THE PURE ROTATIONAL SPECTRUM OF IODINE MONOCHLORIDE:

ROTATIONAL PARAMETERS, BORN-OPPENHEIMER BREAKDOWN CORRECTION, AND HYPERFINE CONSTANTS

ICT PRAGUE

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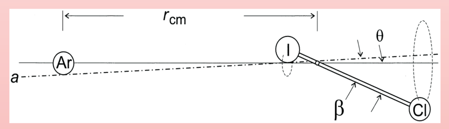
USTL

MOTIVATION

- lack of milli/submillimeter-wave high resolution study
- extension and improvement of previous set of molecular parameters
- data needed for:
  - study of structure and dynamics of Rg···ICl
  - atmospheric study of ozone depletion

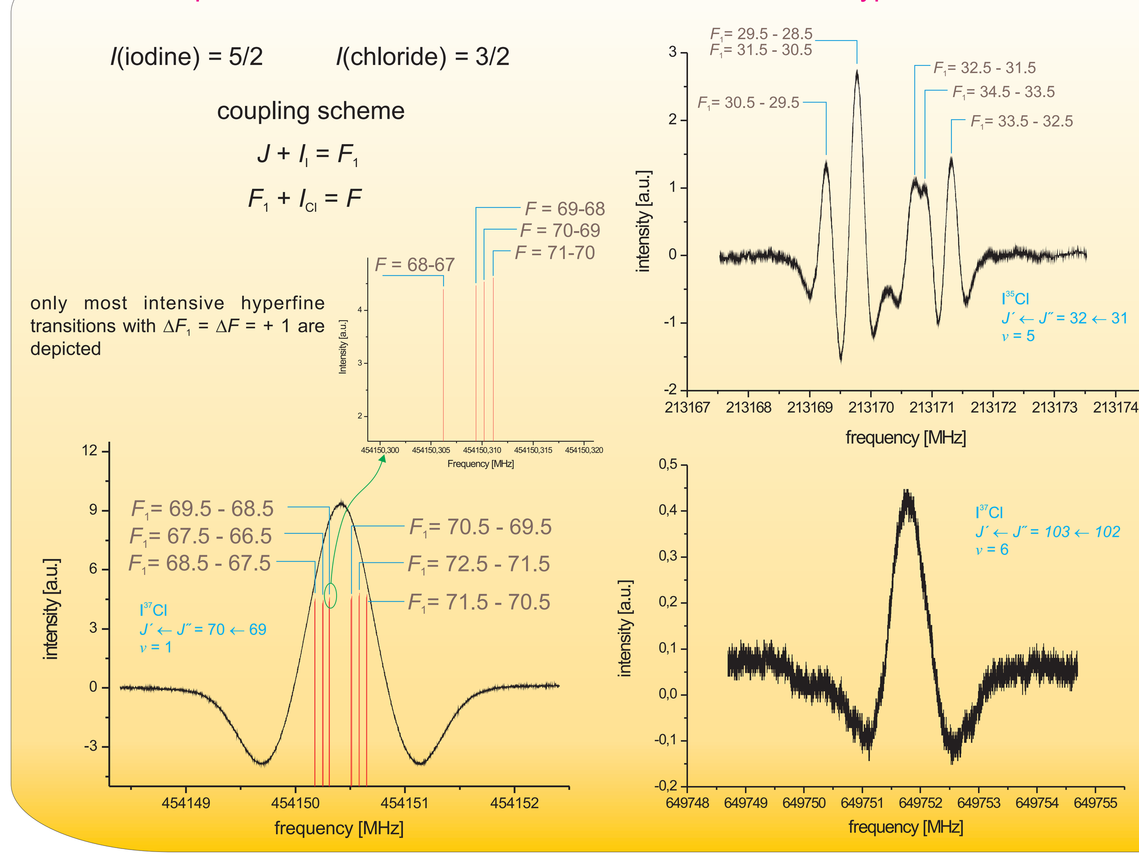


$$ICl \xrightarrow{\text{photodissociation}} Cl\bullet + I\bullet$$

$$Cl\bullet + O_3 \rightarrow O_2 + ClO\bullet$$

