

Conclusions

A variety of up-to-date methods, such as (1+1) two step, (1 + 2)-photon optical-optical double resonance technique, three-step three-color and perturbation facilitated excitation schemes as well as resonance enhanced multiphoton ionization (REMPI) with velocity map imaging (VMI) have been used for study of spectroscopic parameters of the valence, IP and Rydberg states of an iodine molecule. Spectroscopic characteristics of the majority of these states are described well at this point, and these techniques can be utilized for further investigation of the intra- and intermolecular perturbations in the molecule states.

For the precise *ab-initio* calculation of heavy I₂ molecule, both correlation and relativistic effects should be taken into account. High-precision correlation calculations by coupled-cluster and multireference configuration interaction methods within both full electron four-component and relativistic two-component effective core potential frameworks are available for valence states of the I₂. Non-adiabatic perturbations in the *B* state, which manifest in the coupling between the *B* and (*ab*) valence states or the *B* state predissociation are studied in details. The work of Pique *et al.* on the mixing of (*ab*) states is still one of the most cited works on the theory of the hyperfine interaction perturbations in the I₂.

The IP states are well studied experimentally, but high-precision theoretical studies are still required. The *ab-initio* calculations of IP states carried out at the present are fragmental and do not give sufficient accuracy. The molecular orbital or “atom-in-molecule” approaches provide good qualitative and sometimes quantitative description of the optical IP-V transitions. Perturbations caused by *HFI* are still described unsatisfactory.

The experimental and theoretical studies identify two mechanisms for CINAT between the IP states of iodine molecule – “*approach-induced*” for collisions with molecular partners possessing large electric permanent dipole and quadrupole moments, transition dipole moment, and more common “*collision-induced*” one for collisions with rare gas atoms. The approach-induced mechanism manifests itself only in $E0_g^+ \xleftrightarrow{M} D0_u^+$ non-adiabatic transitions and gives large transition cross

sections, including the giant ones, up to $\sim 10^3 \text{ \AA}^2$ that exceed the gas-kinetic cross up to ~ 30 times. This process is highly selective: almost 90% of the products are formed in a single v_D vibrational level with a $\Delta J = \pm 1$ change in the angular momentum. The necessary conditions for this mechanism to occur are the existence of a final v_D level in a quasi-resonance with initially excited v_E level (*ca.* $|\Delta E| \leq 25 \text{ cm}^{-1}$, $M = \text{I}_2(X)$, or larger if transitions are resonant due to rotational transitions in M molecules, $M = \text{H}_2\text{O}$). The features of the approach-induced mechanism can be qualitatively interpreted in the framework of an electrostatic model and the semiclassical Born approximation.

Collisions with rare gas atoms represent a second mechanism for CINAT. For $E \xleftrightarrow{\text{Rg}} D$ energy transfer, much smaller rate constants and significantly broader product state distributions (vibrational and rotational) are observed, especially for $\text{Rg} = \text{Ar} - \text{Xe}$. Strict selection rules for electronic transitions lack for these CINATs, and other IP states of the tier are also populated. The rotational product state distributions obey the high- ΔJ propensity rule, thus being much broader than those observed for approach-induced transitions. Rotational energy transfer can play a significant role as compensating process for the energy difference between the initial and final vibrational energy levels. This fact provides a rationale for why CINAT with rare gas collisions results in broad vibrational product state distributions.

Studies of non-adiabatic transitions between IP states in van der Waals complexes provide more detailed and direct information on the non-adiabatic dynamics than CINAT studies due to much more rigid constraints on available energy, angular momentum, and average orientation of the interacting particles. They facilitate the analysis of the symmetry selection and propensity rules for electronic and vibrational predissociations of complexes and provide spectroscopic data to test directly the theoretical *PESs*.

