Gas-Phase Spectroscopy of Metai Ion–Crown Ether Complexes

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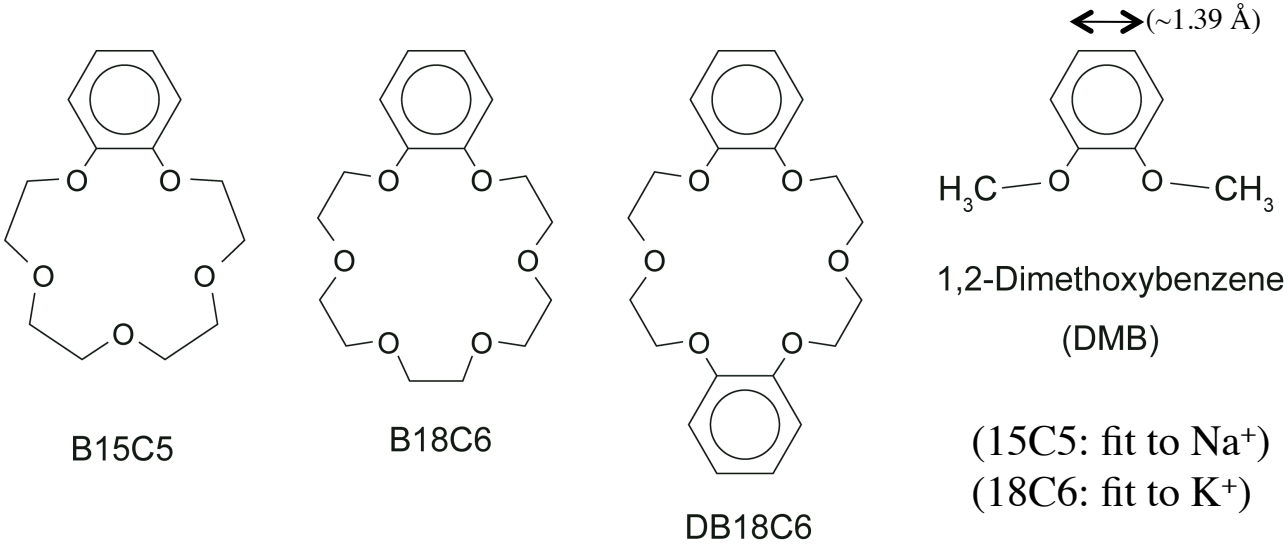
Crown Ether

- Benzo-18-crown-6 was first discovered by Pedersen in 1967.
- Used for many applications.

- Mass spectrometric studies of metal ion-CE complexes
  - Dearden (1991), Brodbelt (1992), Armentrout (1996), Brutschy (1997),
- IR spectroscopy of metal ion-CE complexes
  - Lisy (2009), Martinez-Haya (2009)
- UV spectroscopy of metal ion-CE complexes
  - Kim (2009)
- UV and IR spectroscopy of jet-cooled CE
  - Ebata (2007), Zwier (2009)

Gas-Phase Spectroscopy of Metai Ion–Crown Ether Complexes

- Crown Ethers and DMB



- Metal Ions (ionic radii in Å)*
  - Li^+ (0.59), Na^+ (0.99), K^+ (1.37), Rb^+ (1.52), Cs^+ (1.67)
  - Mg^{2+} (0.57), Ca^{2+} (1.06), Sr^{2+} (1.18), Ba^{2+} (1.35)
  - Ni^{2+}, Mn^{2+}, Cu^+

*R. D. Shannon, Acta Cryst. **A32**, 751 (1976).

- 1:1 and 1:2 complexes at ~4 K → 70 complexes

Outline

- Experimental

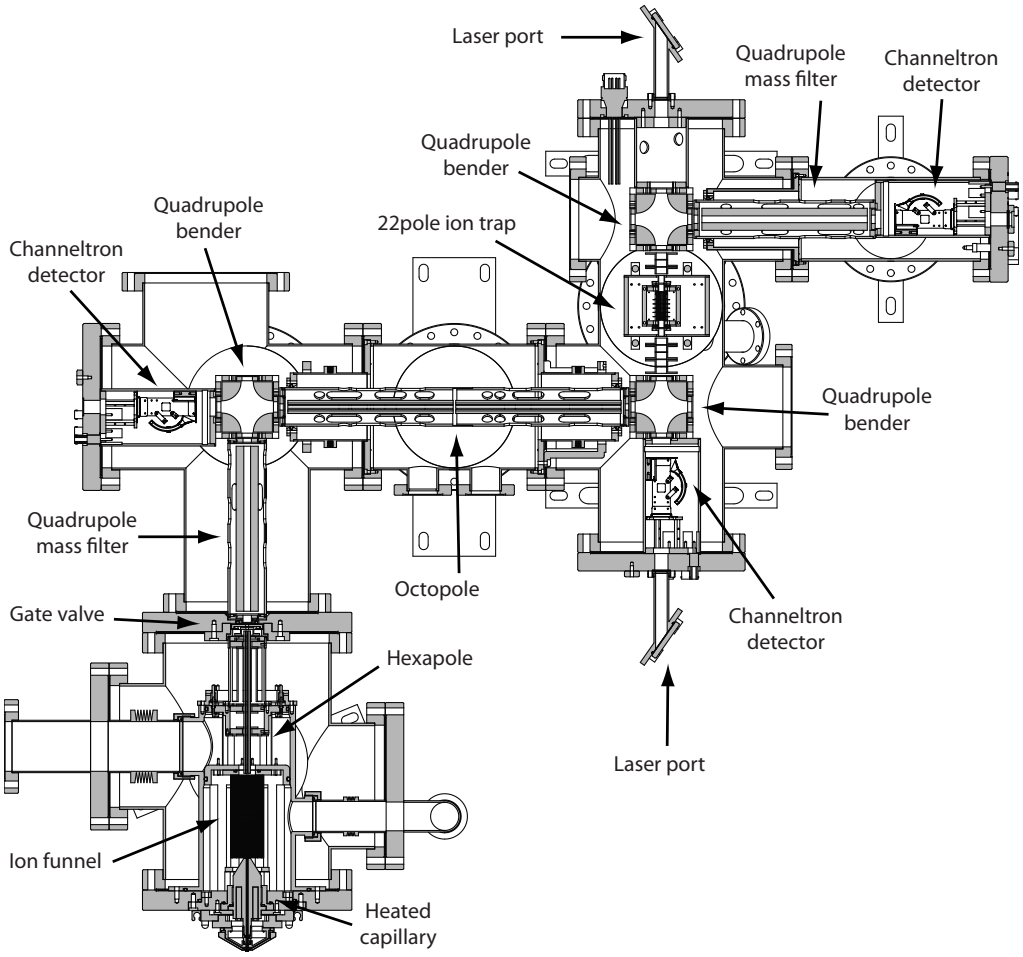
- M^+–DMB (M = Li, Na, K, Rb, and Cs)