$$I\bullet + O_3 \rightarrow O_2 + IO\bullet$$

EXPERIMENT



used spectrometers: submillimeter-wave ones in Lille and in Miyama

measurement range: frequency range 200 - 1200 GHz

$29 \leq J'' \leq 180$

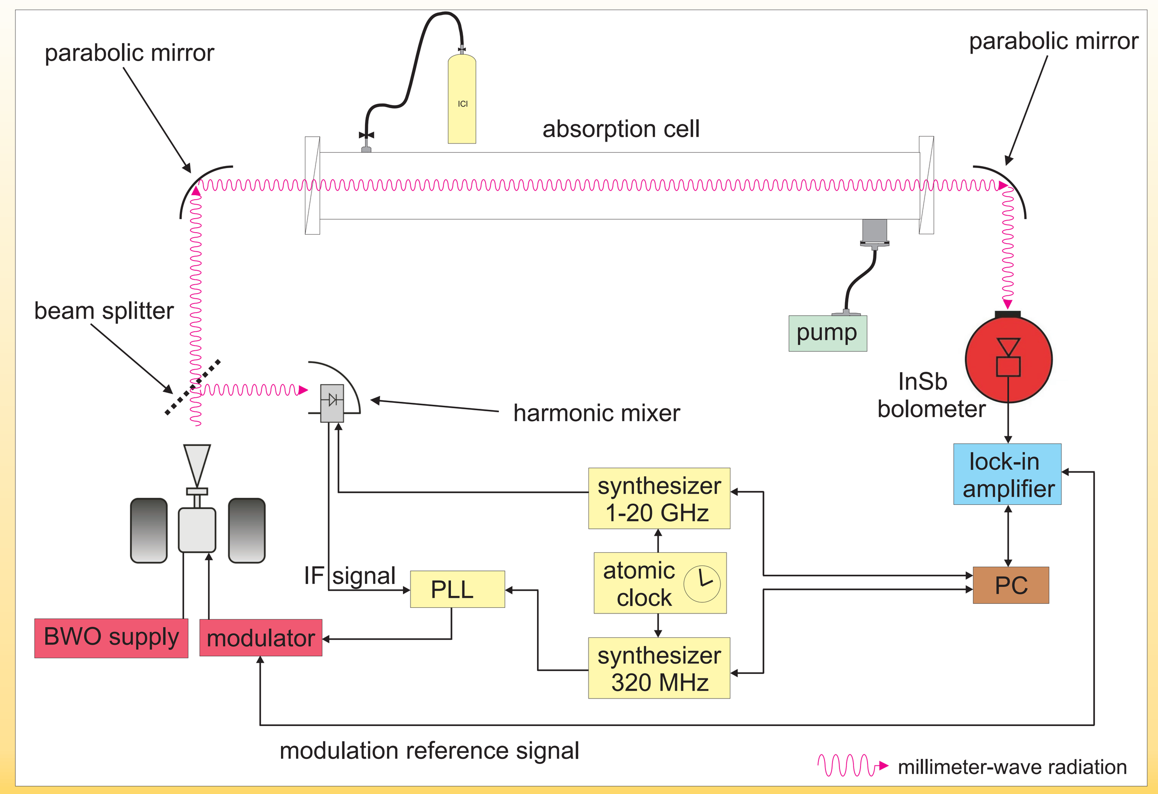
$0 \leq v \leq 7$

sample: commercial product (98%, Sigma Aldrich)

pressure of sample: 3 μbar

temperature of sample:
$v \leq 4$ - room temperature
$v > 4$ - hot water temperature
$177 \leq J'' \leq 180$ - DC discharge

Due to natural abundance of ^{35}Cl (75.8%) and ^{37}Cl (24.2%) of atomic chlorine both isotopologues I^{35}Cl and I^{37}Cl could be measured.



Schematic diagram of the Lille milli/submillimeter-wave spectrometer.