Another very interesting and challenging problem is studies of molecular structures in which interaction of the electrophilic region of a halogen atom (acceptor of electrons) and a nucleophilic region of the other or the same molecular structure (donor of electrons) occurs. This specific interaction specializes as halogen bond (XB). XBs are mostly due to electrostatic interaction, but polarizing, exchange and dispersion ones are of great importance, also. XB is considered as a specific subset of intermolecular interactions according to IUPAC recommendation since 2013 (earlier it has been regarded as a special case of donor-acceptor, exchange or van der Waals (vdW) interaction). Halogen bonds manifest themselves in weakly-bound complexes with molecular partners, mainly. A large number of complexes of dihalogens, and interhalogens, XY, with two- and triatomic molecules and organic species *in the ground states* has been studied using spectroscopy and supersonic molecular beam technique. The excited electronic states of these complexes are promising objects for studies providing abundant information on spectroscopic parameters as well as mechanism of population and decay of these complexes.

Appendix

Table A1 The electronic energy (T_e), vibrational constant (ω_e), unharmonicity ($\omega_e x_e$), rotational constant for the $v = 0$ vibrational level (B_e), equilibrium internuclear distance (R_e), dissociation limit, dissociation energy for the $v = 0$ vibrational level, and radiative lifetime of the valence and ion-pair states of the iodine molecules

State	T_e , cm $^{-1}$	ω_e , cm $^{-1}$	$\omega_e x_e$, cm $^{-1}$	B_e , 10 $^{-2}$ cm $^{-1}$	R_e , Å	Diss. limit	D_0 , cm $^{-1}$	τ_{rad} , ns	Transitions observed	Refs.
X_0^+	0	214.520797	0.6079224	3.736794	2.666	aa	12440.23		$F_0^+, D_0^+, B_0^+ \leftrightarrow X; F_1^+ \rightarrow X$	[1, 2]
A^2_u	10042.0(2)	108.28(8)	1.15(2)	2.813(1)	3.0730 (8)	aa	9984.7	$\sim 6 \cdot 10^6$	$D^2_g \leftrightarrow A^1$	[3]
A^1_u	10907.416(9)	92.95(2)	1.56(1)	2.7398318(2)	3.114	aa	1641.3	$\sim 450 \cdot 10^3$	$A \leftarrow X_0^+, c^1_g, c^1_g \rightarrow A; \beta^1_g \rightarrow A;$ $G^1_g \rightarrow A$	[4]
B^0_u	12190	20.5	0.29			aa	350		$g^0_u \rightarrow B^1$	[5, 6]
a^1_g	12141.177(4)	23.623(6)	0.483(3)	1.43(1)	4.311	aa	394.35		$B_0^+ \rightarrow a^1_g$	[7]
C^1_u	19916.3 ^b	20.8 ^b	0.51 ^b	1.342	4.45	aa	224		$C \leftarrow X_0^+$	[8]
a^0_g	123303.402(1)	17.68(2)	0.4285(9)	1.233(6)	4.642(2)	aa	235.09		$B_0^+ \rightarrow a^0_g$	[7]
(1) 2_g	12309(2)	20(1)	0.5(1)	1.42(8)	4.34(1)	aa	238 (2)		$\delta^2_u \rightarrow (1)2_g$	[9]
B_0^+	15769.0485	125.6724	0.752677	2.903876	3.024800	ab	4318.853	see Fig.3.4	$B \leftrightarrow X_0^+, f^0_g, E_0^+ \rightarrow B$	[10]
(2) 0_g^+	19286.4(5)	64.4(2)	1.23(1)		3.645	ab	832.0(2)		$F^0_u \rightarrow (2)0_g^+$	[11]
c^1_g	19685(2)	29.5(4)	0.51(4)	1.62(2)	4.05(2)	ab	450(2)		$H^1_u, \gamma^1_u \rightarrow c$	[12]
(2) 2_u	19827(2)	25.6(4)	0.611(2)	1.47(4)	4.25	ab	297			[13, 14]
c^1_g	19880.5(2)	24.4(1)		1.427(5)	4.315(5)	ab	258(2)		$\gamma^1_u \rightarrow c^1$	[15, 16]
$0_g^-(ab)$	19744.5(2)	29.5(4)	0.51(4)	1.62(2)	4.052(2)	ab	391.3(3)		$h^0_u \rightarrow 0_g^-(ab)$	[17]
(3) 1_u	19913(1)	22.29(2)	0.611(2)	1.401(1)	4.355(3)	ab	237(2)		$\beta^1_g, G^1_g \rightarrow 3(1_u)$	[14]
(4) 1_u	20030.51	14.948	0.4662	1.234	4.64	ab	112		$\beta^1_g, G^1_g \rightarrow 4(1_u)$	[14]
$0_u^-(ab)$	19967(2)	18.2(9)	0.42(9)	1.335(8)	4.46(1)	ab	184(2)		$g^0_u \rightarrow 0_u^-(ab)$	[14]
$0_u^-(bb)$	27277.6	35.13(3)	0.707(2)	1.738(6)	3.910(7)	bb	458.2		$g^0_u \rightarrow 0_u^-(bb)$	[18]
$0_g^+(bb)$	27305.98(1)	33.340(5)	0.7340(6)	1.702(1)	3.9509	bb	430.67		$0_g^+(bb) \leftarrow B_0^+$; $B_0^+ \leftarrow 0_g^+(bb)$	[19]