- M^+–Crown Ether (M = Li, Na, K, Rb, and Cs)
- M^+–(Crown Ether)$_2$ (M = Li, Na, K, Rb, and Cs)

- M^{2+}–Crown Ether (M = Mg, Ca, Sr, and Ba)
- M^{2+}–(Crown Ether)$_2$ (M = Mg, Ca, Sr, and Ba)

- Transition Metal Ion–Crown Ether complexes

Experimental



Svendsen, Lorenz, Boyarkin, and Rizzo, Rev. Sci. Instrum., **81**, 073107 (2010).

B15C5, B18C6, DB18C6
1,2-Dimethoxybenzene

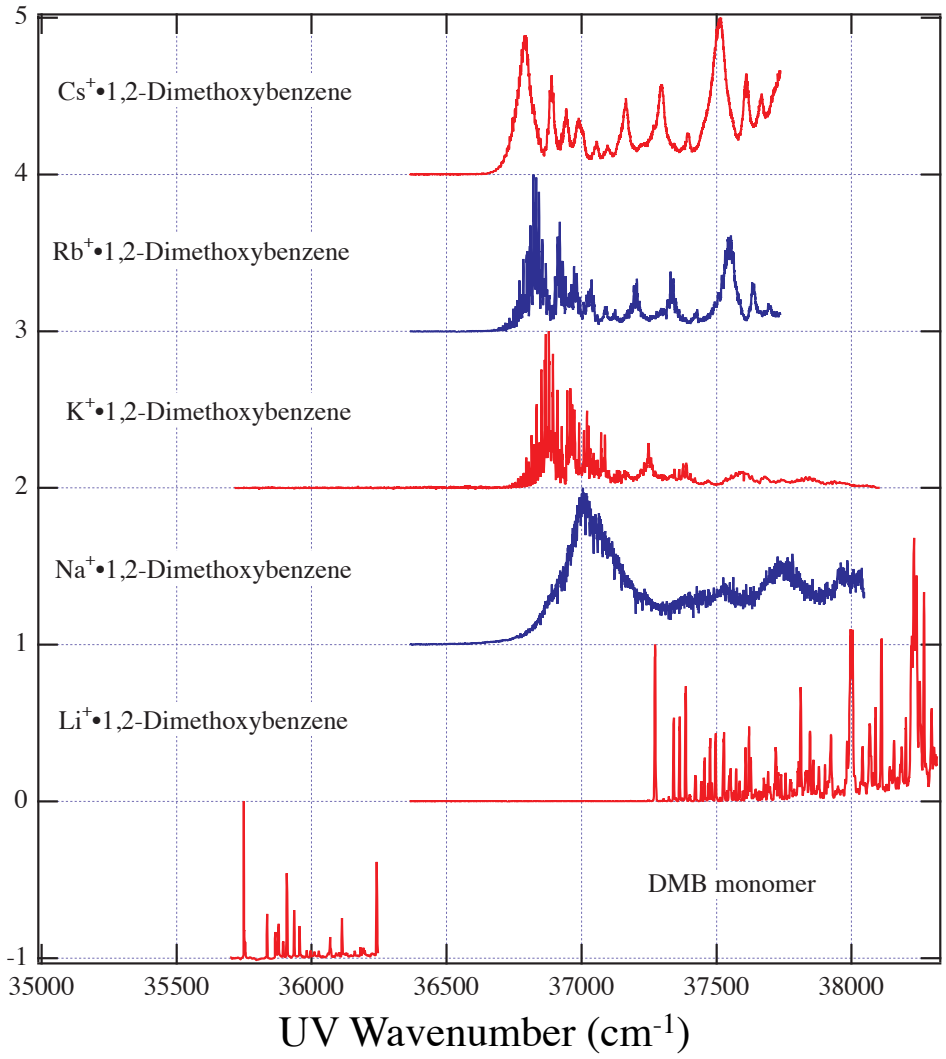
LiCl, NaCl, KCl, RbCl, CsCl
$MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$

