Quadrupole interaction in the solid halogens – a new (not final) look

H. Haas

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Experimentalists credo (old):
If theory and experiment do not agree, theory must be wrong

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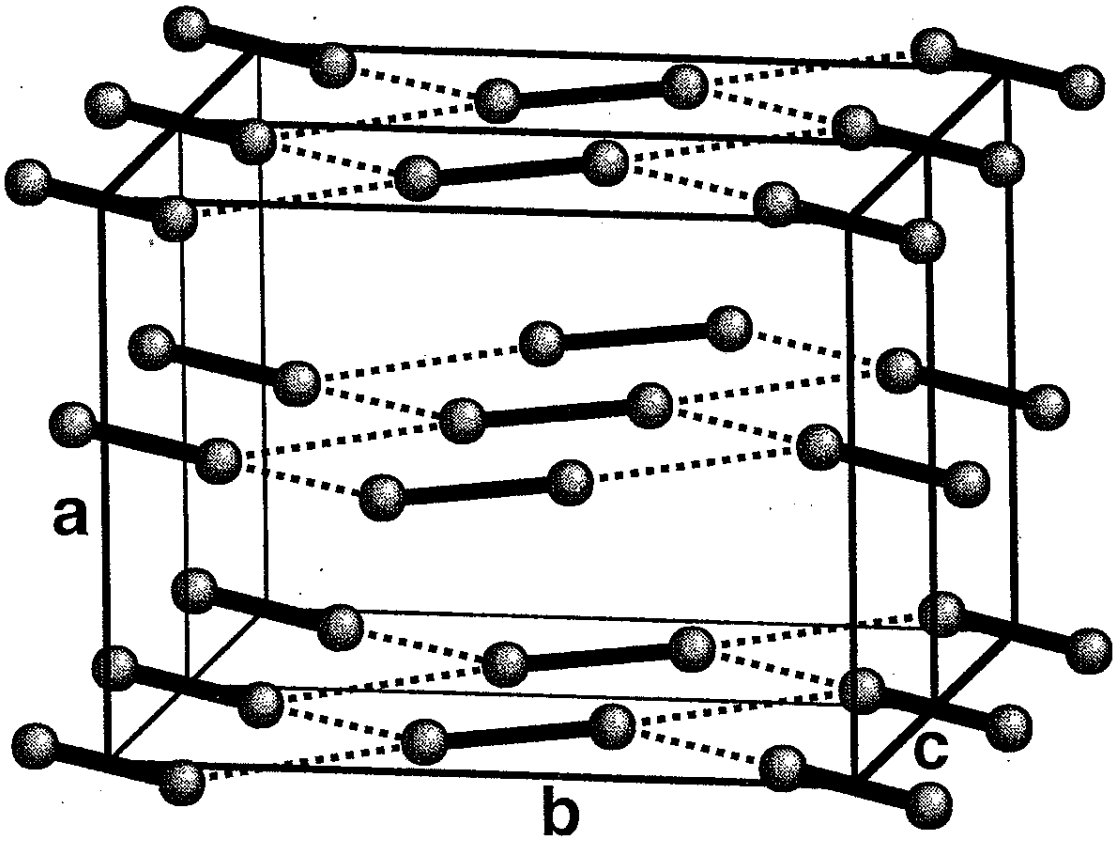
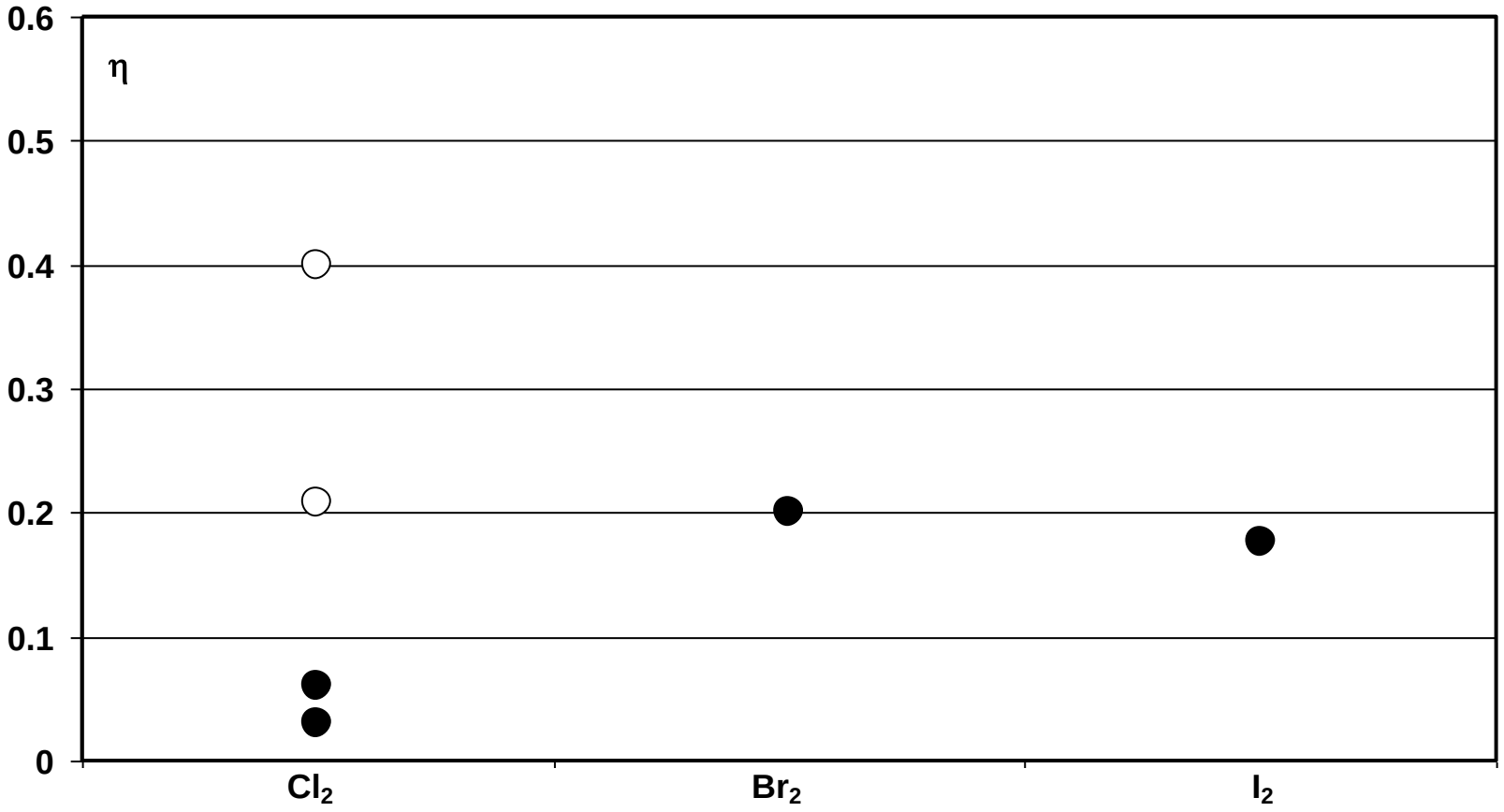
I will try to convince you:
If theory and experiment do agree, they may both be wrong !

