

Rovibrational States of HBF⁺ and HCO⁺ Isotopologues up to high J Theory and Experiment

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Previous published experimental work

Magnetic-field-modulated diode laser IR spectroscopy

K. Kawaguchi, E. Hirota, Chem. Phys. Lett. **82** (1985) 1750.

Microwave spectroscopy

G. Cazzoli, C. Degli Esposti, L. Dore, P. G. Favero, J. Mol. Spectrosc. **119** (1986) 467; **121** (1987) 278.

S. Saito, S. Yamamoto, K. Kawaguchi, J. Chem. Phys. **86** (1987) 2597.

Early theoretical spectroscopic work

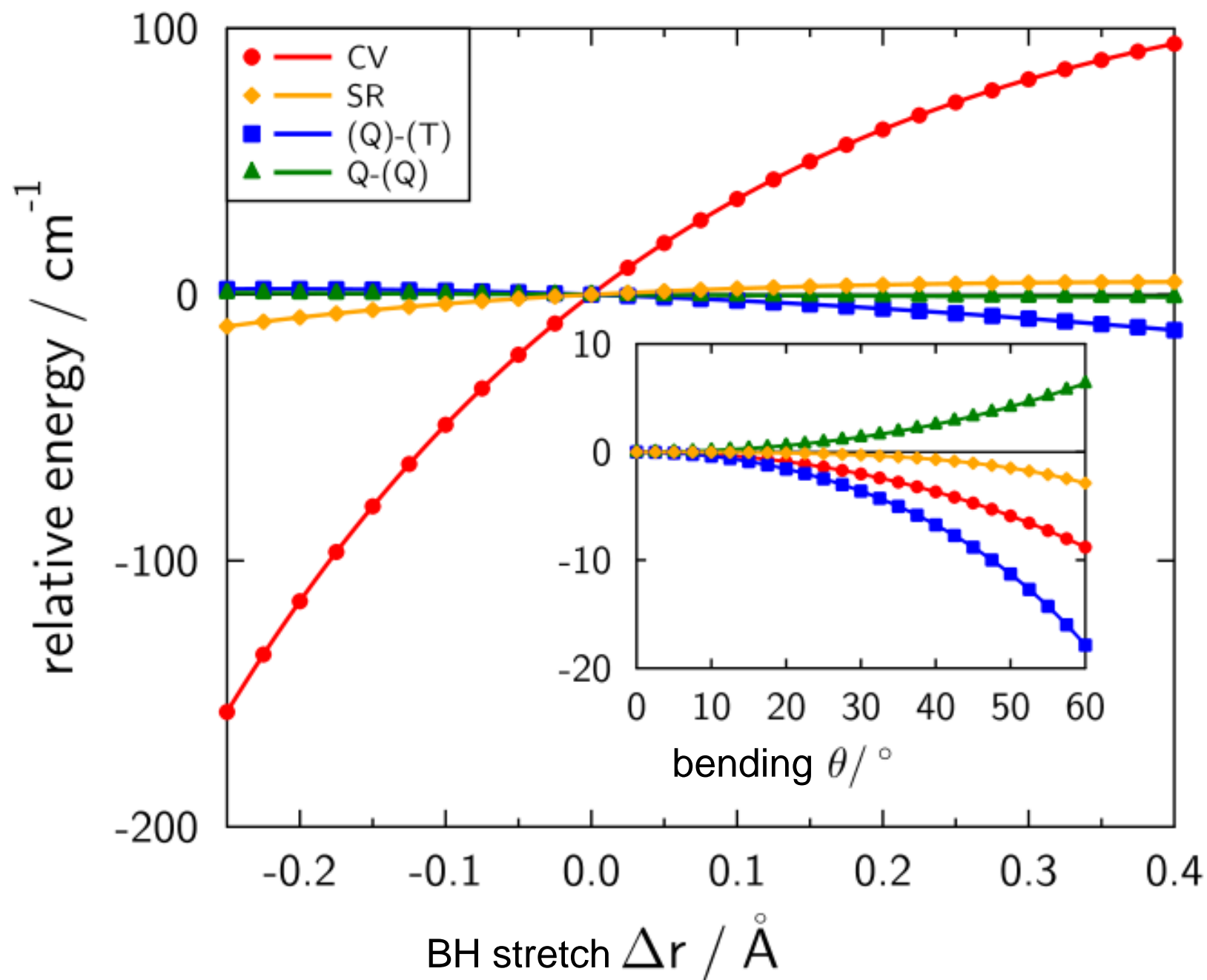
P. Botschwina, J. Mol. Spectrosc. **118** (1986) 76.