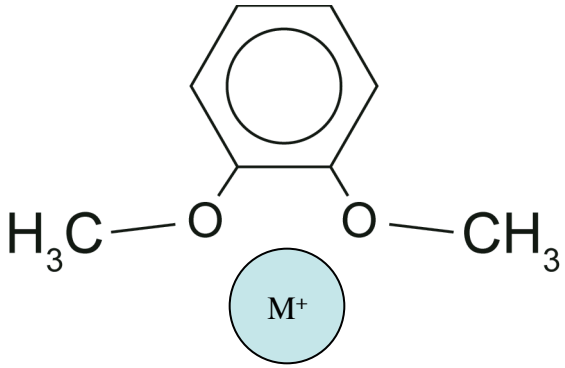
$NiCl_2 \bullet 6H_2O$
$MnCl_2$
$CuSO_4$ (dissolved in H_2O)

in Methanol
20–200 μM

UV power 1–1.5 mJ/pulse
IR power 4–5 mJ/pulse

UV Spectra of M^+•DMB





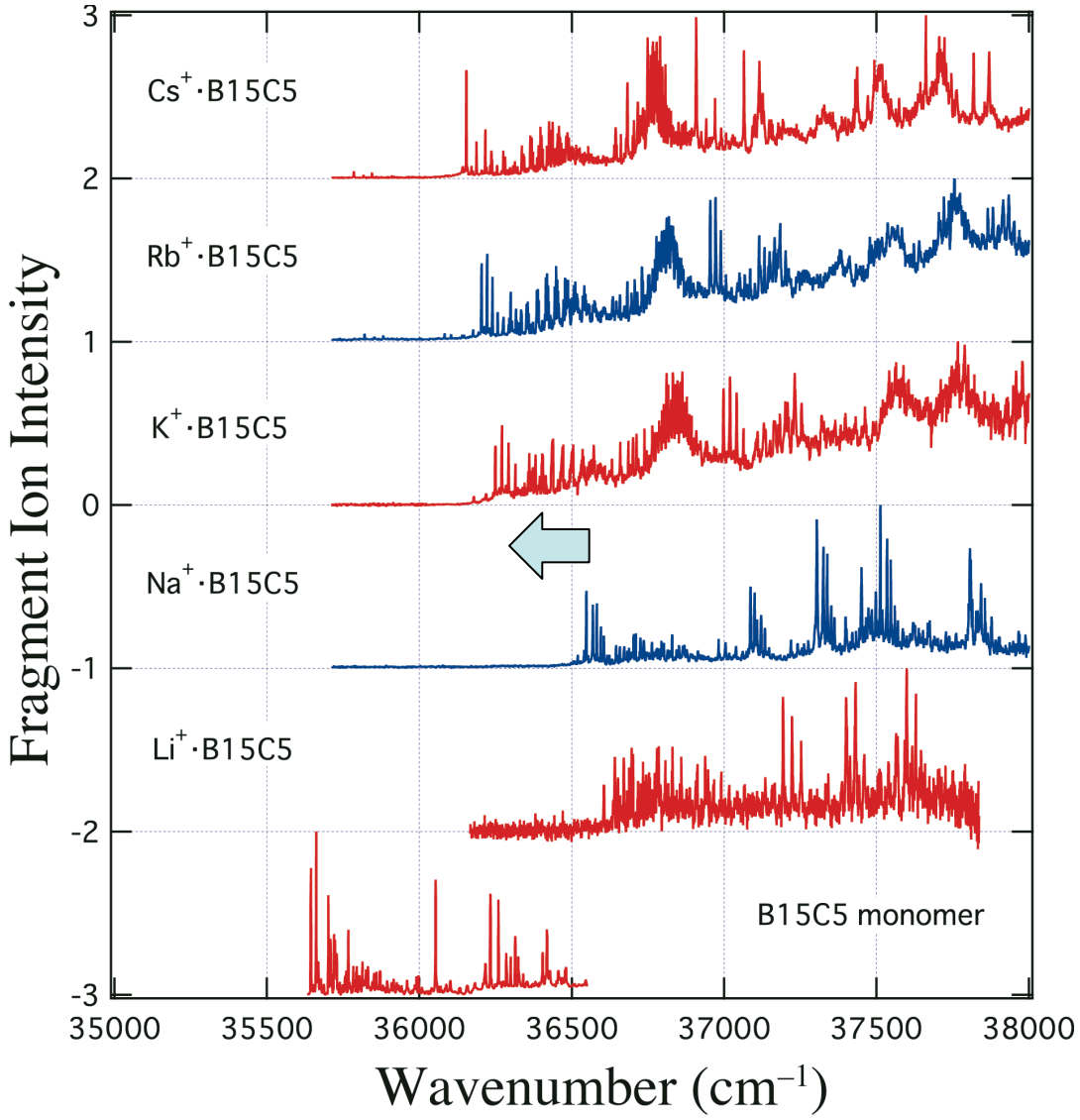
gradually shift to the red from Na^+ to Cs^+

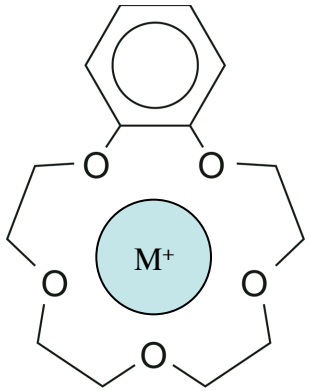
Platt and co-workers, JPCA, **109**, 9456 (2005)

General trend:

Stronger interaction → higher transition energy

UV Spectra of $M^+ \cdot B15C5$



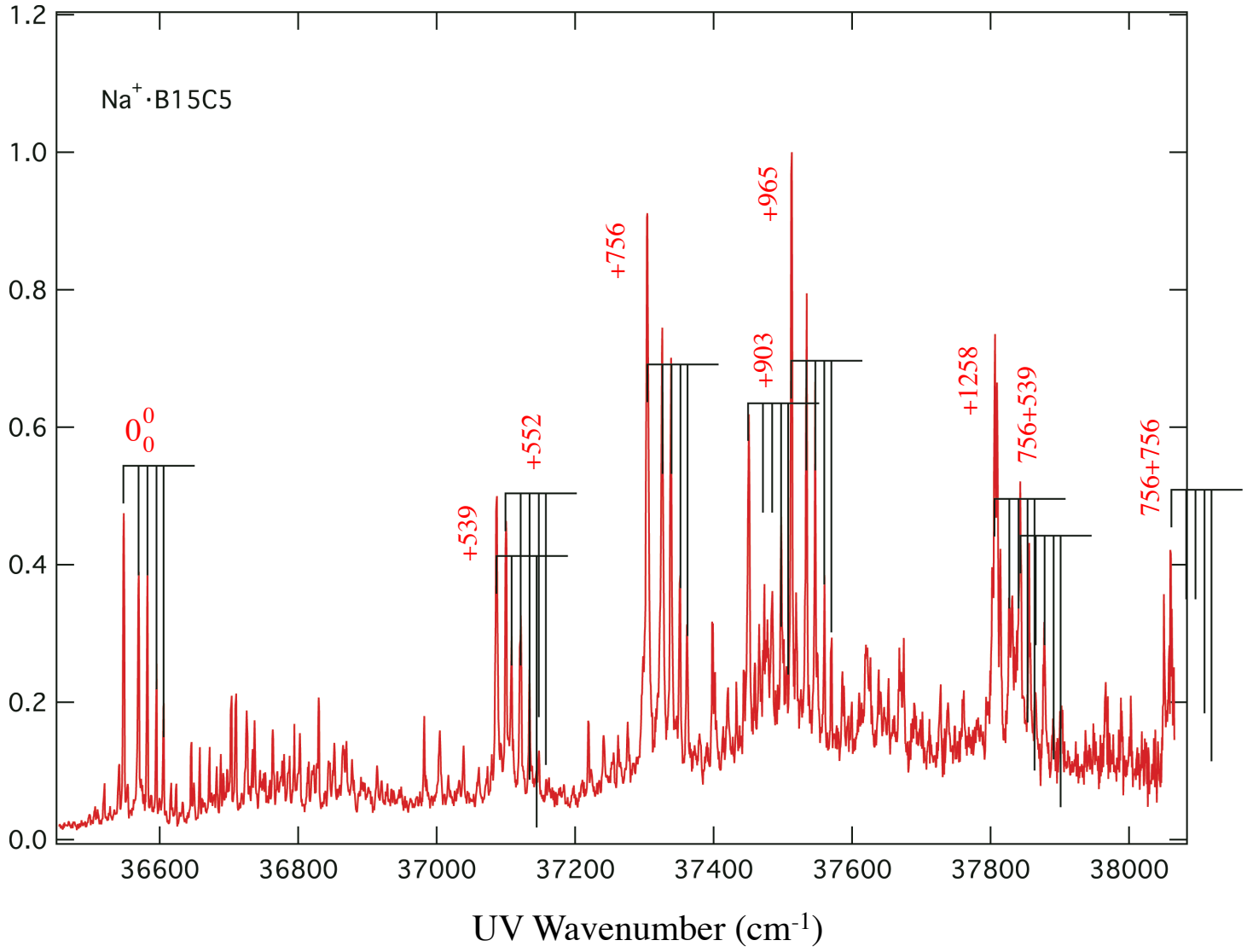


large shift
between Na^+ and K^+

Zwier and co-workers,
JPCA, **113**, 8055 (2009).

Large structural change between Na^+ and K^+?

UV Spectrum of $Na^+ \cdot B15C5$



UV Spectrum of Benzene

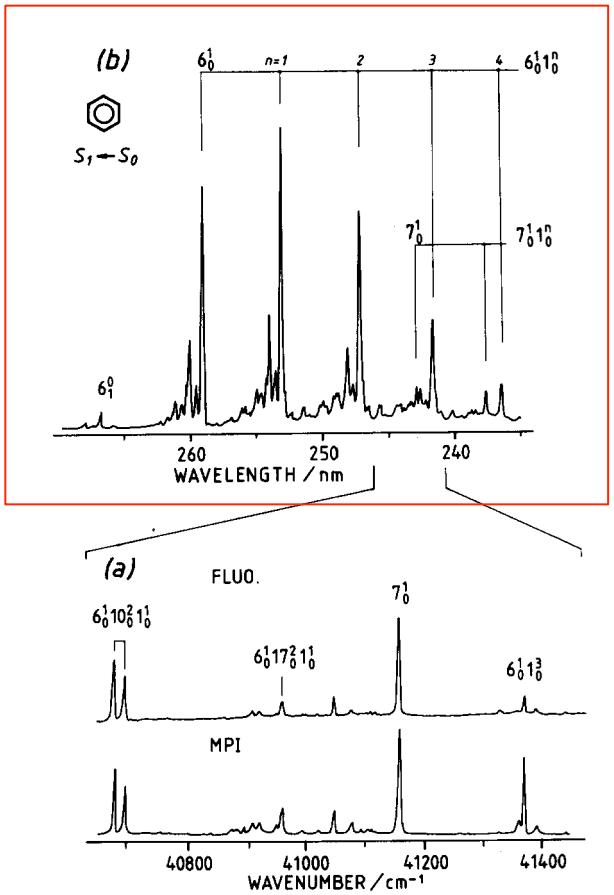


FIG. 1. (a) Fluorescence excitation and REMPI spectra in the vicinity of the onset of channel three simultaneously measured for jet-cooled benzene; (b) Absorption spectrum of benzene vapor. Sample pressure is 126 mTorr.