The structure of the solid halogens



The experimental situation



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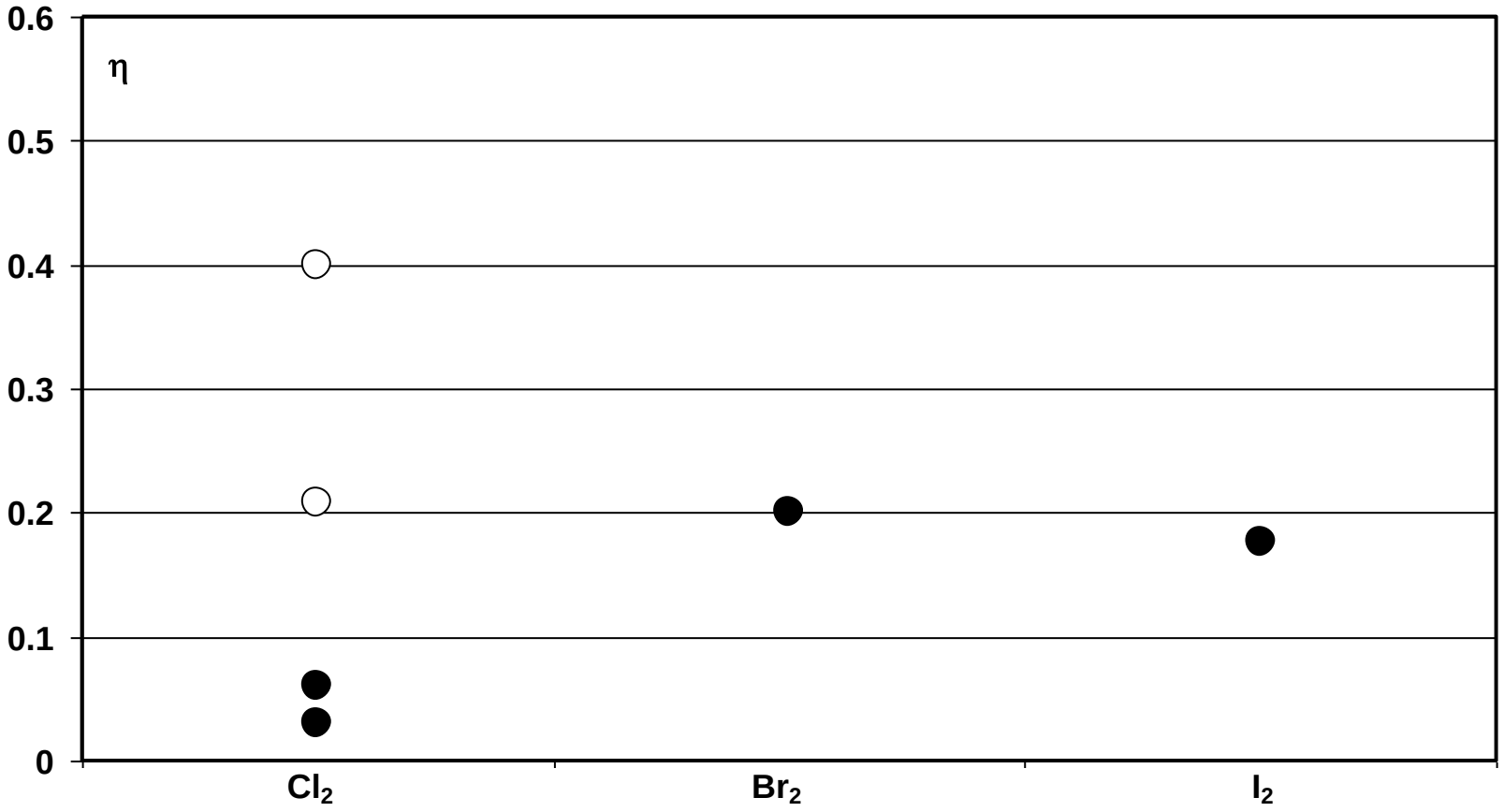


A mess !

Ab initio Calculations of the Electric Field Gradients in Solids in Relation to the Charge Distribution *

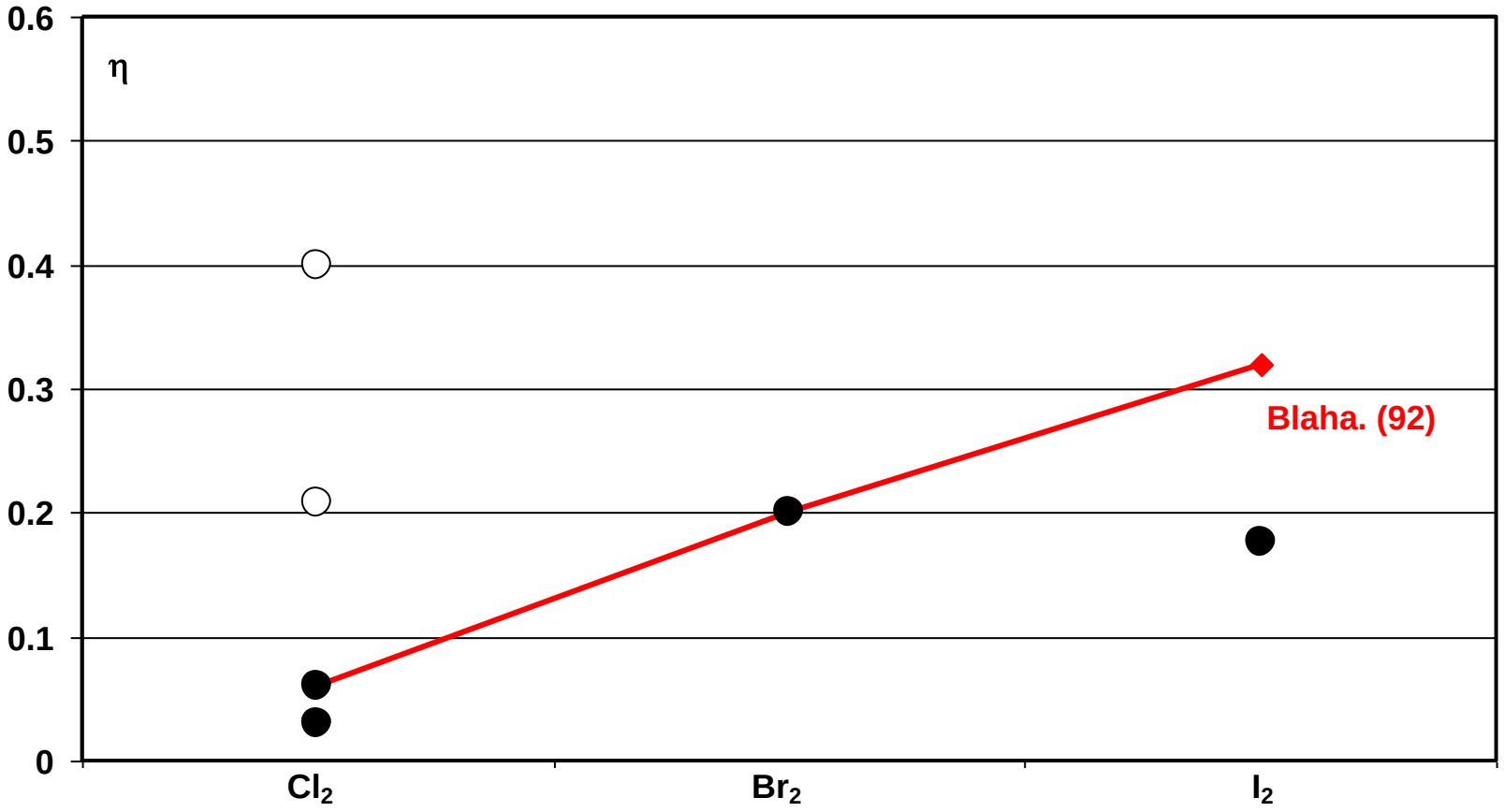
Karlheinz Schwarz and Peter Blaha
Institut für Technische Elektrochemie, Technische Universität Wien, Vienna, Austria