DUNHAM ANALYSIS

The newly observed transitions including more than 400 lines with unresolved hyperfine structures and more than 320 hyperfine lines were connected together with previous data observed at centimeter wavelengths (J''= 0-1, v = 0-1)[1] and with 23 millimeter-wave lines (J''= 12-44, v = 0-3)[2]. The final dataset with more than 900 transitions of both isotopologues I^{35}Cl and I^{37}Cl were fitted to the customary Dunham[3] expression:

$$E_{v,J} = \sum_{i,j} Y_{i,j} (v + \frac{1}{2})^i J^j (J+1)^j$$

where the $Y_{i,j}$ are Dunham parameters, which are listed for both isotopologues in table below.

	$^{127}I^{35}Cl$			$^{127}I^{37}Cl$		
	This work	Hedderich et al.	Willis et al.	This work	Hedderich et al.	Willis et al.
Y_{01}	3422.41375(39)	3422.36043(45)	3422.3638(20)	3277.46257(54)	3277.41437(120)	3277.4173(19)
Y_{11}	-15.973392(138)	-15.96824(42)	-15.9751(43)	-14.969420(156)	-14.96207(117)	-14.9710(40)
$Y_{21} \times 10^{-3}$	-35.843(62)	-38.946(96)	-35.2(26)	-32.871(85)	-37.653(419)	-32.3(24)
$Y_{31} \times 10^{-3}$	-0.4751(113)		-0.6(4)	-0.4264(145)		-0.5(3)
$Y_{41} \times 10^{-6}$	-8.54(72)			-7.50(89)		
$Y_{02} \times 10^{-3}$	-1.2080331(209)	-1.20698(18)	-1.2081(6)	-1.1078713(278)	-1.10752(90)	-1.108(6)
$Y_{12} \times 10^{-6}$	-5.8758(80)	-6.2755(285)	-5.9(6)	-5.2733(99)	-5.103(84)	-5.5(6)
$Y_{22} \times 10^{-6}$	-0.13244(228)			-0.11631(257)		
$Y_{32} \times 10^{-9}$	-2.545(196)			-2.187(222)		
$Y_{03} \times 10^{-10}$	-2.5908(130)	-5.396(360)	-2.639(3)calculated	-2.2753(155)	-10.61(105)	-2.318(3)calculated
$Y_{13} \times 10^{-12}$	-16.098(266)			-13.835(289)		
$Y_{04} \times 10^{-15}$	-0.438(45)			-0.368(77)		

Errors quoted in parentheses are one standard deviation. All parameters are given in MHz.

The parameters $Y_{i,j}$ derived by Hedderich[4] from infrared measurement show large deviations from ours, which do not agree within the errors. In particular his higher order constants (Y_{21},Y_{02},Y_{12},Y_{03}) deviate significantly from our derived parameters. These inconsistencies are the reason, why we did not use the IR data in our fits. All data included in our fit are pure rotational transitions with experimental accuracy in the range 2-30 KHz. The exception are 4 lines measured in the THz region (J''=177-180, v = 0) possessed of accuracy 125-200 kHz.

MASS INVARIANT ANALYSIS

In addition to the standard Dunham parameters $Y_{i,j}$, the mass invariant parameters $U_{i,j}$ and the Born-Oppenheimer breakdown correction (BOB) Δ_{01}(Cl) have been determined. The experimental data have been analyzed using the expression:

$$E_{v,J} = \sum_{i,j} U_{i,j} \mu^{-(\frac{i}{2}+j)} (1 + \frac{m_e}{M_{Cl}} \Delta^{Cl}_{i,j})(v + \frac{1}{2})^i J^j (J+1)^j$$

where M_{Cl} is atomic mass of chlorine, m_e is the electron mass and μ is the reduced mass of the molecule. The results of this isotopically invariant study are listed in table below. The first order Born-Oppenheimer breakdown correction Δ_{01} for chlorine is well determined. The BOB correction for iodine was not consider, since there is no other stable isotope than ^{127}I.