Composite potential energy functions (PEFs) for HBF⁺ and HCO⁺

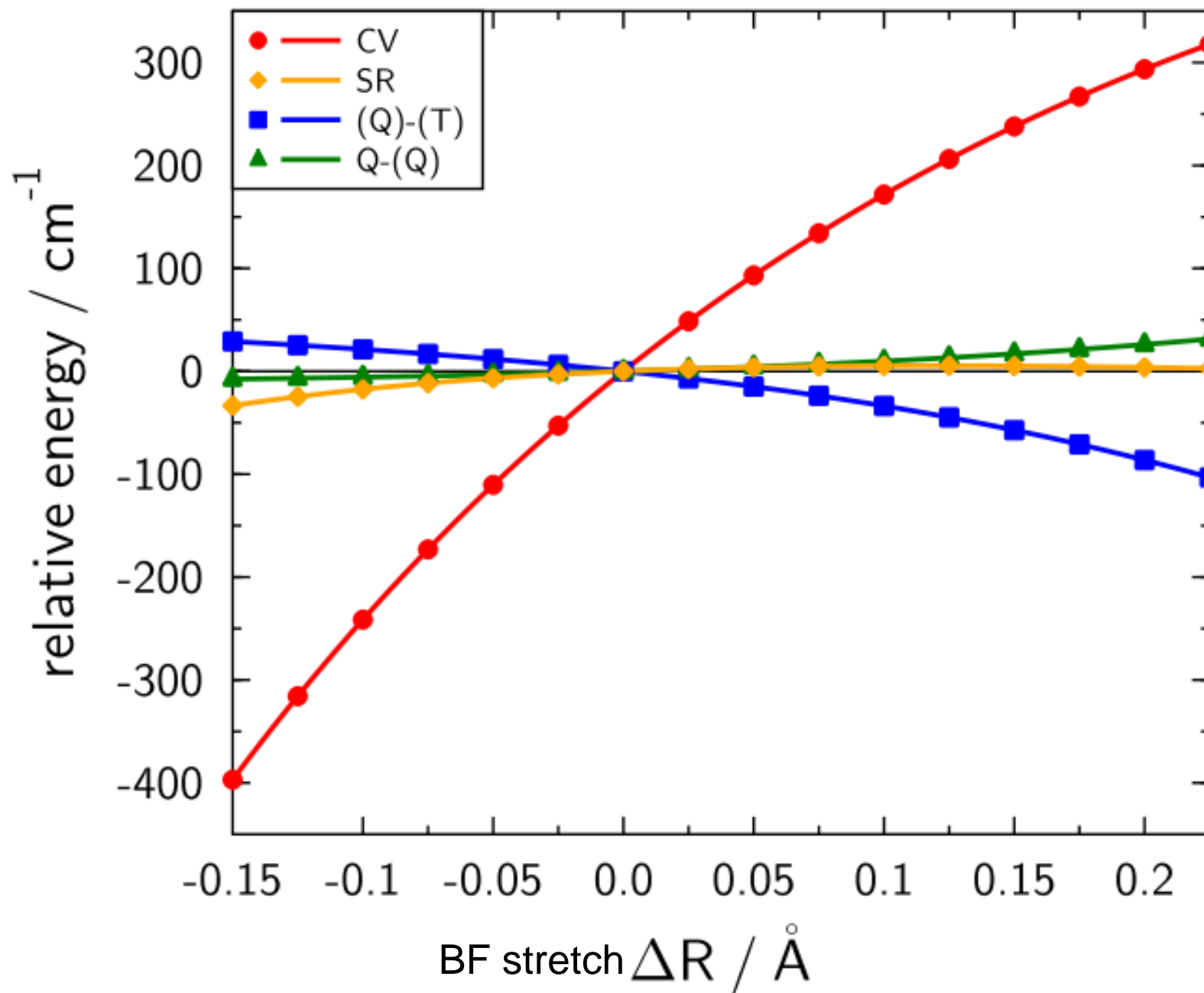
- Basic contribution by explicitly correlated coupled cluster theory
fc-CCSD(T)-F12b with scaling of triple substitutions (T*)
AO basis: cc-pVQZ-F12 } **F12bs**
- Core-core and core-valence correlation (**CV**): CCSD(T)/cc-pCV6Z
- Scalar relativity (**SR**): 2nd order Douglas-Kroll-Hess fc-CCSD(T)/cc-pVQZ(-DK)
- Higher-order correlation (HC) up to CCSDTQ:
 - (Q)-(T)** CCSDT(Q) – CCSD(T) / cc-pVTZ
 - Q-(Q)** CCSDTQ – CCSDT(Q) / cc-pVDZ
- Diagonal Born-Oppenheimer-Correction (**DBOC**): CCSD / cc-pCVQZ