Z. Naturforsch. **47 a,** 197–202 (1992); received August 3, 1991

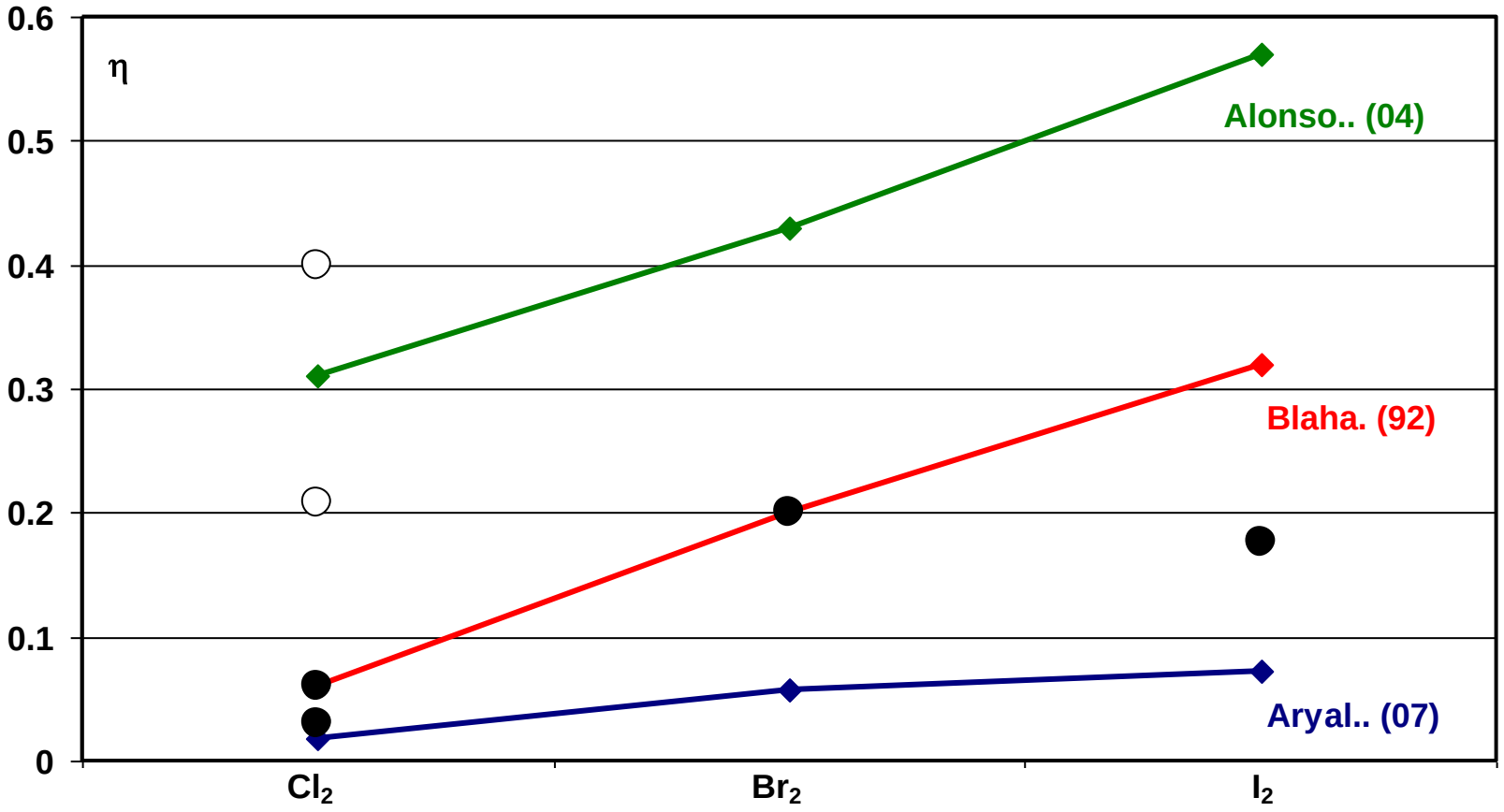
Table 3. Electric field gradient of solid Cl_2, Br_2, and I_2. Most experimental data are taken from [20] except for Cl_2 as specified.

		Cl_2	Br_2	I_2
Isotope		^{35}Cl	^{79}Br	^{127}I
$Q/mb = 10^{-31}\ m^2$		−82.5	331	−789
EFG	theory	+53.7	+96.6	+118.8
$(10^{21}\ V/m^2)$	exp.	±54.6	±95.6	±113.0
η	theory	0.07	0.19	0.32
	exp.	0.06 [21]	0.20	0.18
		0.4 [22]		
		0.2 [23]		

The advent of theory



More new theories



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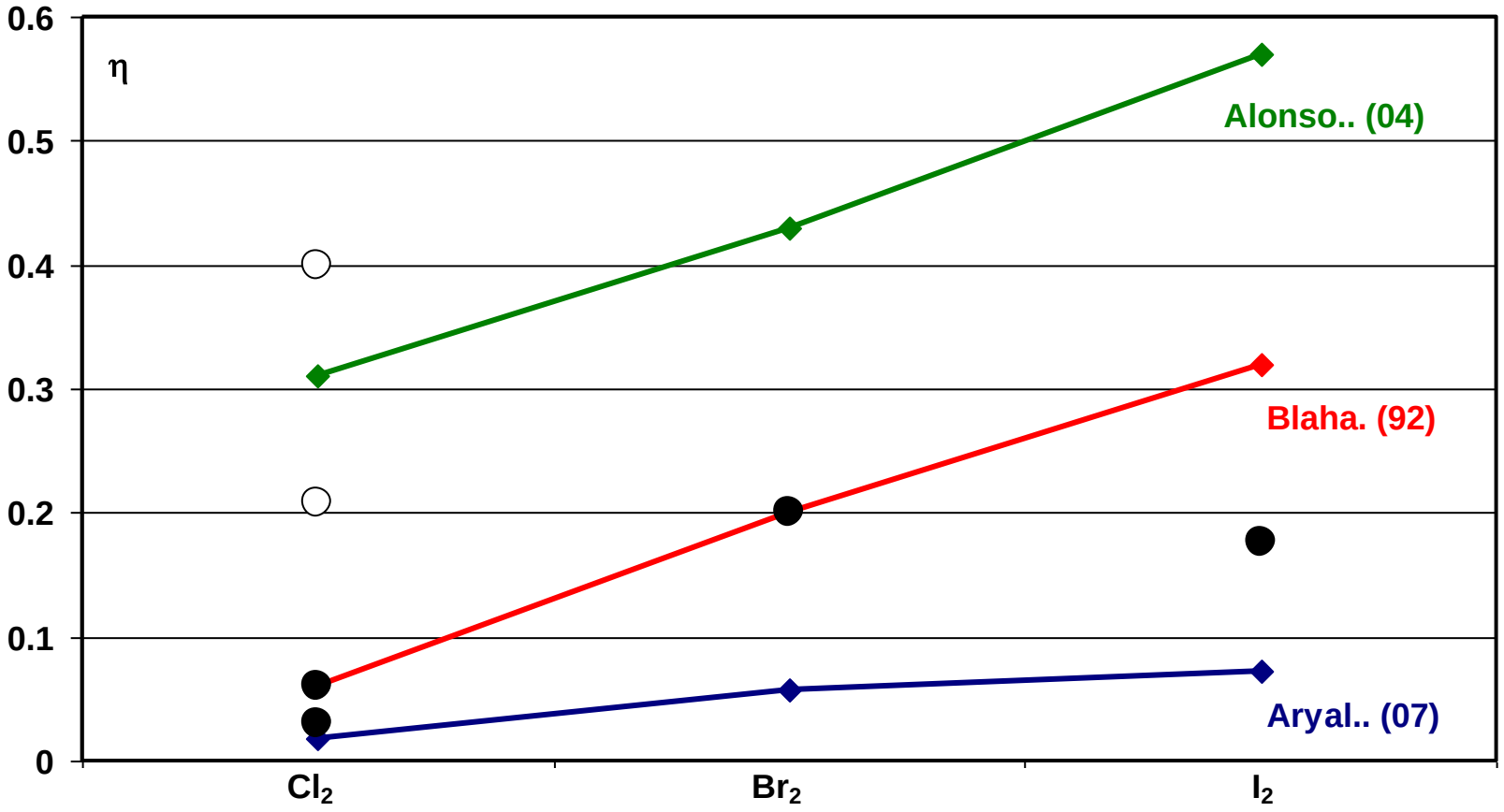
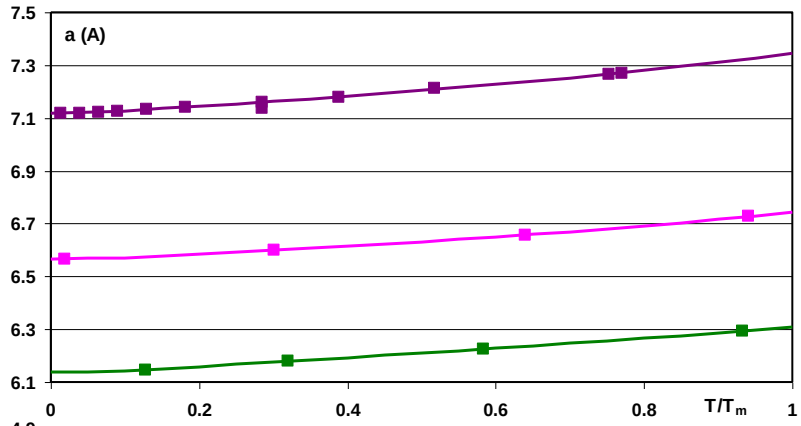
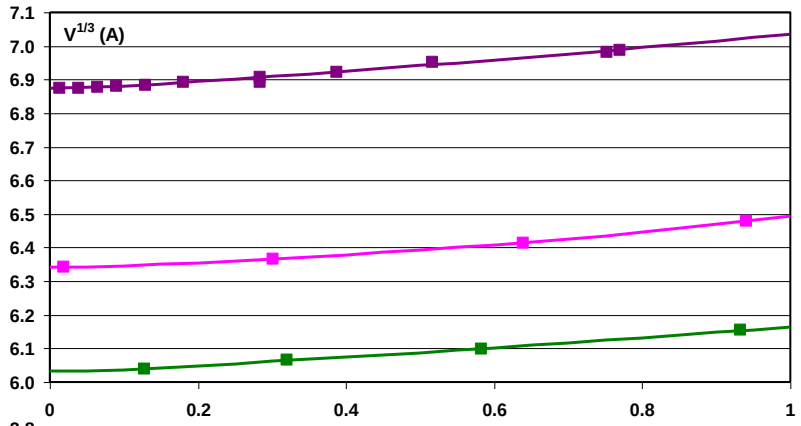
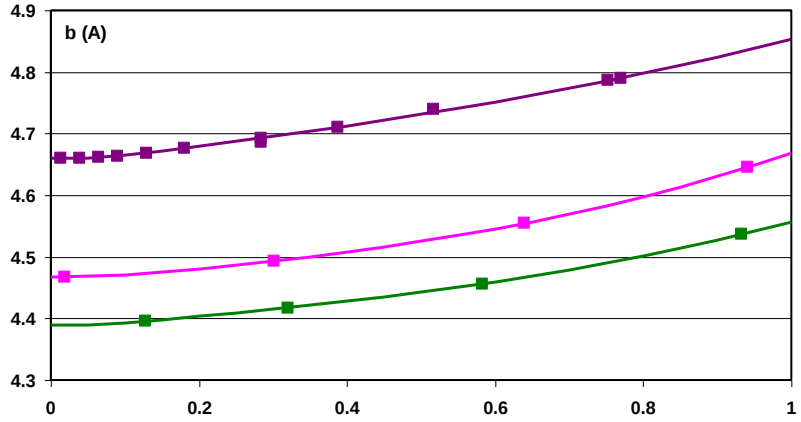