Suzuki and Ito, J. Chem. Phys., **91**, 4564 (1989).

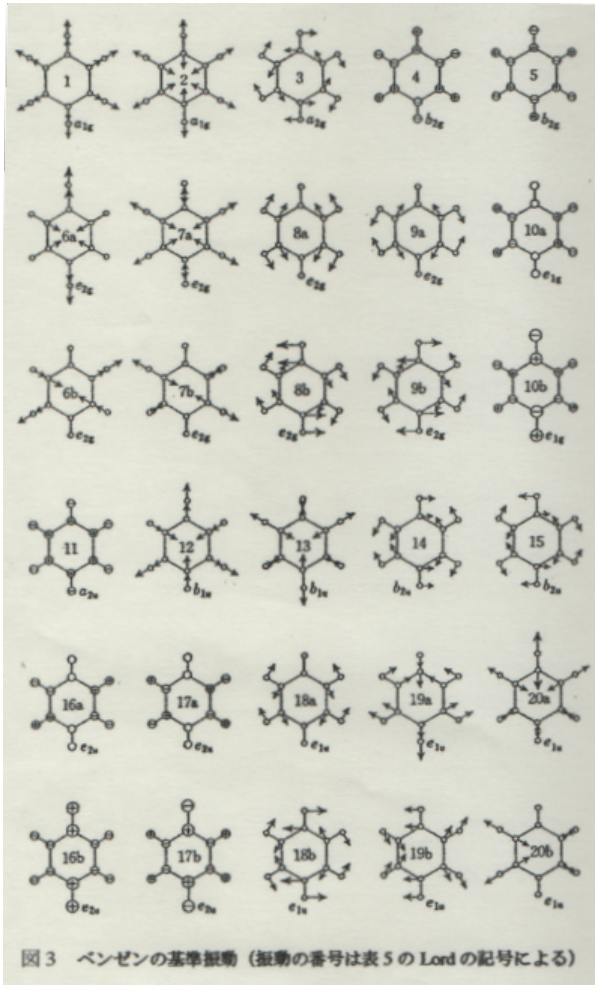
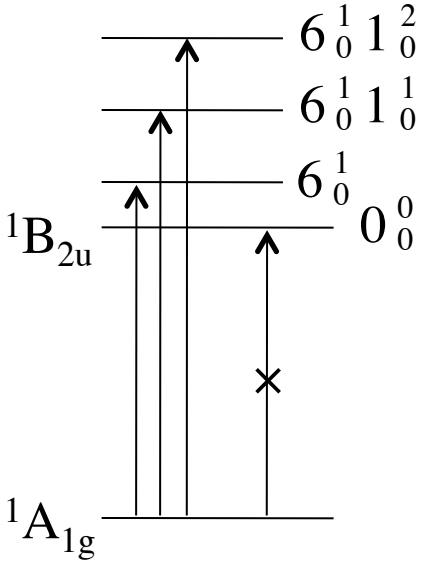
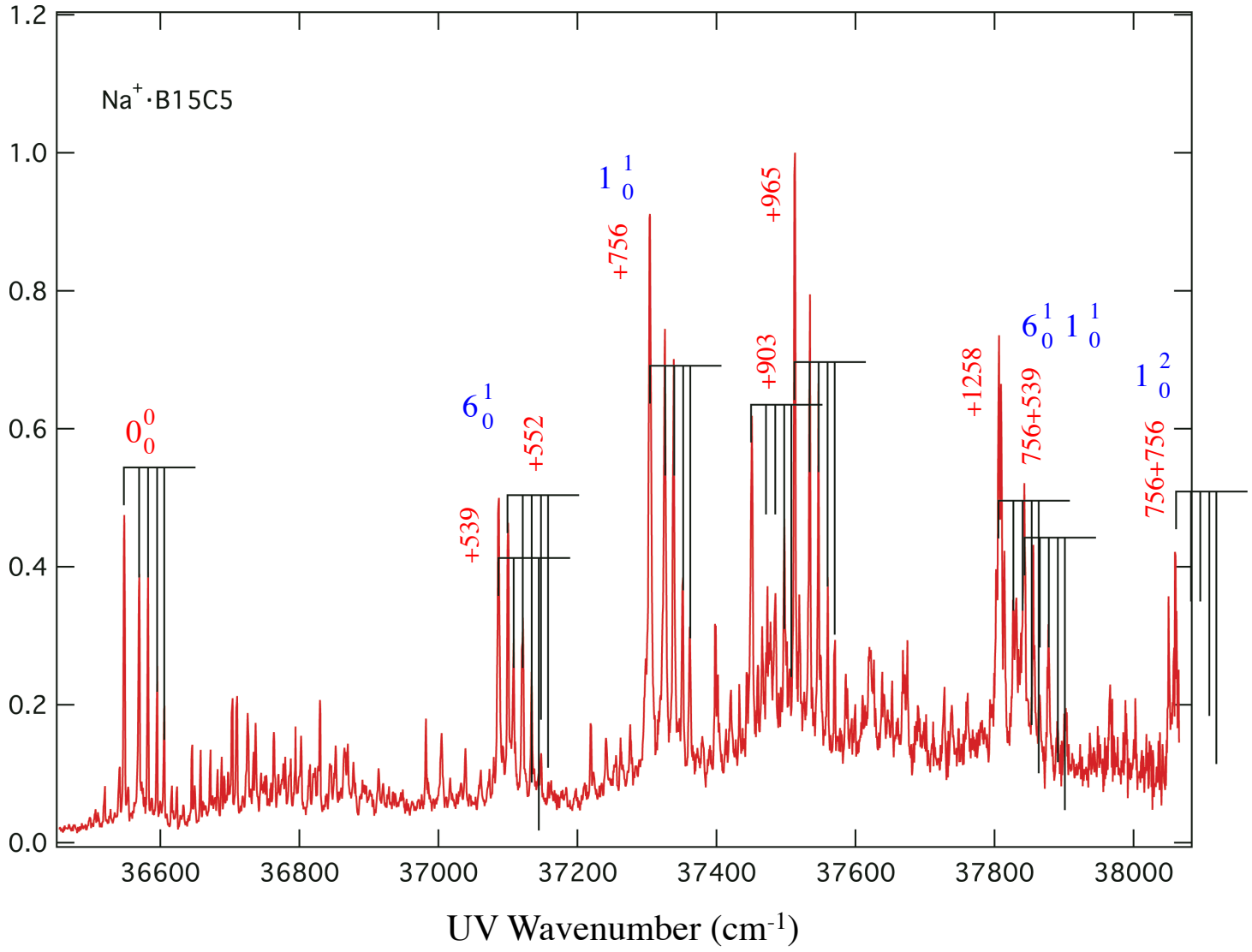


