	0.060	3.923	34.90	12 (Exp.)
$1u\,^3\Delta_u \rightarrow I(^2P_{\frac{1}{2}})+I(^2P_{\frac{1}{2}})$	27373.9	3.394	379	0.047	4.036	29.24	13 (Exp.)

Table S2 Spectroscopic constants of the I_2 states which correlate to the $I(^2P_{\frac{3}{2}})+I(^2P_{\frac{3}{2}})$, $I(^2P_{\frac{1}{2}})+I(^2P_{\frac{3}{2}})$ and $I(^2P_{\frac{1}{2}})+I(^2P_{\frac{1}{2}})$ asymptotes.

I_2 state → ion-pair asymptote	T_e cm^{-1}	T_e eV	D_e cm^{-1}	D_e eV	R_e Å	ω_e cm^{-1}	Ref.
$D': 2_g \rightarrow I^+(^3P_2)+I^-(^1S_0)$	40388.3	5.008	31781	3.940	3.600	103.95	14,15 (Exp.)
$\beta: 1_g \rightarrow I^+(^3P_2)+I^-(^1S_0)$	40821.0	5.061	31349	3.887	3.607	105.02	16 (Exp.)
$D: 0_u^+ \rightarrow I^+(^3P_2)+I^-(^1S_0)$	41026.3	5.087	31143	3.861	3.581	95.08	17 (Exp.)
$E: 0_g^+ \rightarrow I^+(^3P_2)+I^-(^1S_0)$	41410.3	5.134	30759	3.814	3.634	101.41	18 (Exp.)
$\gamma: 1_u \rightarrow I^+(^3P_2)+I^-(^1S_0)$	41621.3	5.160	30548	3.788	3.672	95.01	18 (Exp.)
$\delta: 2_u \rightarrow I^+(^3P_2)+I^-(^1S_0)$	41787.8	5.181	30382	3.767	3.781	100.63	19 (Exp.)
$f: 0_g^+ \rightarrow I^+(^3P_0)+I^-(^1S_0)$	47026.1	5.830	31591	3.917	3.574	104.19	20 (Exp.)
$F: 0_u^+ \rightarrow I^+(^3P_0)+I^-(^1S_0)$	47217.3	5.854	31400	3.893	3.600	96.30	11 (Exp.)
$g: 0_g^- \rightarrow I^+(^3P_1)+I^-(^1S_0)$	47085.8	5.838	32171	3.989	3.559	104.07	6 (Exp.)
$G: 1_g \rightarrow I^+(^3P_1)+I^-(^1S_0)$	47559.1	5.897	31697	3.930	3.530	106.60	11 (Exp.)
$H: 1_u \rightarrow I^+(^3P_1)+I^-(^1S_0)$	48280.3	5.986	30976	3.841	3.630	107.96	11,21 (Exp.)
$0_u^- \rightarrow I^+(^3P_1)+I^-(^1S_0)$	48646.5	6.031	30610	3.795	3.780	102.34	22 (Th.)
$F'0_u^+ \rightarrow I^+(^1D_2)+I^-(^1S_0)$	51706.2	6.411	34191	4.239	3.480	131.00	11,23 (Exp.)
$1_g \rightarrow I^+(^1D_2)+I^-(^1S_0)$	53216.3	6.598	32680	4.052	3.522	106.93	24 (Exp.)
$2_u \rightarrow I^+(^1D_2)+I^-(^1S_0)$	54262.7	6.728	31634	3.922	3.530	108.49	25 (Exp.)
$2_g \rightarrow I^+(^1D_2)+I^-(^1S_0)$	54489.6	6.756	31407	3.894	3.522	108.26	26 (Exp.)
$1_u \rightarrow I^+(^1D_2)+I^-(^1S_0)$	54706.2	6.783	31191	3.867	3.708	105.29	25 (Exp.)
$0_g^+ \rightarrow I^+(^1D_2)+I^-(^1S_0)$	55409.9	6.870	30487	3.780	3.825	97.10	20 (Exp.)
$0_u^+ \rightarrow I^+(^1S_0)+I^-(^1S_0)$	65800.0	8.158	35871	4.447	3.500	100.00	27 (Th.)
$0_g^+ \rightarrow I^+(^1S_0)+I^-(^1S_0)$	69000.0	8.555	32671	4.051	3.800	100.00	27 (Th.)

Table S3 Same caption as Tab. S2 for the I_2 ion-pair states.

I_2^+ state → ionic asymptote	T_e cm^{-1}	T_e eV	D_e cm^{-1}	D_e eV	R_e Å	ω_e cm^{-1}	Ref.
$X^2\Pi_{\frac{3}{2}g} \rightarrow I^+(^3P_2)+I(^2P_{\frac{3}{2}})$	75069.0	9.307	21773	2.700	2.584	239.04	28 (Exp.)
$X^2\Pi_{\frac{1}{2}g} \rightarrow I^+(^3P_2)+I(^2P_{\frac{3}{2}})$	80266.0	9.952	16576	2.055	2.580	229.00	29 (Exp.)
$A^2\Pi_{\frac{3}{2}u} \rightarrow I^+(^3P_2)+I(^2P_{\frac{3}{2}})$	86367.0	10.708	10381	1.287	2.948	138.10	28 (Exp.)
$A^2\Pi_{\frac{1}{2}u} \rightarrow I^+(^3P_2)+I(^2P_{\frac{3}{2}})$	95254.1	11.810	1588	0.197	2.980	120.00	8,30

Table S4 Same caption as Tab. S2 for the lowest energy states of I_2^+ which correlate to the $I+(^3P_2)+I(^2P_{\frac{3}{2}})$ asymptote.