$1_u(bb)$	27373.88(4)	29.24(1)	0.635(2)	1.631(2)	4.036(5)	bb	364.82	$\beta 1_g \leftarrow 1_u(bb)$	[20]
$D^+ 2_g$	40388.2(1)	103.960(9)	0.2080(3)	2.056(2)	3.594(2)	$^3P_2 + ^1S_0$	31719.1	$D \leftrightarrow A$	[3]
$\beta 1_g$	40821.04(2)	105.023(4)	0.2258(3)	2.0420(2)	3.607	$^3P_2 + ^1S_0$	31259.8	$\beta \leftarrow A 1_u; \beta \leftarrow 1_u(bb)$	[21]
$D0_u^+$	41026.307	95.0784	0.10838	2.06785	3.584	$^3P_2 + ^1S_0$	31095.5	$D \leftrightarrow X; D \rightarrow a 1_g^+$	[22]
$E0_g^+$	41411.8	101.3628	0.197930	1.99692	3.647	$^3P_2 + ^1S_0$	30706.8	$D \rightarrow (2)0_g^+$	
$\gamma 1_u$	41621.444(6)	94.739(4)	0.1709(7)	1.9586(1)	3.68305	$^3P_2 + ^1S_0$	30510.5	$E \leftrightarrow B0_u^+; E \rightarrow A 1_u C 1_u$	[23]
$\delta 2_u$	41787.780(8)	100.644(3)	0.2102(3)	1.8586(2)	3.78744 (5)	$^3P_2 + ^1S_0$	30331.2	$\gamma \leftarrow X0_g^+;$ $\gamma \rightarrow a 1_{g^+} c 1_{g^+} c 1_g$	[24]
$f0_g^+$	47026.2	104.1447	0.211335	2.0803	3.5737	$^3P_0 + ^1S_0$	31538.9	$\delta \rightarrow (1)2_g^+$	[25]
$g0_g^-$	47085.777(7)	104.065(2)	0.1936(9)	2.0822(6)	3.572	$^3P_1 + ^1S_0$	31479.4	$f \leftrightarrow B0_u^+; f \rightarrow A 1_u C 1_u$	[23]
$F0_u^+$	47217.35	96.31275	0.4125426	2.05413	3.5963	$^3P_0 + ^1S_0$	31351.6	$g \leftarrow B0_u^+ \sim 0_u^-(ab)$	[26]
$G1_g$	47558.645(4)	106.656(2)	0.2233(3)	2.10892(8)	3.5493	$^3P_1 + ^1S_0$	31005.3	$F0_u^+ \leftrightarrow X0_g^+$	[27, 28]
$H1_u$	48280.337(3)	107.960(1)	0.2647(1)	1.99046(7)	3.6534	$^3P_1 + ^1S_0$	36282.8	$G \leftrightarrow (3)1_u(4)1_u B0_u^+, A1_u$	[29]
$h0_u^-$	48646.548(6)	102.344(2)	0.2186(3)	1.859(6)	3.7804	$^3P_1 + ^1S_0$	29917.5	$H \leftarrow B0_u^+ \sim c 1_g$	[17]
$F^+0_u^+$	51706.237(2)	131.00(1)	0.5162(1)	2.19489(5)	3.4791	$^1D_2 + ^1S_0$	30.486	$h \leftarrow B0_u^+ \sim 0_u^-(ab)$	[17]
$f^+0_u^-$	55409.9	96.98	0.1865	1.8156	3.8250	$^1D_2 + ^1S_0$	26.800	$F^+ \rightarrow X0_g^+$	[30]
$1_g^+(D_2)$	53216.288(7)	106.932(3)	0.2077(3)	2.1420(5)	3.5218	$^1D_2 + ^1S_0$	29.988	$f^+ \leftrightarrow B0_u^+$	[23, 31]