図3 ベンゼンの基準振動（振動の番号は表5のLordの記号による）

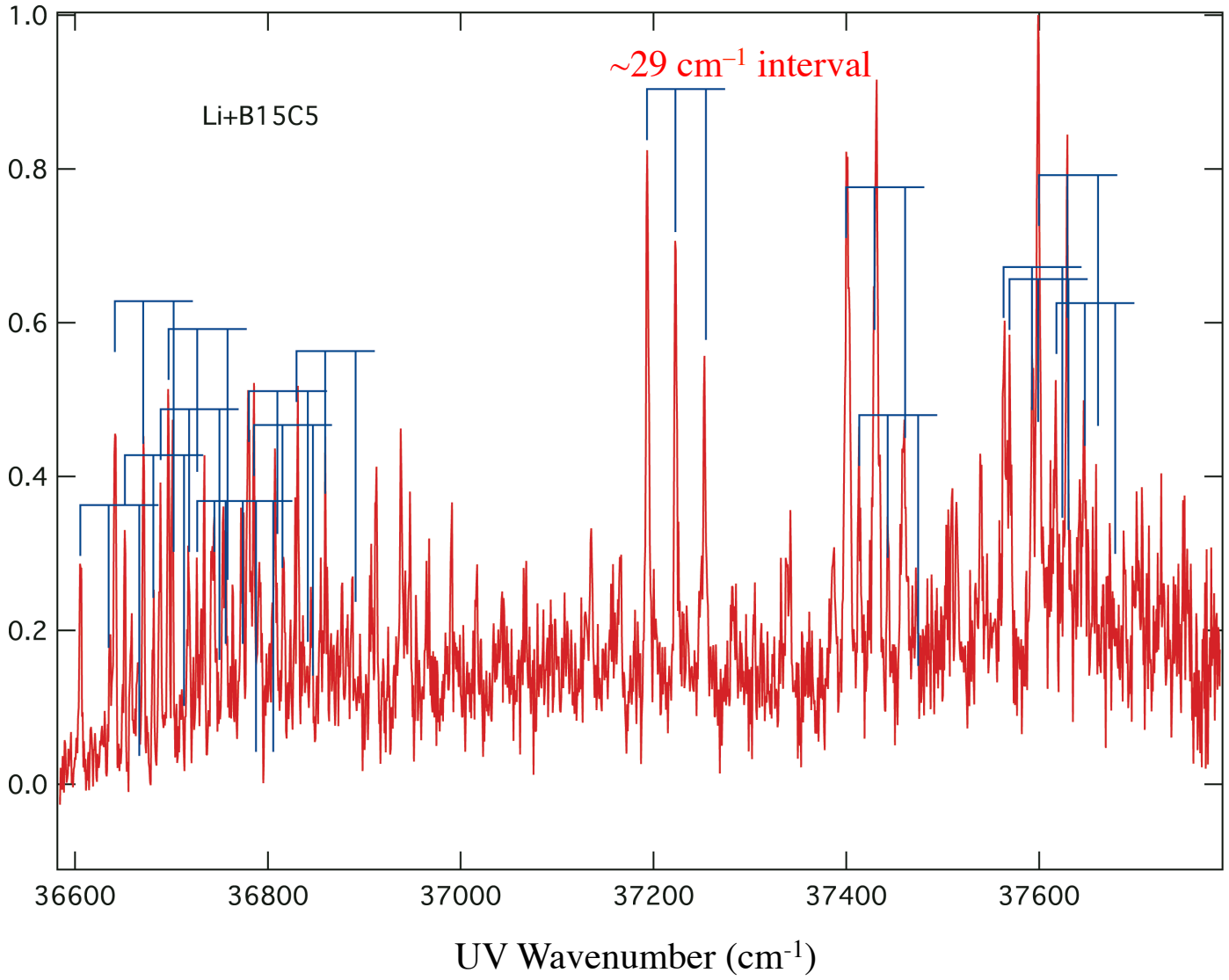


Mode	Freq. in S_0 (cm^{-1})	Freq. in S_1 (cm^{-1})
1	993	923
6	606	522
16	404	244