Program systems employed: MOLPRO 2012.1 (including Kallay's MRCC)
 CFOUR V1.0

Significance of smaller PEF contributions



Dependence of smaller PEF contributions on ΔR



Results of fc-CCSD(T) calculations with different basis sets for HBF⁺ ^a

Method	Basis	r_e (BH)	R_e (BF)	B_e	ω_1	ω_2	ω_3
fc-CCSD(T)	VTZ	1.17448	1.21740	1.20240	2864.3	740.6	1635.7
	VQZ	1.17466	1.21306	1.20959	2858.3	734.9	1639.8
	V5Z	1.17455	1.21237	1.21078	2858.0	736.6	1639.1
	V6Z	1.17455	1.21216	1.21115	2857.3	737.3	1639.3
	V7Z	1.17456	1.21208	1.21127	2857.2	736.7	1639.3
fc-CCSD(T)-F12b	VQZ-F12	1.17458	1.21202	1.21136	2857.8	737.1	1639.6
fc-CCSD(T*)-F12b	VQZ-F12	1.17460	1.21215	1.21114	2857.4	736.8	1638.9

^a Equilibrium bond lengths in Å, B_e and ω_1 - ω_3 in cm⁻¹

Triples-scaled and unscaled CCSD(T)-F12b with VQZ-F12 basis comparable with standard CCSD(T) at V7Z.

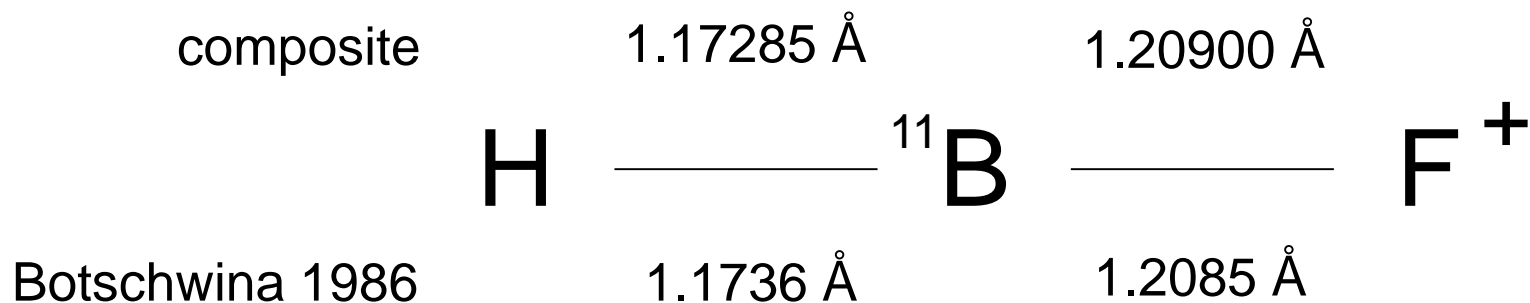
Range of calculated potential energy surface (PES) points

$$-0.25 \text{ \AA} \leq \Delta r \leq 0.4 \text{ \AA}, -0.15 \text{ \AA} \leq \Delta R \leq 0.225 \text{ \AA} \text{ and } 0^\circ \leq \theta \leq 60^\circ$$

Analytical form of PEF: $V - V_e = \sum_{ijk} C_{ijk} \Delta r^i \Delta R^j \theta^k \quad (k = \text{even})$

Diagonal stretching terms up to 8th power, diagonal angular terms up to 10th power, off-diagonal terms up to sextic. 38 non-redundant parameters in total