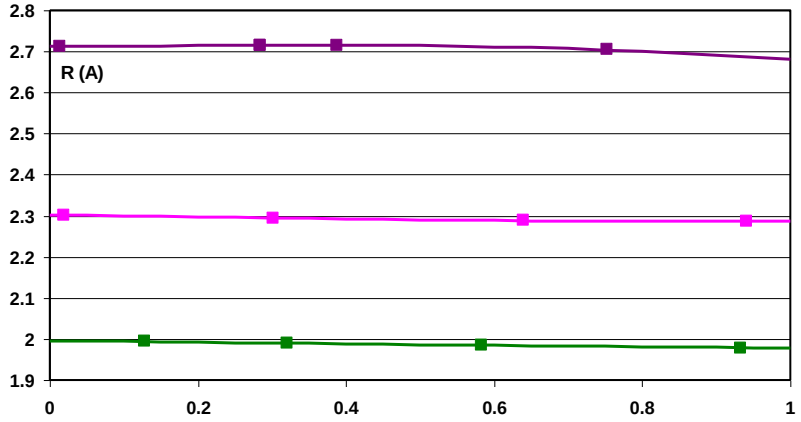
A mess !

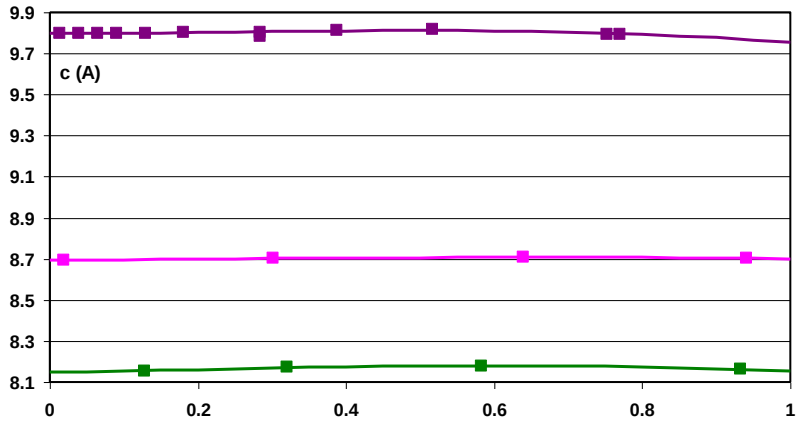
Structural parameters as function of temperature