Transitions observed are also presented (see Chap. 3 for details)

^aRadiative lifetime for the $v = 0$ vibronic level [33]

^b*ab-initio* calculation [34]

References

1. Gerstenkom, S., Luc, P.: Description of the absorption spectrum of iodine recorded by means of Fourier Transform Spectroscopy : the (B-X) system. *J. Phys.* **46**, 867–881 (1985). <https://doi.org/10.1051/jphys:01985004606086700>
2. Martin, F., Bacis, R., Churassy, S., Vergès, J.: Laser-induced-fluorescence Fourier transform spectrometry of the $X0_g^+$ state of I_2 : Extensive analysis of the $B0_u^+ \rightarrow X0_g^+$ fluorescence spectrum of $^{127}I_2$. *J. Mol. Spectrosc.* **116**, 71–100 (1986). [https://doi.org/10.1016/0022-2852\(86\)90254-7](https://doi.org/10.1016/0022-2852(86)90254-7)
3. Zheng, X., Fei, S., Heaven, M.C., Tellinghuisen, J.: Spectroscopy of metastable species in a free-jet expansion: The $D' \leftarrow A'$ transition of I_2 . *J. Chem. Phys.* **96**, 4877–4883 (1992). <https://doi.org/10.1063/1.462895>
4. Appadoo, D.R.T., Le Roy, R.J., Bernath, P.F., Gerstenkorn, S., Luc, P., Vergès, J., Sinzelle, J., Chevillard, J., D'Aignaux, Y.: Comprehensive analysis of the A–X spectrum of I_2 : An application of near-dissociation theory. *J. Chem. Phys.* **104**, 903–913 (1996)
5. Viswanathan, K.S., Tellinghuisen, J.: The 2880-A Emission Spectrum of I_2 : Ion-Pair States near $47\,000\text{ cm}^{-1}$. *J. Mol. Spectrosc.* **101**, 285–299 (1983)
6. Motohiro, S., Nakajima, S., Aoyama, K., Kagi, E., Fujiwara, H., Fukushima, M., Ishiwata, T.: Analysis of the $0_g^- (^3P_1) - B ^3\Pi(0_u^-)$ system of I_2 by perturbation-facilitated optical-optical double resonance. *J. Chem. Phys.* **117**, 9777–9784 (2002)
7. Churassy, S., Martin, F., Bacis, R., Vergès, J., Field, R.W.: Rotation–vibration analysis of the $B0_u^+ - a1_g$ and $B0_u^+ - a'0_g^+$ electronic systems of I_2 by laser-induced fluorescence Fourier-transform spectroscopy. *J. Chem. Phys.* **75**, 4863–4868 (1981)
8. Inard, D., Cerny, D., Nota, M., Bacis, R., Churassy, S., Skorokhodov, V.: $E0_g^+ \rightarrow A1_u$ and $E0_g^+ \rightarrow B''1_u$ laser-induced fluorescence in molecular iodine recorded by Fourier-transform spectroscopy. *Chem. Phys.* **243**, 305–321 (1999). [https://doi.org/10.1016/S0301-0104\(99\)00077-4](https://doi.org/10.1016/S0301-0104(99)00077-4)
9. Bature, V.V., Cherepanov, I.N., Lukashov, S.S., Poretsky, S.A., Pravilov, A.M.: Molecular parameters for weakly bound $2_g(aa, ab)$ and $0_u^-(ab)$ states of molecular iodine and dipole moment functions of transitions to these states. *J. Phys. B At. Mol. Opt. Phys.* **49**, 125101. (8pp) (2016)
10. Barrow, R.F., Yee, K.K. $B0_u^+ - X0_g^+$ system of $^{127}I_2$: rotational analysis and long-range potential in the $B0_u^+$ state. *J. Chem. Soc., Faraday Trans. 2.* **69**, 684–700 (1973). <https://doi.org/10.1039/F29736900684>
11. Ishiwata, T., Ohtoshi, H., Sakaki, M., Tanaka, I.: Spectroscopic study on the iodine molecule by a sequential three-photon excitation. *J. Chem. Phys.* **80**, 1411–1416 (1984)
12. Jewsbury, P.J., Ridley, T., Lawley, K.P., Donovan, R.J.: Parity mixing in the valence states of I_2 probed by optical-optical double-resonance excitation of ion-pair. *J. Mol. Spectrosc.* **157**, 33–49 (1993). <https://doi.org/10.1006/jmsp.1993.1003>
13. Tellinghuisen, J.: $D' \rightarrow 2_u(^3\Delta)$ transition in I_2 . Analysis by classical and quantum spectral simulations. *J. Phys. Chem.* **87**, 5136–5140 (1983)
14. Bature, V.V., Cherepanov, I.N., Lukashov, S.S., Poretsky, S.A., Pravilov, A.M.: Spectroscopic constants and potential energy curves of some iodine valence ungerade weakly bound states. *J. Phys. B At. Mol. Opt. Phys.* **48**, 055101. (8pp) (2015). <https://doi.org/10.1088/0953-4075/48/5/055101>
15. Ridley, T., Lawley, K.P., Donovan, R.J.: Observation of weakly bound valence states of I_2 . *J. Chem. Phys.* **127**, 154306–154312 (2007)
16. Akopyan, M.E., Lukashov, S.S., Maslennikova, Y.D., Poretsky, S.A., Pravilov, A.M.: Hyperfine coupling of the iodine $E0_g^+, v_E = 19$ and $\gamma1_u, v_\gamma = 18$ ion-pair states. *J. Phys. B At. Mol. Opt. Phys.* **40**, 1173–1181 (2007). <https://doi.org/10.1088/0953-4075/40/6/008>
17. Motohiro, S., Nakajima, S., Ishiwata, T.: Perturbation-facilitated optical-optical double resonance spectroscopy of the $h0_u^+ (^3P_1)$ and $H1(^3P_1)$ ion-pair states of I_2 . *J. Chem. Phys.* **117**, 187–196 (2002)