Equilibrium structure



Harmonic vibrational wavenumbers (in cm⁻¹) : **2862.2**, **738.3**, **1643.8**

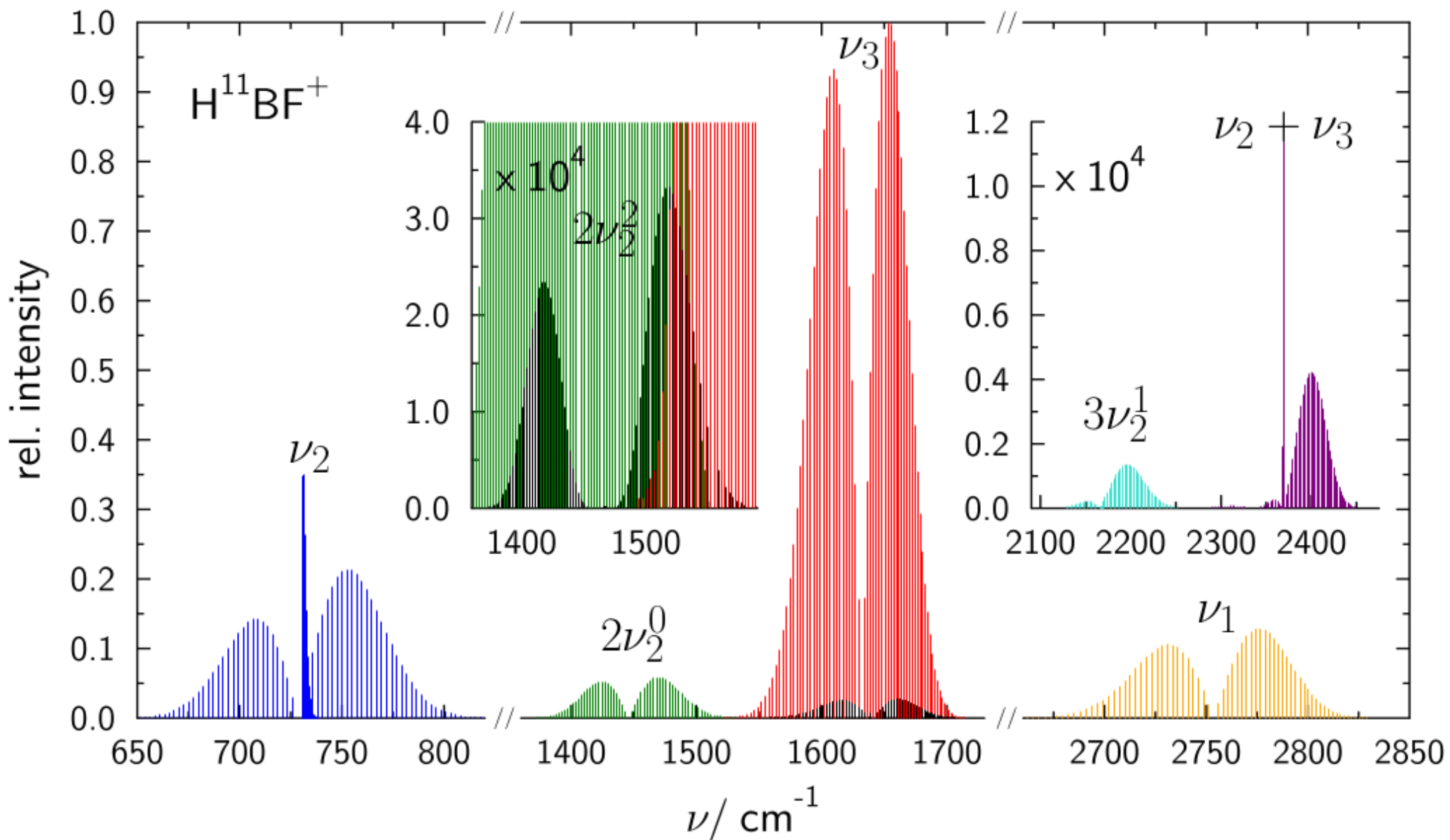
Rovibrational energies and wavefunctions from variational calculations with Watson's isomorphous Hamiltonian for linear molecules using Sebald's program

Some effective spectroscopic parameters (in cm^{-1}) for H^{11}BF^+ and D^{11}BF^+ ^a

Isotopologue	State	G_v	B_v	$10^6 D_v$	$10^{12} H_v$
H^{11}BF^+	(0,0 ⁰ ,0)		1.21118 (1.21165)	2.649 (2.649)	2.199
	(0,1 ¹ ,0)e	730.74	1.21141	2.674	2.294
	(0,1 ¹ ,0)f	730.74	1.21676	2.727	2.979
	(0,0 ⁰ ,1)	1631.91 (1633.22)	1.20256 (1.20301)	2.598 (2.574)	7.032
	(1,0 ⁰ ,0)	2753.50	1.20257	2.617	2.304
D^{11}BF^+	(0,0 ⁰ ,0)		0.97152 (0.97186)	1.653 (1.645)	1.776
	(0,1 ¹ ,0)e	587.66	0.97245	1.681	1.902
	(0,1 ¹ ,0)f	587.66	0.97670	1.717	2.478
	(0,0 ⁰ ,1)	1504.49	0.96599	1.645	1.931
	(1,0 ⁰ ,0)	2168.94	0.96299	1.619	2.457