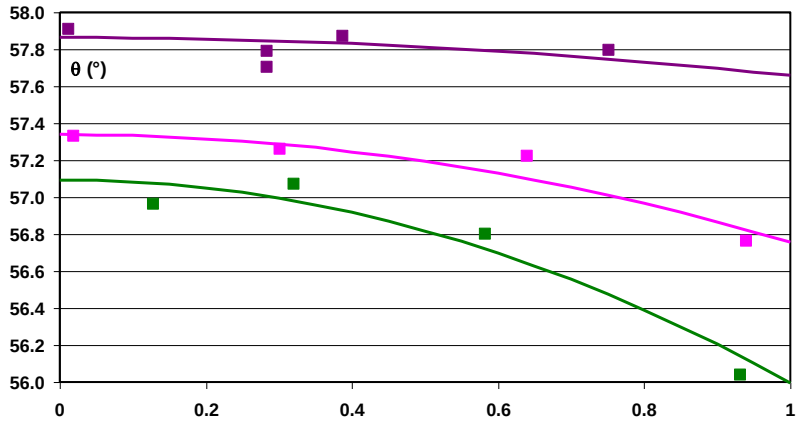












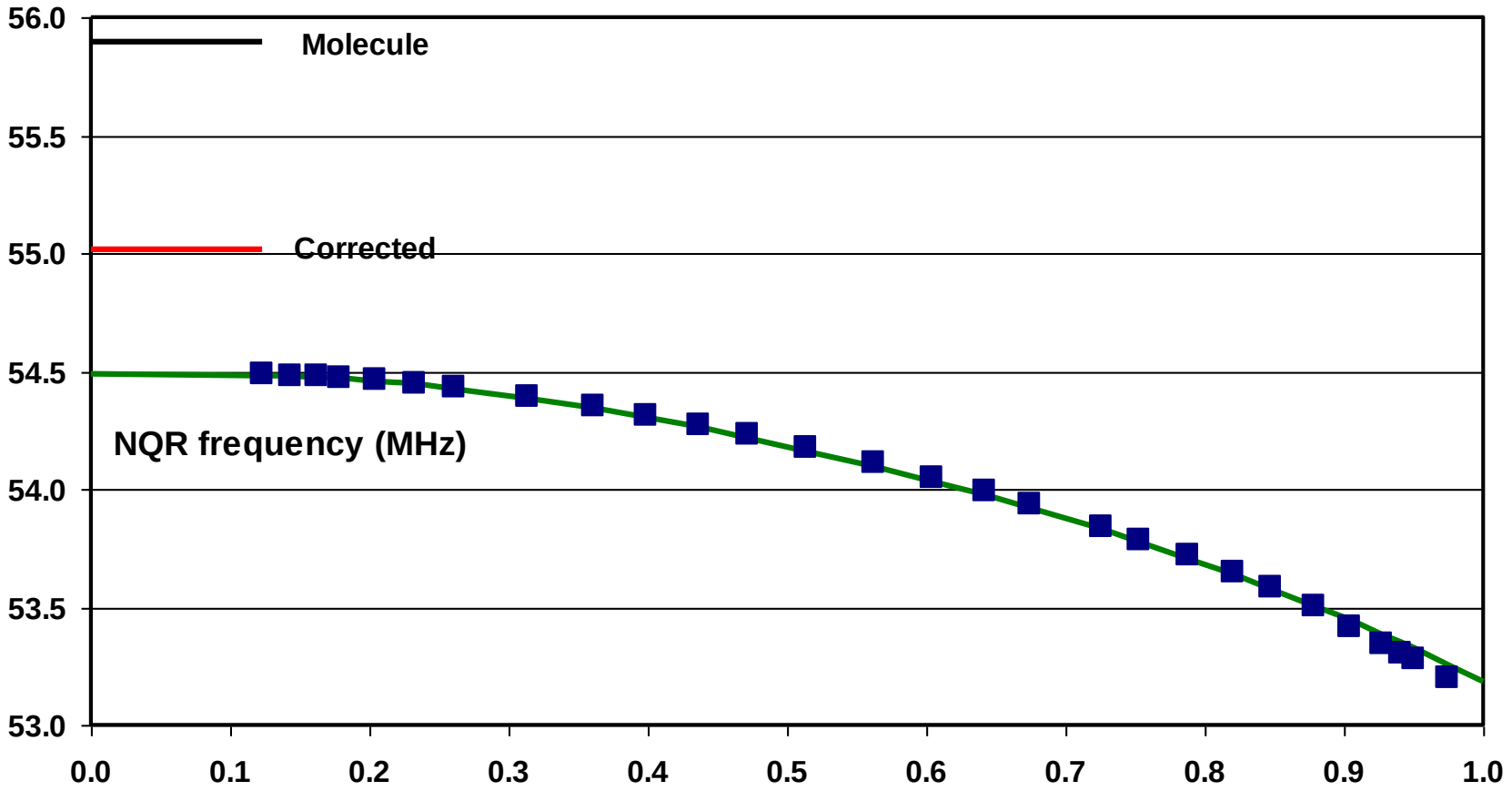
Structural data extrapolated to T = 0

	Cl_2	Br_2	I_2
R_{mol} (A)	1.9881	2.2809	2.6660
R_{sol} (A)	1.9950	2.3006	2.7124
θ (^{o})	57.093	57.339	57.863
a (A)	6.1360	6.5672	7.1191
b (A)	4.3889	4.4678	4.6600
c (A)	8.1492	8.6938	9.7962

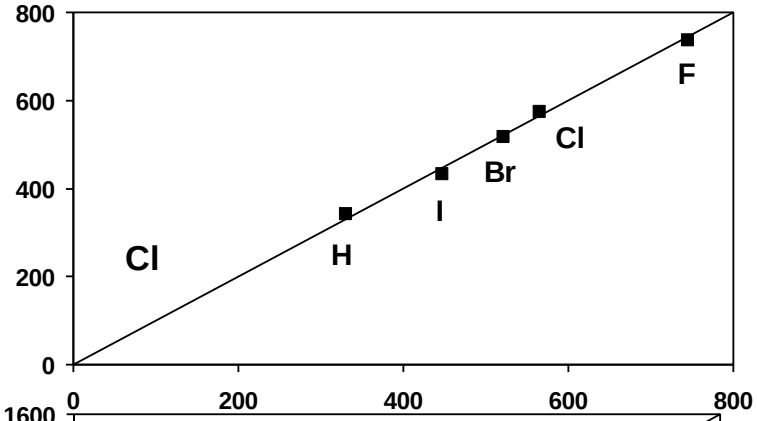
Experimental frequencies (MHz) extrapolated to T = 0

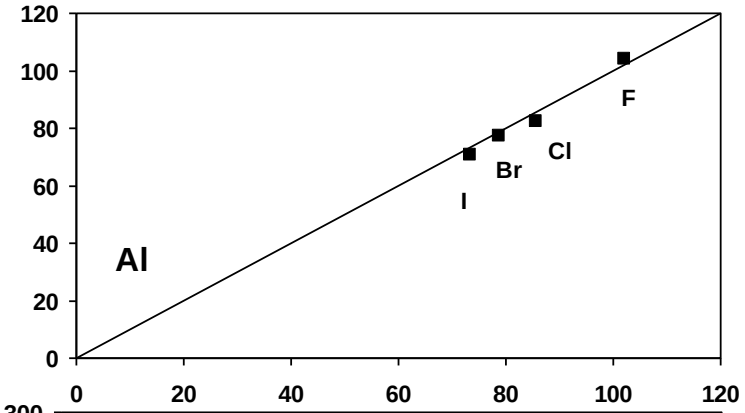
	Cl_2	Br_2	I_2
ν_Q (mol)	**111.79**	**810.0**	**2452.6**
ν_Q (sol)	**108.97**	**763.1**	**2156.2**
ν_Q^0 (sol)	**109.79**	**768.2**	**2160.0**

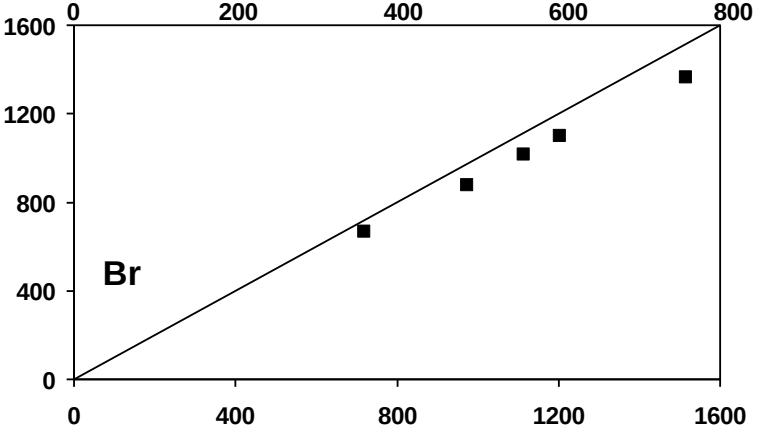
Temperature dependence Cl_2 (Nakamura 67)

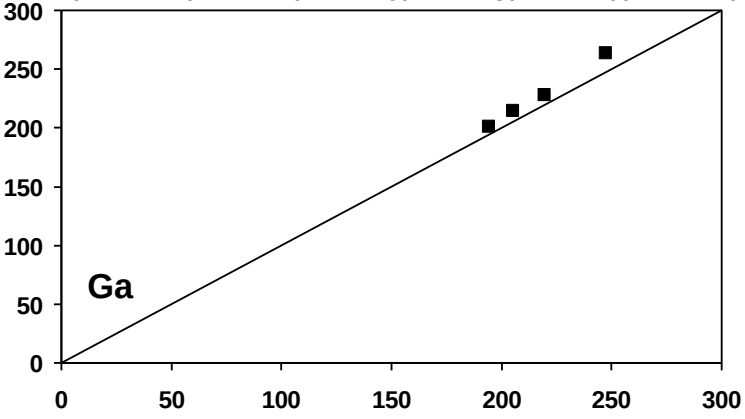


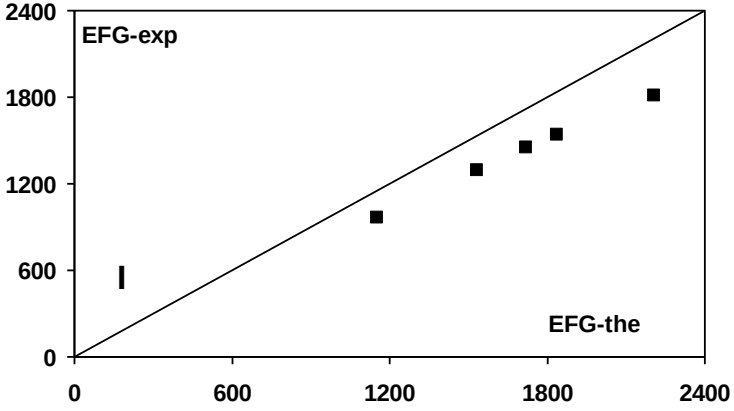
Halogen Q (with H. Petrilli)

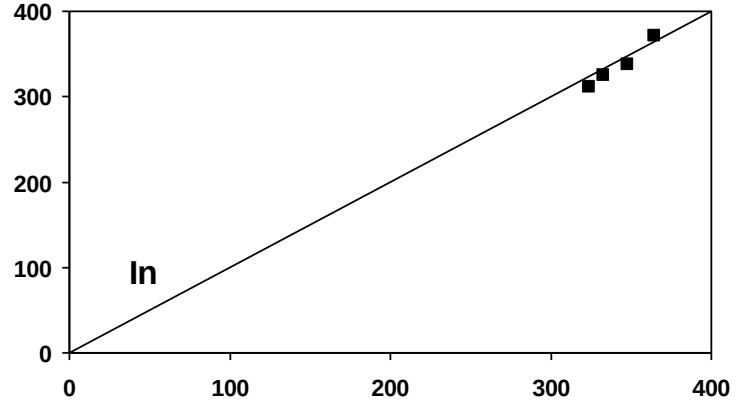












WIEN2k results (10^{21} V/m^2)

	Cl_2	Br_2	I_2
EFG(mol)	57.27	112.99	152.88
EFG(sol)	54.11	97.86	119.75
$\delta\nu/\nu_0$(cal)	0.055	0.134	0.217
$\delta\nu/\nu_0$(exp)	0.018	0.052	0.119