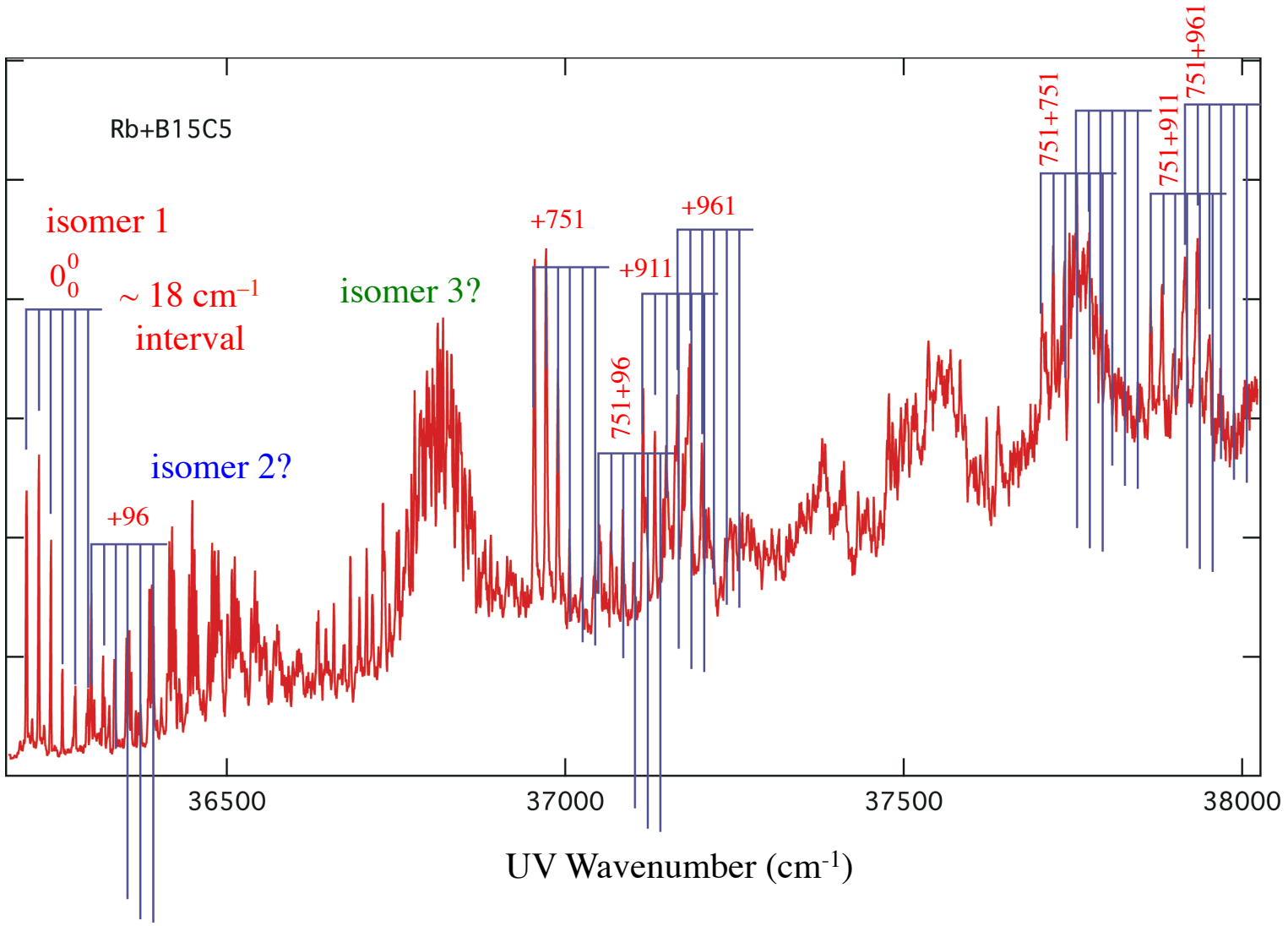
UV Spectrum of Na^+•B15C5



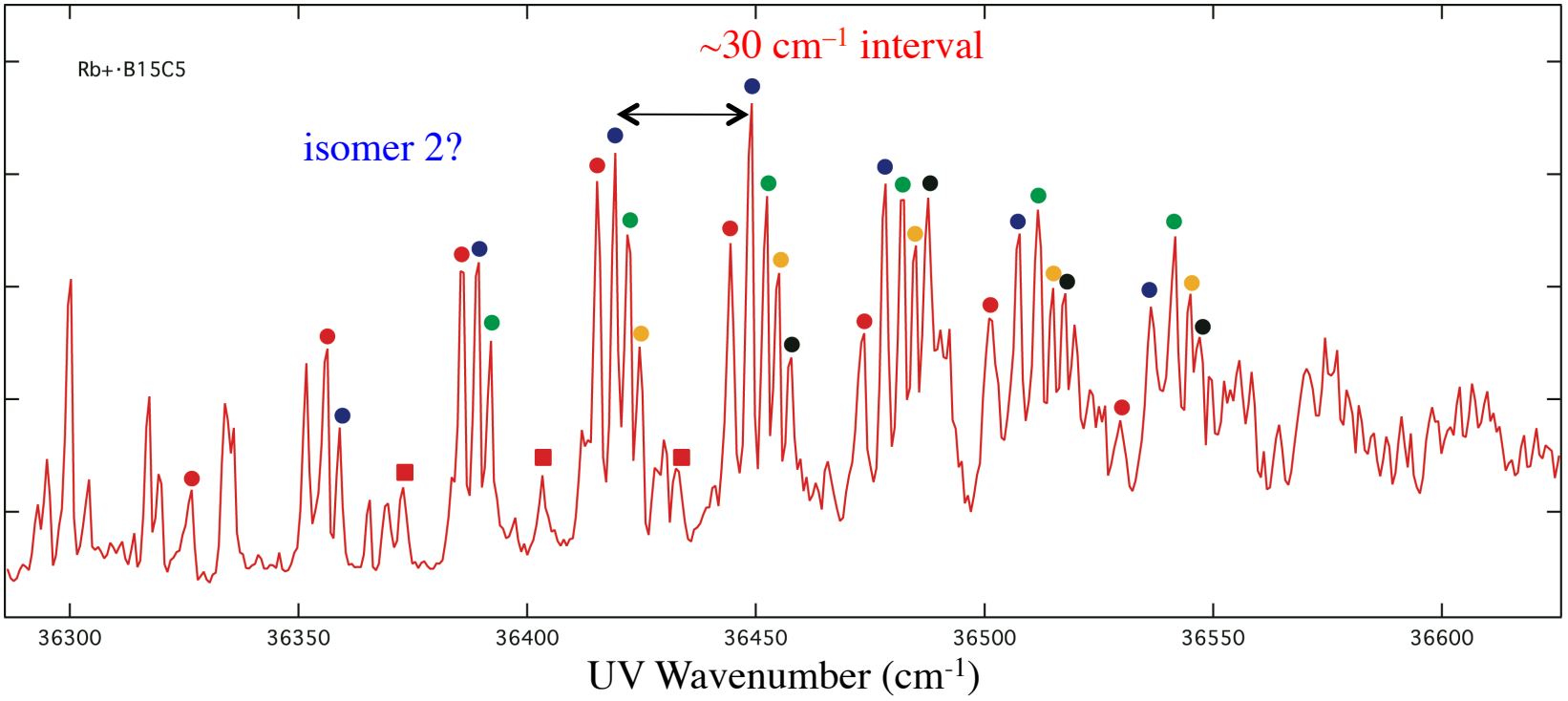
UV Spectrum of $Li^+ \bullet B15C5$