^a Experimental values in parentheses

Calculated IR spectra of different bands of H^{11}BF^+ at 296 K

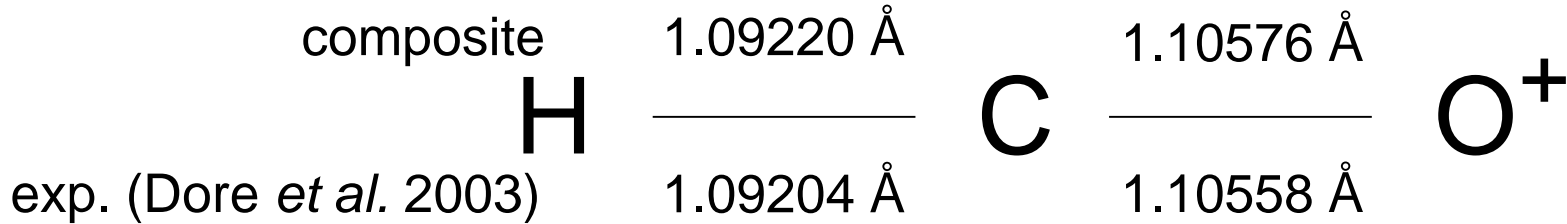


Experimental results (in cm^{-1}) for ν_1 bands of H^{11}BF^+ and H^{10}BF^+

Isotopologue	Line	Obs.	c.-o.	Spectroscopic Parameters		
					Experimental	Theoretical
H^{11}BF^+	R(4)	2766.0259	0.0007			
	R(3)	2763.6909	-0.0006	B'	1.203012(24)	1.20257
	R(2)	2761.3370	-0.0005	$D' \times 10^6$	2.665 [fixed]	2.304
	R(1)	2758.9655	-0.0003	B''	1.211649038(17)	1.21118
	R(0)	2756.5764	0.0001	$D'' \times 10^6$	2.665(5)	2.649
	P(1)	2751.7466	0.0006	ν_0	2754.1704(4)	2753.50
H^{10}BF^+	P(14)	2737.6666	0.0000			
	P(13)	2740.4246	0.0003	B'	1.248092(19)	1.24760
	P(12)	2743.1654	-0.0005	$D' \times 10^6$	2.882(86)	2.804
	P(11)	2745.8866	0.0000	B''	1.25766756(33)	1.25718
	P(9)	2751.2739	0.0006	$D'' \times 10^6$	2.853(9)	2.840
	P(8)	2753.9408	-0.0002	ν_0	2774.5938(9)	2773.90
	P(7)	2756.5882	-0.0001			

Some results for HCO⁺

Equilibrium structure



State	G_v (cm ⁻¹)	B_v (MHz)	D_v (kHz)	H_v (Hz)
(0,0 ⁰ ,0)		44581.7 (0.03%)	82.82 (0.002%)	0.07
(0,1 ¹ ,0)	829.2	44665.1 (0.03%)	84.46 (0.02%)	0.08
(0,0 ⁰ ,1)	2183.0	44287.9 (0.03%)	82.89 (0.06%)	0.07
(1,0 ⁰ ,0)	3088.3	44228.7 (0.03%)	82.06 (0.008%)	0.07
(1,1 ¹ ,1)	6050.8	44027.6 (0.03%)	85.74 (1.8%)	0.32
(2,0 ⁰ ,0)	6077.7	43910.4 (0.03%)	79.29 (0.2%)	-0.13
(1,0 ⁰ ,2)	7383.9	43676.8 (0.03%)	83.70 (1.3%)	0.07

$J_{\text{max}} = 40$, relative deviations with respect to experiment in parentheses

Conclusions

- Rovibrational states and line intensities of transitions among them calculated from composite PEF and CCSD(T)-F12b electric dipole moment function
- A total of 13 lines assigned in the ν_1 bands of H^{11}BF^+ and H^{10}BF^+ with the aid of the theoretical results
- tentative assignment of some hot band lines arising from the lowest excited vibrational state
- ongoing work devoted to a variety of rovibrational transitions of HCO^+ isotopologues, including line intensities and life times of rovibrational excited states

Publication on HBF^+ Isotopologues

P. Botschwina, P. Sebald, B. Schröder, A. Bargholz, K. Kawaguchi, T. Amano, Rovibrational States of HBF^+ Isotopologues up to High J : Theory and Experiment, J. Mol. Spectrosc., DOI: 10.1015/j.jms.014.05.008