18. Baturo, V.V., Cherepanov, I.N., Lukashov, S.S., Poretsky, S.A., Pravilov, A.M., Zhironkin, A. I.: Heterogeneous and hyperfine interactions between valence states of molecular iodine correlating with the $I(^2P_{1/2}) + I(^2P_{1/2})$ dissociation limit. *J. Chem. Phys.* **144**, 184309–184308 (2016). <https://doi.org/10.1063/1.4948630>
19. Akopyan, M.E., Baturo, V.V., Lukashov, S.S., Poretsky, S.A., Pravilov, A.M.: Spectroscopic constants and the potential energy curve of the iodine weakly bound 0_g^+ state correlating with the $I(^2P_{1/2}) + I(^2P_{1/2})$ dissociation limit. *J. Phys. B At. Mol. Opt. Phys.* **46**, 055101. (9pp) (2013). <https://doi.org/10.1088/0953-4075/46/5/055101>
20. Akopyan, M.E., Baturo, V.V., Lukashov, S.S., Poretsky, S.A., Pravilov, A.M.: Spectroscopic constants and the potential energy curve of the iodine weakly-bound 1_u state correlating with the $I(^2P_{1/2}) + I(^2P_{1/2})$ dissociation limit. *J. Phys. B, At. Mol. Opt. Phys.* **025101**(7pp), 48 (2014)
21. Perrot, J.P., Broyer, M., Chevaleyre, J., Femelat, B.: Extensive study of the $1_g(^3P_2)$ ion pair state of I_2 . *J. Molec. Spectr.* **98**, 161–167 (1983)
22. Tellinghuisen, J.: The D state of I_2 : A case study of statistical error propagation in the computation of RKR potential curves, spectroscopic constants, and Frank-Condon factors. *J. Mol. Spectrosc.* **217**, 212–221 (2003). [https://doi.org/10.1016/S0022-2852\(02\)00055-3](https://doi.org/10.1016/S0022-2852(02)00055-3)
23. Wilson, P.J., Ridley, T., Lawley, K.P., Donovan, R.J.: Double resonance ionisation nozzle cooled spectroscopy (DRINCS) of the $E(^3P_2)$, $f(^3P_0)$ and $f'(^1D_2)$ 0_g^+ ion-pair states of I_2 . *Chem. Phys.* **182**, 325–339 (1994). [https://doi.org/10.1016/0301-0104\(94\)00047-6](https://doi.org/10.1016/0301-0104(94)00047-6)
24. Ishiwata, T., Motohiro, S., Kagi, E., Fujiwara, H., Fukushima, M.: Optical-optical double-resonance spectroscopy of the $1_u(^3P_2)$ and $2_u(^3P_2)$ states of I_2 through the $A^3\Pi(1_u)$ state. *Bull. Chem. Soc. Jpn.* **73**, 2255–2261 (2000). <https://doi.org/10.1246/bcsj.73.2255>
25. Ishiwata, T., Yotsumoto, T., Motohiro, S.: Optical–optical double resonance spectroscopy of I_2 through the parity mixed valence states. *Bull. Chem. Soc. Jpn.* **74**, 1605–1610 (2001). <https://doi.org/10.1246/bcsj.74.1605>