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Conclusion:

Present DFT overestimates the frequency shift due to the intermolecular interaction by a factor 2 to 2.5

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Conclusion:

Present DFT overestimates the frequency shift due to the intermolecular interaction by a factor 2 to 2.5

Assumption:

The calculated intermolecular interaction overestimates η by a similar factor

Final results

	Cl_2	Br_2	I_2
EFG(mol)	57.27	112.99	152.88
EFG(sol)	54.11	97.86	119.75
$\delta\nu/\nu_0$(cal)	0.055	0.134	0.217
$\delta\nu/\nu_0$(exp)	0.018	0.052	0.119
η(cal)	0.071	0.183	0.320
η(cor)	0.023	0.071	0.176

Comparison with experiments

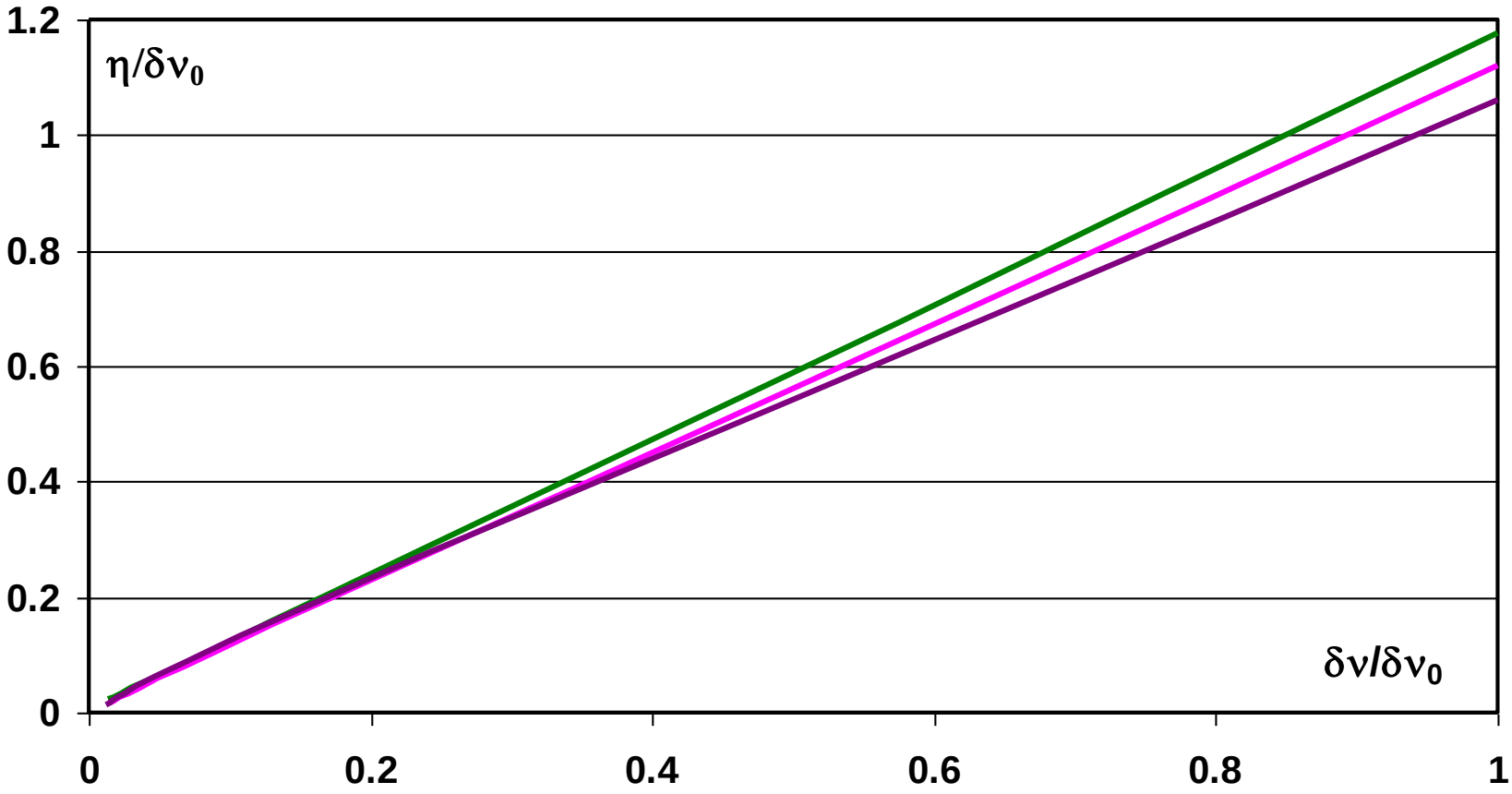
	Cl_2	Br_2	I_2
EFG(mol)	57.27	112.99	152.88
EFG(sol)	54.11	97.86	119.75
$\delta\nu/\nu_0$(cal)	0.055	0.134	0.217
$\delta\nu/\nu_0$(exp)	0.018	0.052	0.119
η(cal)	0.071	0.183	0.320
η(cor)	0.023	0.071	0.176
η(pub)	0.0-0.2	0.200	0.175

Conclusions:

Experiment for Br_2 must be grossly wrong

The low value of η (>.3) for Cl_2 is favored

Expanded lattice calculations



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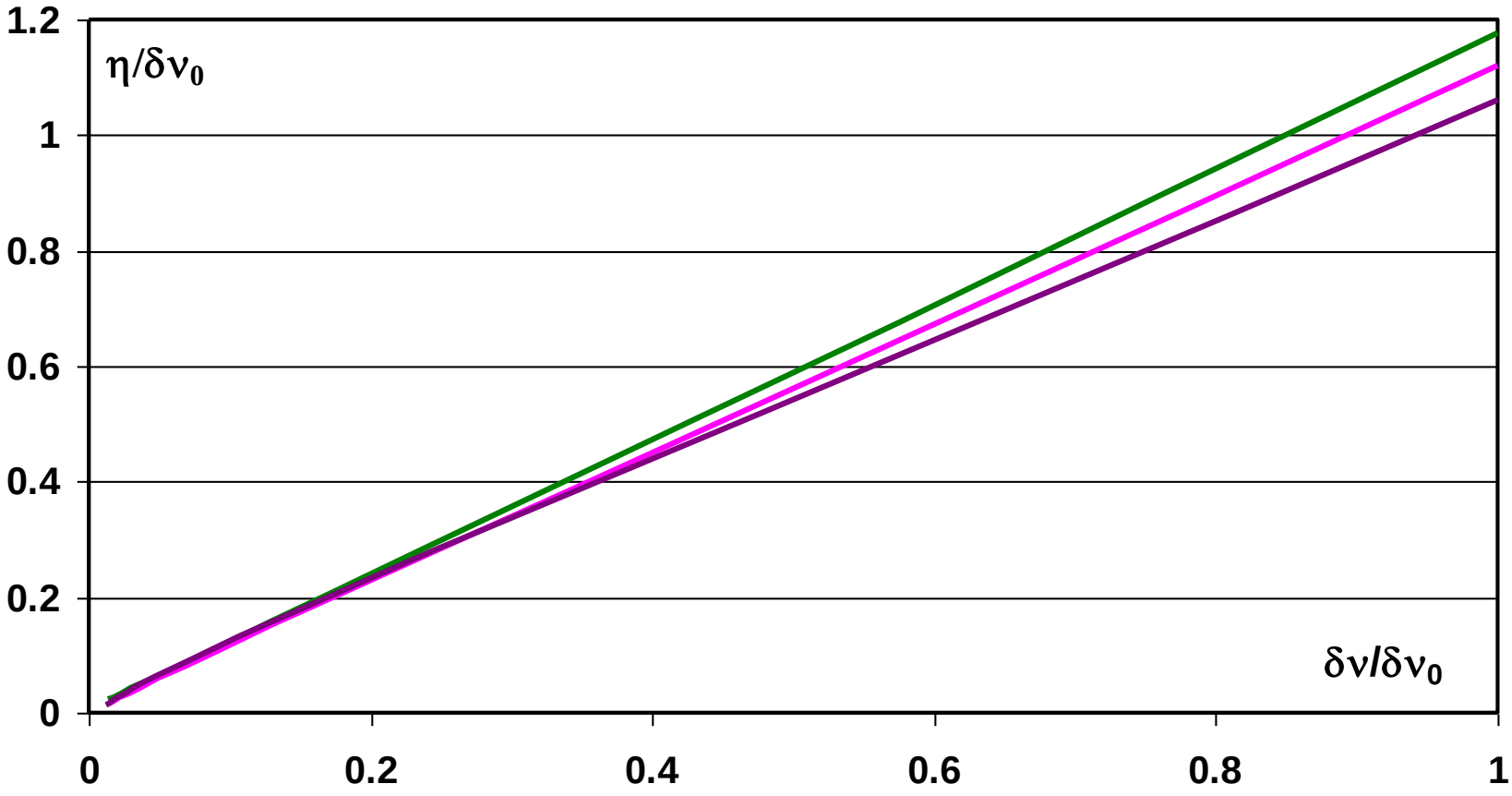
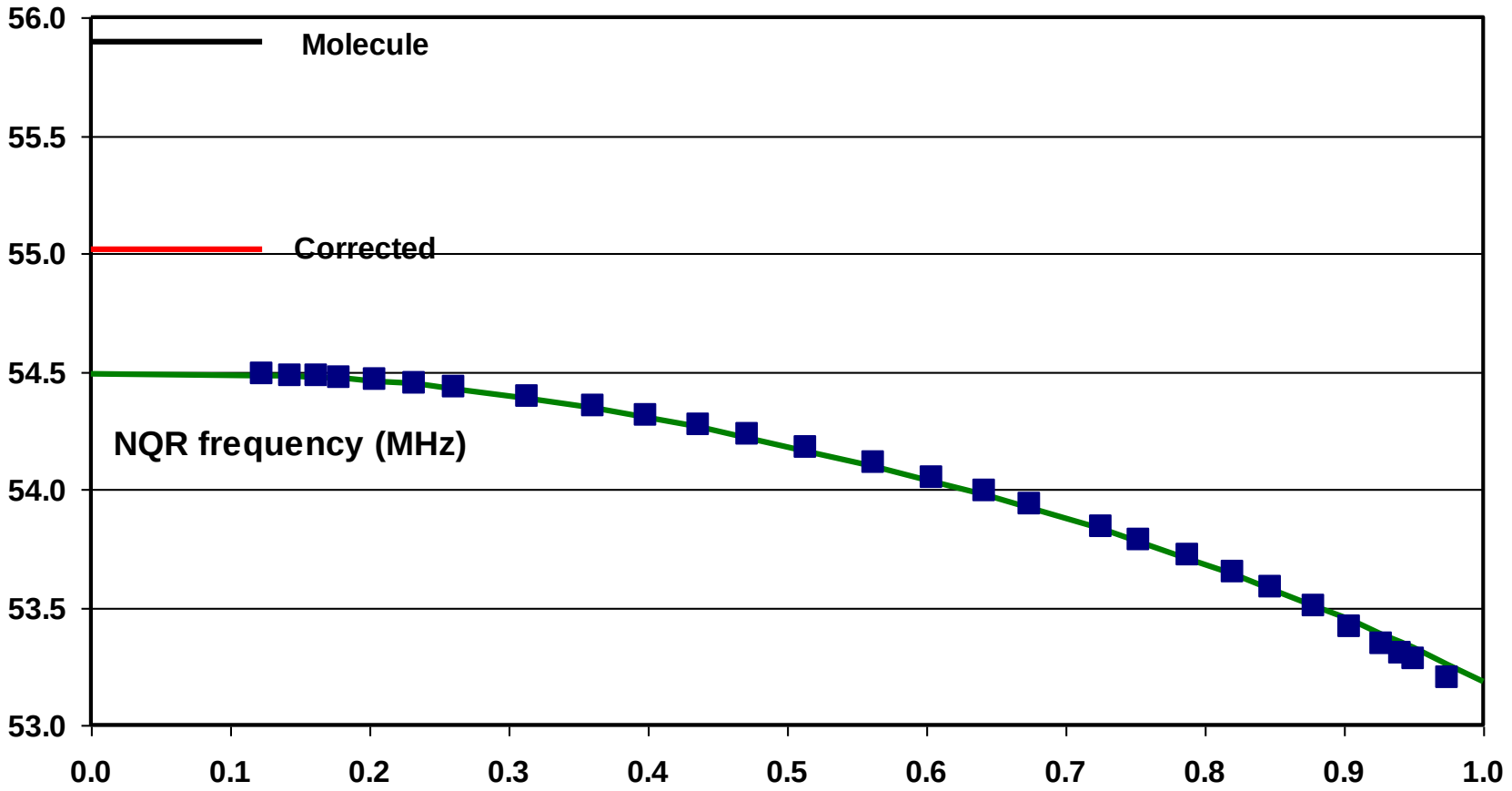


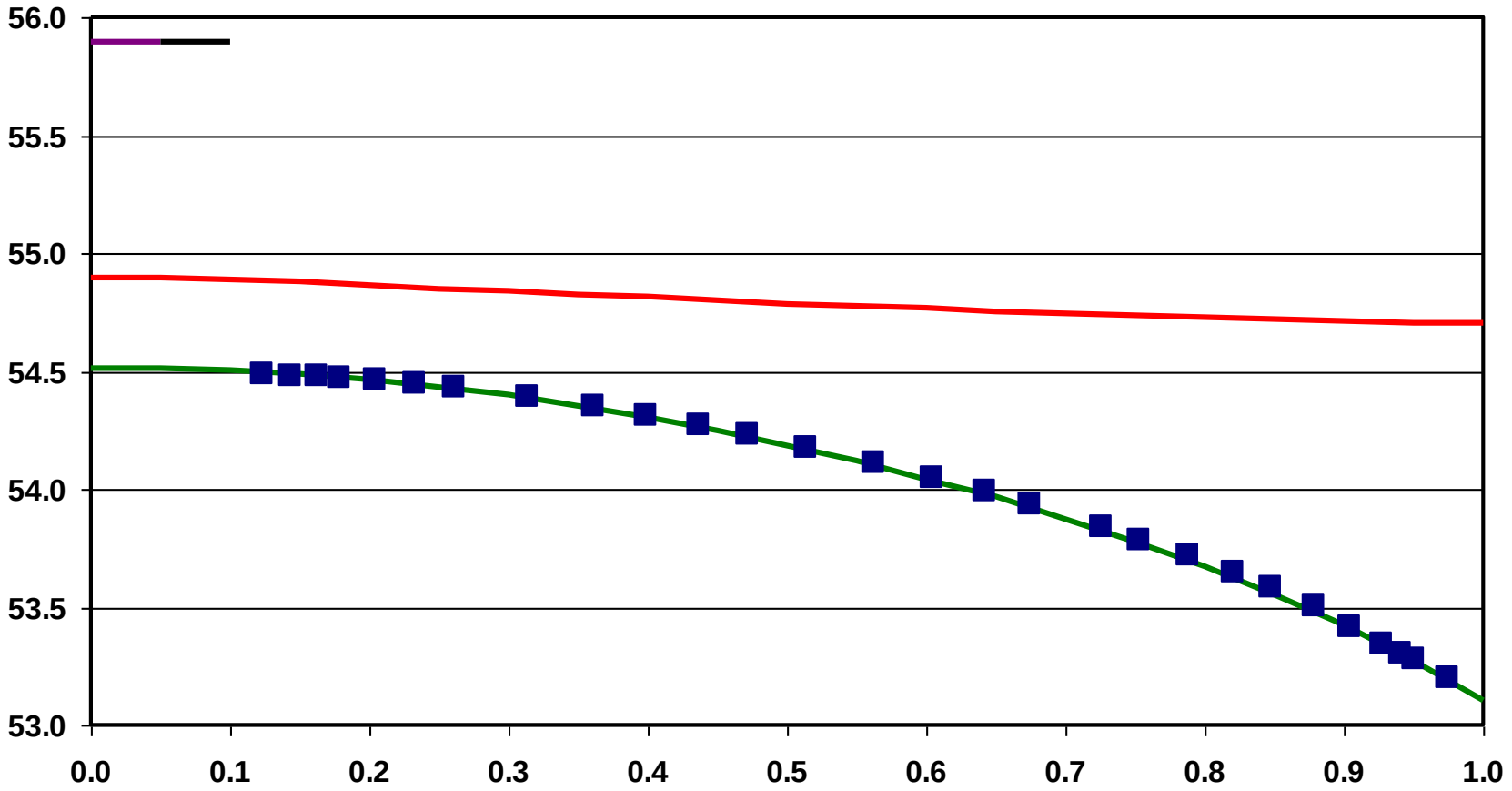
Conclusion:

With proper choice of the degree of expansion, fixed to the result at T=0, one can compute the EFG also for high T

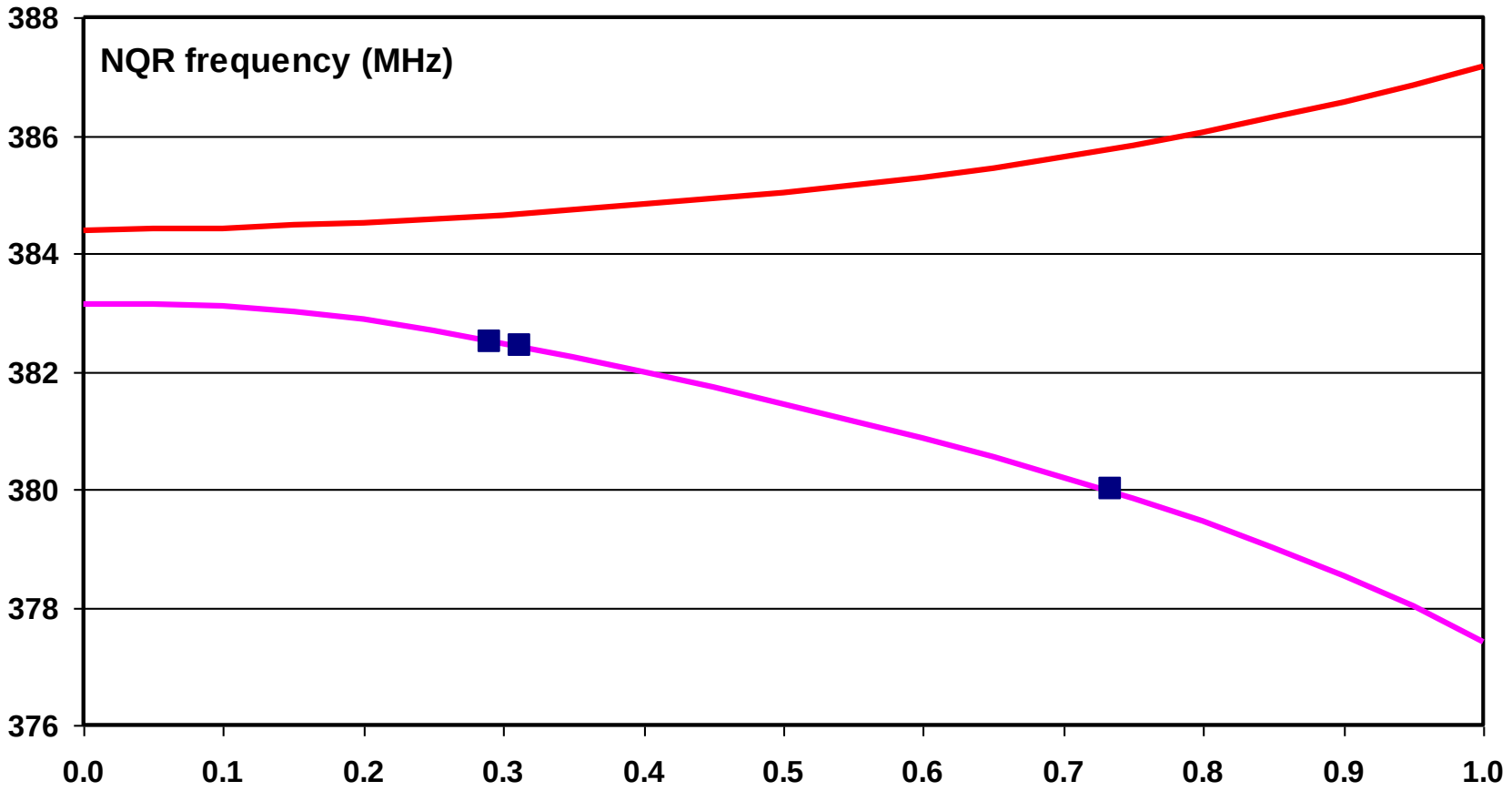
Temperature dependence Cl_2 (Nakamura 67)



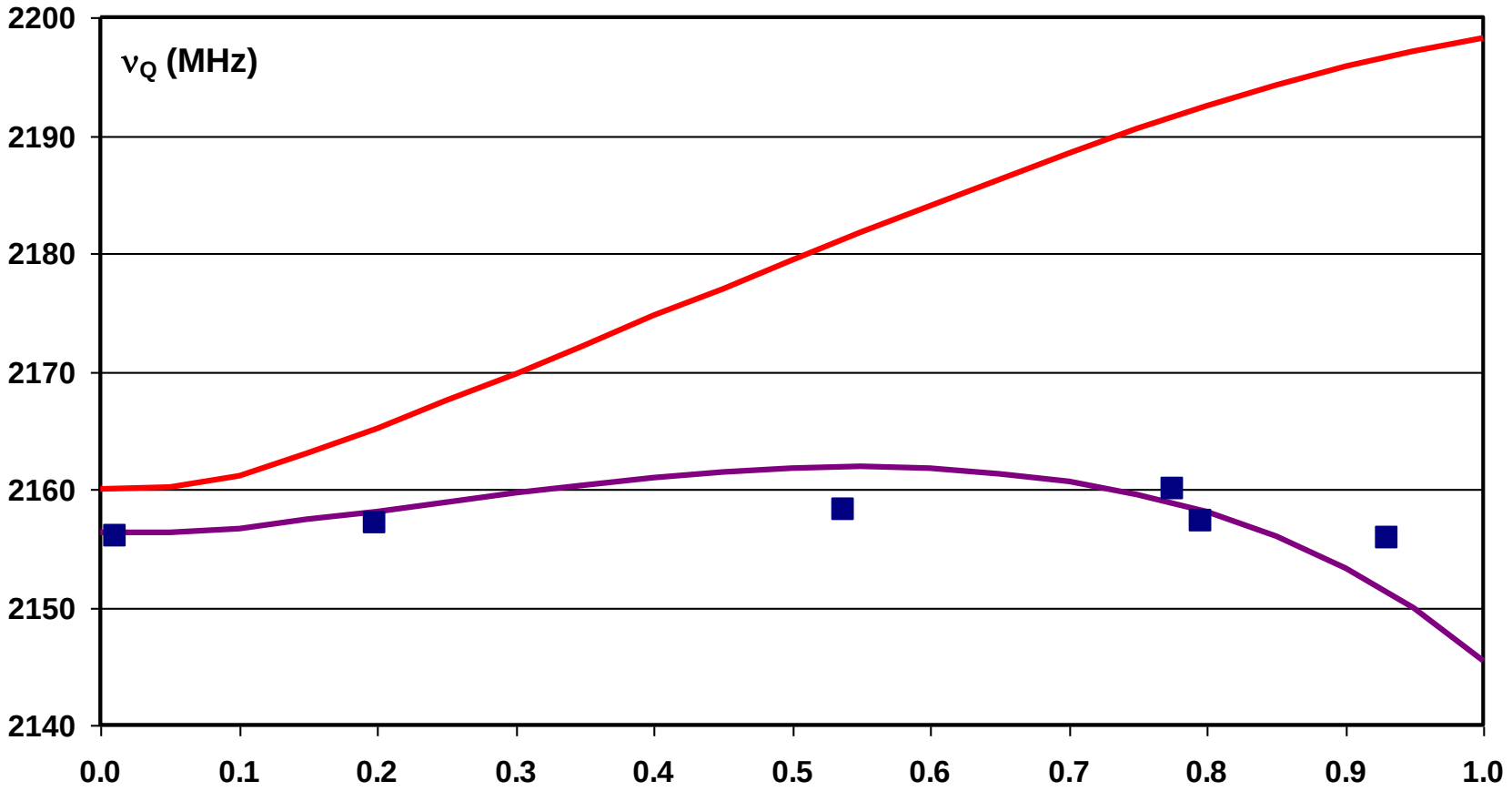
Temperature dependence Cl_2 (new)



Temperature dependence Br_2



Temperature dependence I_2



General conclusions

- **We need a proper theory for treatment of the intermolecular interaction !**
- **For better calculations one would require more accurate crystal structure data**
- **A remeasurement of η for solid Br_2 is highly recommended**
- **Interesting effects are predicted for the temperature dependence of the NQR frequency for Br_2 and I_2**