Notes and references

1 G. A. Garcia, L. Nahon and I. Powis, Rev. Sci. Instrum., 2004, **75**, 4989–4996.

2 P. Luc, J. Molec. Spectrosc., 1980, **80**, 41–55.

3 R. Bacis, D. Cerny and F. Martin, J. Molec. Spectrosc., 1986, **118**, 434–447.

4 J. B. Koffend, A. M. Sibai and R. Bacis, Journal De Physique, 1982, **43**, 1639–1651.

5 S. Gerstenkorn, P. Luc and J. Vergès, J. Phys. B: At. Mol. Opt. Phys., 1981, **14**, L193–L196.

6 S. Motohiro, S. Nakajima, K. Aoyama, E. Kagi, H. Fujiwara, M. Fukushima and T. Ishiwata, J. Chem. Phys., 2002, **117**, 9777–9784.

7 S. Churassy, F. Martin, R. Bacis, J. Vergès and R. W. Field, J. Chem. Phys., 1981, **75**, 4863–4868.

8 W. A. deJong, L. Visscher and W. C. Nieuwpoort, J. Chem. Phys., 1997, **107**, 9046–9058.

9 V. V. Baturo, I. N. Cherepanov, S. S. Lukashov, S. A. Poretsky and A. M. Pravilov, J. Phys. B: At. Mol. Opt. Phys., 2016, **49**, 125101.

10 S. Hoshino, T. Ishiwata, Y. Nakano, M. Fukushima, H. Fujiwara, M. Araki and K. Tsukiyama, J. Phys. Chem. A, 2019, **123**, 7590–7596.

11 P. J. Jewsbury, T. Ridley, K. P. Lawley and R. J. Donovan, J. Molec. Spectrosc., 1993, **157**, 33–49.

12 V. V. Baturo, I. N. Cherepanov, S. S. Lukashov, S. A. Poretsky and A. M. Pravilov, J. Phys. B: At. Mol. Opt. Phys., 2015, **48**, 055101.

13 M. E. Akopyan, V. V. Baturo, S. S. Lukashov, S. A. Poretsky and A. M. Pravilov, J. Phys. B: At. Mol. Opt. Phys., 2015, **48**, 025101.

14 J. Tellinghuisen, J. Molec. Spectrosc., 1982, **94**, 231–252.

15 J. Tellinghuisen, S. Fei, X. Zheng and M. C. Heaven, Chem. Phys. Lett., 1991, **176**, 373–378.

16 J. P. Perrot, M. Broyer, J. Chevaleyre and B. Femelat, J. Molec. Spectrosc., 1983, **98**, 161–167.

17 J. Tellinghuisen, J. Molec. Spectrosc., 2003, **217**, 212–221.

18 G. W. King, I. M. Littlewood and J. R. Robins, Chem. Phys., 1981, **56**, 145–156.

19 T. Ishiwata, T. Yotsumoto and S. Motohiro, Bull. Chem. Soc. Jpn., 2001, **74**, 1605–1610.

20 T. Ishiwata, J. Yamada and K. Obi, J. Molec. Spectrosc., 1993, **158**, 237–245.

21 S. Motohiro and T. Ishiwata, J. Molec. Spectrosc., 2000, **204**, 286–290.

22 V. A. Alekseyev, Opt. Spectrosc., 2005, **99**, 719–730.

23 T. Ishiwata, A. Tokunaga, T. Shinzawa and I. Tanaka, J. Molec. Spectrosc., 1986, **117**, 89–101.

24 T. Ishiwata, H. Takekawa and K. Obi, J. Molec. Spectrosc., 1993, **159**, 443–457.

25 S. Motohiro, A. Umakoshi and T. Ishiwata, J. Molec. Spectrosc., 2001, **208**, 213–218.

26 Y. Nakano, H. Ukeguchi and T. Ishiwata, J. Chem. Phys., 2004, **121**, 1397–1404.

27 V. A. Alekseev, Opt. Spectrosc., 2014, **116**, 329–336.

28 L.-h. Deng, Y.-y. Zhu, C.-l. Li and Y.-q. Chen, J. Chem. Phys., 2012, **137**, 054308.

29 M. C. R. Cockett, J. G. Goode, K. P. Lawley and R. J. Donovan, J. Chem. Phys., 1995, **102**, 5226–5234.

30 A. J. Yencha, M. C. R. Cockett, J. G. Goode, R. J. Donovan, A. Hopkirk and G. C. King, Chem. Phys. Lett., 1994, **229**, 347–352.