26. Motohiro, S., Nakajima, S., Aoyama, K., Kagi, E., Fujiwara, H., Fukushima, M., Ishiwata, T.: Analysis of the $0_g^-(^3P_1) - B'^3\Pi(0_u^-)$ system of I_2 by perturbation-facilitated optical–optical double resonance. *J. Chem. Phys.* **117**, 9777–9784 (2002). <https://doi.org/10.1063/1.1516790>
27. Hoy, A.R., Brand, J.C.D.: The $F0_u^+$ state of diatomic iodine: Effects of configuration interaction. *Chem. Phys.* **109**, 109–115 (1986). [https://doi.org/10.1016/0301-0104\(86\)80189-6](https://doi.org/10.1016/0301-0104(86)80189-6)
28. Ishiwata, T., Kusayanagi, T., Hara, T., Tanaka, I.: An analysis of the $F(0_u^+)$ ion-pair state of I_2 by optical-optical double resonance. *J. Mol. Spectrosc.* **119**, 337–351 (1986). [https://doi.org/10.1016/0022-2852\(86\)90029-9](https://doi.org/10.1016/0022-2852(86)90029-9)
29. Kagi, E., Yamamoto, N., Fujiwara, H., Fukushima, M., Ishiwata, T.: Optical–Optical Double Resonance Spectroscopy of the $1_g(^3P_1) - A^3\Pi(1_u) - X^1\Sigma_g^+$ Transition of I_2 . *J. Mol. Spectrosc.* **216**, 48–51 (2002). <https://doi.org/10.1006/jmsp.2002.8676>
30. Ishiwata, T., Tokunaga, A., Shinzawa, T., Tanaka, I.: An analysis of the $F'0_u^+$ ion-pair state of I_2 by optical-optical double resonance. *J. Mol. Spectrosc.* **117**, 89–101 (1986). [https://doi.org/10.1016/0022-2852\(86\)90094-9](https://doi.org/10.1016/0022-2852(86)90094-9)
31. Ishiwata, T., Yamada, J., Obi, K.: Optical-optical double-resonance spectroscopy of the $I_2 0_g^+(^1D)$ ion-pair state. *J. Mol. Spectrosc.* **158**, 237–245 (1993). <https://doi.org/10.1006/jmsp.1993.1068>
32. Ishiwata, T., Takekawa, H., Obi, K.: Optical-optical double-resonance spectroscopy of the $I_2 1_g(^1D)$ ion-pair state. *J. Mol. Spectrosc.* **159**, 443–457 (1993). <https://doi.org/10.1006/jmsp.1993.1141>
33. Lawley, K.P., Jewsbury, P., Ridley, T., Langridge-Smith, P., Donovan, R.: Einstein A-coefficients and transition dipole moments for some ion-pair to valence transitions in I_2 . *Molec. Phys.* **75**, 811–828 (1992)
34. de Jong, W.A., Visscher, L., Nieuwpoort, W.C.: Relativistic and correlated calculations on the ground, excited, and ionized states of iodine. *J. Chem. Phys.* **107**, 9046–9058 (1997). <https://doi.org/10.1063/1.475194>

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