

A NEW ACCURATE FIT OF THE HYPERFINE STRUCTURE OF MOLECULAR IODINE

CHRISTIAN J. BORDÉ, F. DU BURCK AND A. N. GONCHAROV

*Laboratoire de Physique des Lasers, Université Paris-Nord, Villetaneuse, France
Tel +33-608221484, Fax +33-608018459, E-mail: borde@lpl.univ-paris13.fr*

Recent measurements of hyperfine splittings of I_2 have been performed both by stimulated Raman spectroscopy [1-3] and by saturation spectroscopy [4], from which, the rotation dependence of the hyperfine coupling constants has been investigated in detail in the lower state. With these new data, it is possible to analyze independently the ground and excited states of this molecule and to obtain an improved predictive fit of iodine lines used as optical frequency standards.

Our starting point is an ensemble of recent measurements in Raman spectroscopy of the $X^1\Sigma_{0+g}, v''=0$ rovibronic states of iodine for values of J higher than those already published for $J = 13$ and 15 ^{1,2,3}. They correspond to the iodine transitions R(26) 62-0, R(54) 70-0 and R(55) 71-0 in coincidence with the 501,7 nm line of the argon laser:

$J = 26$	Frequency (kHz)	$J = 54$	Frequency (kHz)
4, 24 \rightarrow 4, 23	-27 286, 30(16)	4, 51 \rightarrow 4, 50	-175 580, 2(11)
4, 29 \rightarrow 4, 28	-30 008, 09(16)	4, 52 \rightarrow 4, 51	-13 557, 2(10)
4, 26 \rightarrow 4, 25	165 407, 08(16)	4, 57 \rightarrow 4, 56	-14 177, 7(10)
4, 23 \rightarrow 4, 22	-166 565, 24(16)	2, 54 \rightarrow 2, 53	375 052, 6(10)
4, 30 \rightarrow 4, 29	200 066, 42(16)	4, 52 \rightarrow 2, 53	174 722, 7(10)
4, 27 \rightarrow 4, 26	-201 288, 48(15)	4, 56 \rightarrow 2, 55	-191 995, 7(20)
2, 27 \rightarrow 2, 26	-352 929, 70(17)	4, 54 \rightarrow 2, 55	374 730, 9(10)
4, 25 \rightarrow 4, 24	-353 791, 79(17)	4, 54 \rightarrow 4, 53	175 227, 2(10)
2, 26 \rightarrow 2, 25	381 907, 34(16)	4, 56 \rightarrow 4, 55	375 179, 8(10)
4, 28 \rightarrow 4, 27	382 317, 72(17)	4, 58 \rightarrow 4, 57	192 117, 7(20)
		0, 54 \rightarrow 4, 55	175 668, 8(10)
		2, 52 \rightarrow 4, 52	-361 178, 4(10)
		2, 53 \rightarrow 4, 53	535 561, 6(10)
		2, 55 \rightarrow 4, 55	567 174, 2(10)
		4, 54 \rightarrow 0, 54	368 116, 1(10)
		4, 56 \rightarrow 2, 56	376 252, 7(10)

$J = 55$	Frequency (kHz)
3, 56 \rightarrow 3, 55	374 618, 6(15)
5, 52 \rightarrow 3, 52	174 354, 9(10)
3, 53 \rightarrow 5, 53	333 189, 9(10)
5, 54 \rightarrow 1, 54	179 907, 7(10)
3, 55 \rightarrow 5, 55	365 882, 8(10)
1, 56 \rightarrow 5, 56	189 637, 6(10)
3, 58 \rightarrow 5, 58	203 913, 8(10)

It should be noted that for high J values, the strongest lines correspond to $\Delta\varepsilon \neq 0$. The next step is the fit of these Raman data using a four-term Hamiltonian⁵:

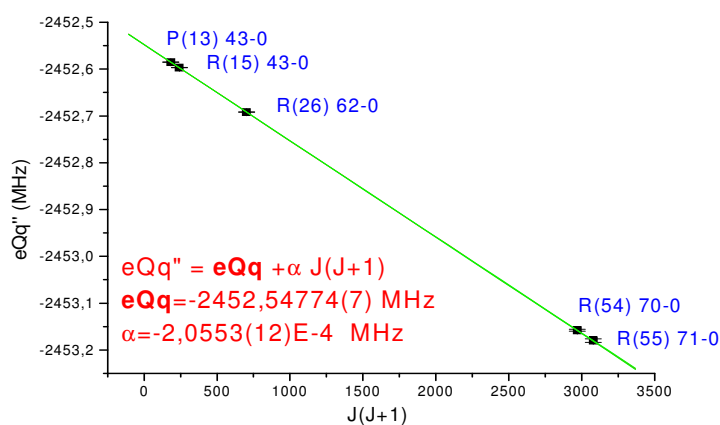
$$H = eqQH_Q + CH_{SR} + dH_{SSS} + \delta H_{SST}$$

The following hyperfine constants are obtained for $J'' = 13, 15, 26, 54$ and 55 :

$X, v'' = 0$	$J'' = 13$	$J'' = 15$
$eqQ(\text{MHz})$	-2452,58514(45)	-2452,59699(45)
$C(\text{kHz})$	3,1536(33)	3,1543(29)
$d(\text{kHz})$	1,528(18)	1,519(18)
$\delta(\text{kHz})$	3,708(22)	3,701(23)

$X, v'' = 0$	$J'' = 26$	$J'' = 54$	$J'' = 55$
$eqQ(\text{MHz})$	-2452,6921(4)	-2453,158(2)	-2453,180(4)
$C(\text{kHz})$	3,153(1)	3,161(5)	fixed
$d(\text{kHz})$	1,50(2)	1,47(8)	fixed
$\delta(\text{kHz})$	3,69(3)	3,56(9)	fixed

One may thus conclude that in the ground state $X^1\Sigma_{0+g} v''=0$, the quadrupole constant eqQ exhibits a linear dependence with $J(J+1)$ and that the magnetic interaction constants C, d, δ are almost constants within this range of J values and with the present accuracy. This confirms previous results of saturation spectroscopy^{5,4} but at a much higher level of accuracy.



Rotational dependence of the electric quadrupole coupling constant in the ground vibronic state of iodine

For example, the crossover c_8 in the P(13) saturation spectrum has a frequency given by ^{5,6} $\nu_{c_8} - \nu_{a_7} - \delta/2\pi = 114341 \pm 1$ kHz and the corresponding Raman line has a frequency ² $\nu_{Raman} = 228679581 \pm 28$ Hz, which yields $114339, 79 \pm 0, 014$ kHz for the previous quantity. Conversely, our results can be applied to the analysis and to the prediction of saturation spectra. From measured main saturation resonances, it is now possible to separate accurately the contributions of the hyperfine energies of both electronic states. As an example, from the measured values of P(13)/R(15) ⁵, we can now obtain the hyperfine constants for all the excited states $B^3\Pi_{0+u}$ $v' = 43$ levels:

$B, v' = 43$	$J' = 12$	$J' = 16$
$eqQ(MHz)$	$-558, 6168(30)$	$-558, 6407(17)$
$C(kHz)$	$190, 313(12)$	$190, 533(6)$
$d(kHz)$	$-100, 03(18)$	$-100, 34(11)$
$\delta(kHz)$	$0, 60(15)$	$0, 61(9)$

From which we may conclude that there are significant changes of eqQ but also of C with J in the electronic excited state. The saturation spectrum of a single rovibronic line has altogether several hundred resonances including all crossovers and weak lines. Thanks to this work, we are now able to determine accurately the positions and **absolute** intensities of all these resonances ^{1,6} for a large range of J values.

References

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