Comments and Addenda

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Re-evaluation of the hyperfine coupling constants for B-X transitions in I_2

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High-precision measurements of the I_2 B-$X(43,0)$ $R(15)$ hyperfine spectrum are reported. The $R(15)$ and previously measured (43,0) $P(13)$ spectra were fitted to 2.6 and 5.4 kHz, respectively. A previous fit of the $P(13)$ which resulted in a nonzero value for the magnetic octupole coupling constant was apparently in error. Extension of such measurements to other rotational vibrational levels in I_2 using an optically pumped laser and two-step excitation is discussed.

In a previous paper[1] we reported precision measurements of the B-$X(43,0)$ $P(13)$ $\Delta F = \Delta J$ hyperfine spectrum in $^{127}I_2$. More recently we performed similar measurements for the B-$X(43,0)$ $R(15)$ $\Delta F = \Delta J$ transitions in I_2. The data for both the $P(13)$ and $R(15)$ transitions were least-squares fitted using the Hamiltonian described in Ref. 1 without, however, the inclusion of magnetic octupole coupling and third-order nuclear electric quadrupole interactions. The measured line positions and their calculated frequencies are displayed in Table I for both the $P(13)$ and $R(15)$ transitions. The fits resulted in standard deviations of 5.4 and 2.6 kHz for the $P(13)$ and $R(15)$ transitions, respectively, with the corresponding differences between upper- and lower-state nuclear electric quadrupole (eQq), magnetic spin-rotation (C), tensor spin-spin (D_t), and scalar spin-spin (D_s) coupling constants displayed in Table II. Inclusion of the magnetic octupole interaction did not significantly improve the fit and resulted in values for the octupole coupling constant which were smaller than their uncertainties. This is in sharp contrast with the results of the fit in Ref. 1 where a nonzero value for the octupole term was obtained. It appears that the fitting of the data in Ref. 1 was in

TABLE I. Measured and calculated frequencies of the B-$X(43,0)P(13)$ and $R(15)$ hyperfine transitions. Line positions are with respect to a_7 and b_{13} for the $P(13)$ and $R(15)$ transitions, respectively, and the notation is the same as in Ref. 1.

Line	Meas. Freq. (kHz)	Meas.-Calc. (kHz)	Line	Meas. Freq. (kHz)	Meas.-Calc. (kHz)
a_1	−386 761	2	b_1	−630 766	2
a_2	−314 901	−3	b_2	−561 042	−1
a_3	−254 994	−1	b_3	−501 613	1
a_4	−178 956	−5	b_5	−294 948	2
a_5	−51 776	5	b_7	−234 335	−5
a_6	−14 224	4	b_{12}	−64 490	0
a_7	0	0	b_{14}	27 406	1
a_8	83 696	2	b_{15}	94 392	1
a_9	94 711	1	b_{17}	160 892	−2
a_{11}	138 964	9	b_{18}	234 748	−3
a_{12}	180 592	3	b_{19}	244 061	0
a_{15}	332 387	5	b_{20}	262 121	1
a_{16}	361 739	−1	b_{21}	316 505	2
a_{17}	405 908	−5			
a_{20}	502 614	4			
a_{21}	562 302	−10			
Std. dev. (kHz)		5.4			2.6

TABLE II. Differences between upper- and lower-state hyperfine coupling constants obtained from the fits in Table I. Uncertainties in constants are two standard deviations.

	$P(13)$	$R(15)$
$eQq' - eQq''$	1 893 924.4 ± 8.6 kHz	1 893 977.8 ± 3.2 kHz
eQq''	−2 451 689.9 ± 100 kHz	−2 453 790.0 ± 50 kHz
$C' - C''$	186.903 ± 0.076 kHz	187.521 ± 0.044 kHz
C'' [a]	0.00	0.00
$D_t' - D_t''$	−101.63 ± 0.50 kHz	−101.88 ± 0.60 kHz
D_t''	2.5 ± 0.5 kHz	2.5 ± 0.5 kHz
$D_s' - D_s''$	−3.18 ± 0.72 kHz	−2.13 ± 0.46 kHz
D_s'' [a]	0.00	0.00

[a] Quantities held fixed.

error, which first became apparent to us when the fitting of the $R(15)$ data yielded a negligible value for the octupole term. In the meantime, Landsberg[2] refitted our data in Ref. 1 and obtained a 6.25-kHz fit without including an octupole interaction. Also, Broyer *et al*[3]. estimated the order of magnitude of the octupole term to be much less than the value obtained in Ref. 1.

In order to develop a detailed model of the structure of the I_2 molecule it is necessary to map out the hyperfine coupling strengths for the ground and excited electronic states as a function of the rotational vibrational level. The precision measurements presented above can be easily extended to study the variation of the hyperfine coupling strengths in the excited electronic B state by replacing the argon laser in the setup described in Ref. 1 with a frequency stabilized tunable laser capable of coupling the lower rotational vibrational levels of the X state to the various rotational vibrational levels in the B state. However, in order to measure coupling constants associated with the high-lying thermally unpopulated levels in the ground electronic state, it is clear that an alternate technique must be used. Recently we have demonstrated[4] hyperfine structure measurements in high-lying ($v'' = 83$) vibrational levels of the X state using an optically pumped laser (OPL) where the gain medium is the molecule under study. More recently we demonstrated a more precise scheme using two-step excitation[5] which requires both a pump and a probe laser to measure the spectra and allows for operation at much lower vapor pressures and weaker power levels than the OPL method.

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