	ICl
U_{01} [MHz amu]	93824.3439(87)
U_{11} [MHz amu$^{3/2}$]	-2292.8291(198)
U_{21} [MHz amu^{2}]	-26.938(47)
U_{31} [MHz amu$^{5/2}$]	-1.870(46)
U_{41} [MHz amu^{3}]	-0.1759(148)
U_{02} [MHz amu^{2}]	-0.9079144(157)
U_{12} [MHz amu$^{5/2}$]	-0.0231220(31)
U_{22} [MHz amu^{3}] × 10^3	-2.729(47)
U_{32} [MHz amu$^{7/2}$] × 10^3	-0.274(21)
U_{03} [MHz amu^{3}] × 10^6	-5.33805(267)
U_{13} [MHz amu$^{7/2}$] × 10^6	-1.7367(287)
U_{04} [MHz amu^{4}] × 10^{10}	-2.474(254)
Δ_{01}(Cl)	-1.3973(104)

Errors quoted in parentheses are one standard deviation.

The ICl equilibrium bond lengths [pm]

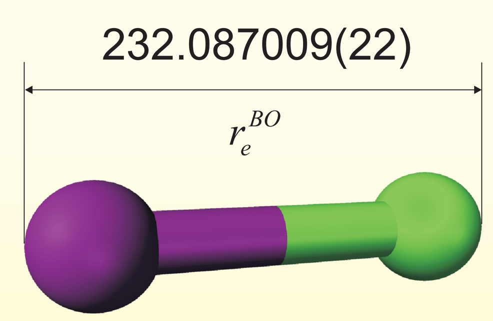
$$r_e^2 \times B_e \times \mu = X$$

μ is the reduced mass of selected species
X = 505379.0094 ± 0.0034 amu MHz Å^2

I^{35}Cl r_e = 232.0887386(24)
I^{37}Cl r_e = 232.0886991(32)

The bond distance in the BOA [pm]

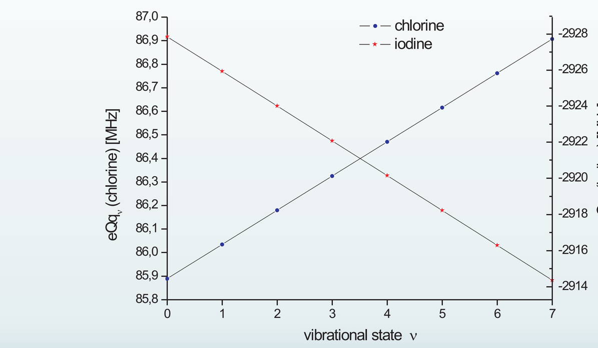
$$r_e^2 \times U_{01} = X$$



HYPERFINE ANALYSIS

	I^{35}Cl	I^{37}Cl
eQq_e(I)	-2928.8234(28)	-2928.8212(30)
eQq_{10}(I)	1.92684(295)	1.88522(289)
eQq_e(Cl)	-85.8161(41)	-67.6122(42)
eQq_{10}(Cl)	-0.1455(43)	-0.1421(42)
c_e(I)	0.020721(59)	0.019813(56)

All parameters are given in MHz and errrors quoted in parentheses are one standard deviation



CONCLUSION

Very accurate rotational transition frequencies of I^{35}Cl and I^{37}Cl are now available in milli/submillimeter-wave region. They span ground vibrational state and excited vibrational states up to v = 7. The hyperfine analysis have enabled determination of equilibrium nuclear electric quadrupole coupling parameters and their vibrational dependencies for iodine and chlorine along with determination of nuclear magnetic spin-rotational constant of iodine. For the first time the higher order Dunham parameters Y_{31},Y_{41},Y_{22},Y_{32},Y_{13}, and Y_{04} were determined. On the basis of the presented data, the rotational spectrum of both ICl isotopologues can be predicted into THz-region with high level of confidence.

References

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Acknowledgement

This work was supported through the European Commission (grants PERG02-GA-2007-224936 "PRAMICIDIS" and MRTN-CT-2004-512302) and the Ministry of Education, Youth and Sports of the Czech Republic (grants OC111, OC186 within the frame of the EU COST 729 Action and the Research program LC06071). S.B. gratefully acknowledges JSPS (Japan Society for the Promotion of Science) through the Invitation Fellowship Program ID S-0871 for financial support.

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