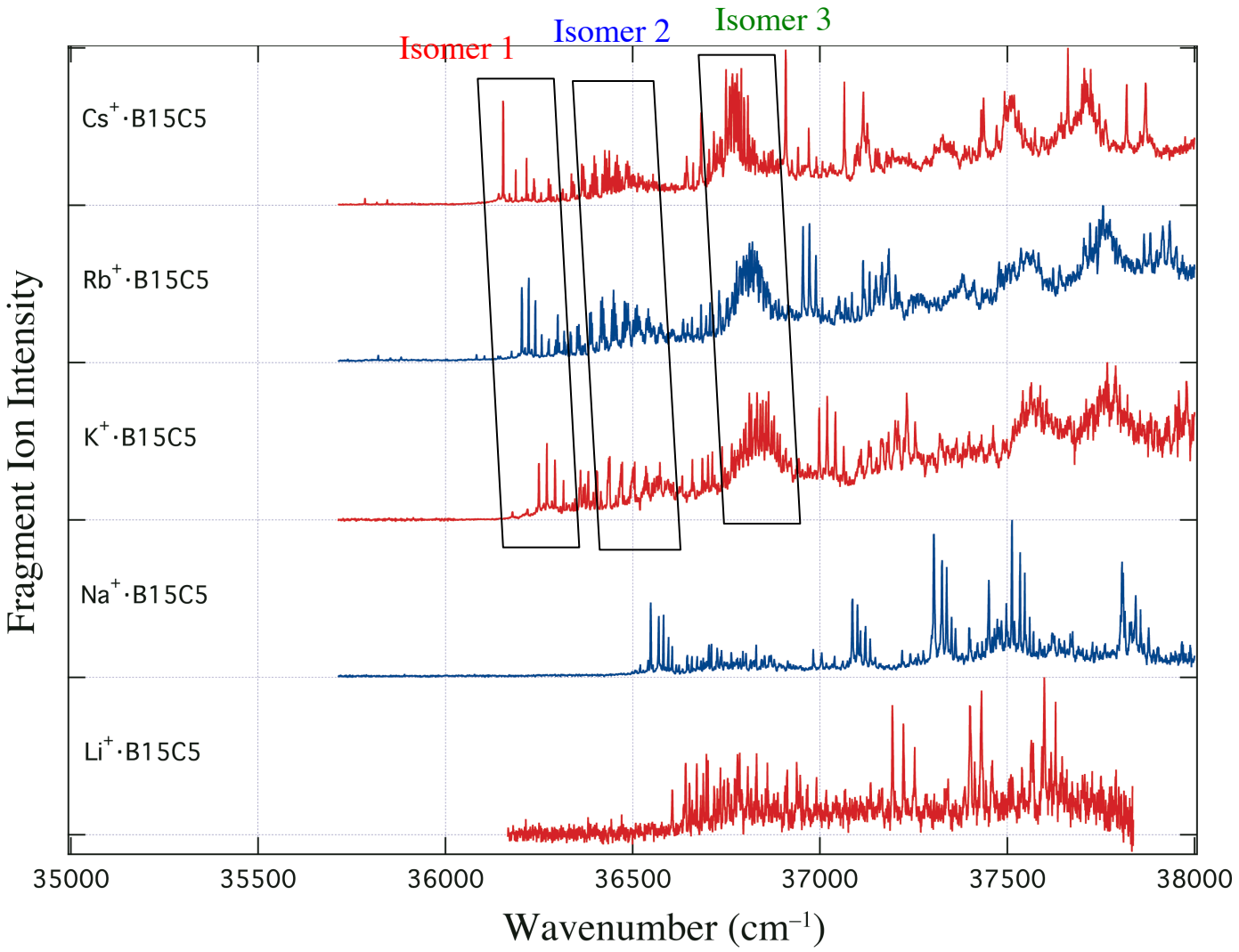
UV Spectrum of $Rb^+ \bullet B15C5$



UV Spectrum of $Rb^+ \cdot B15C5$

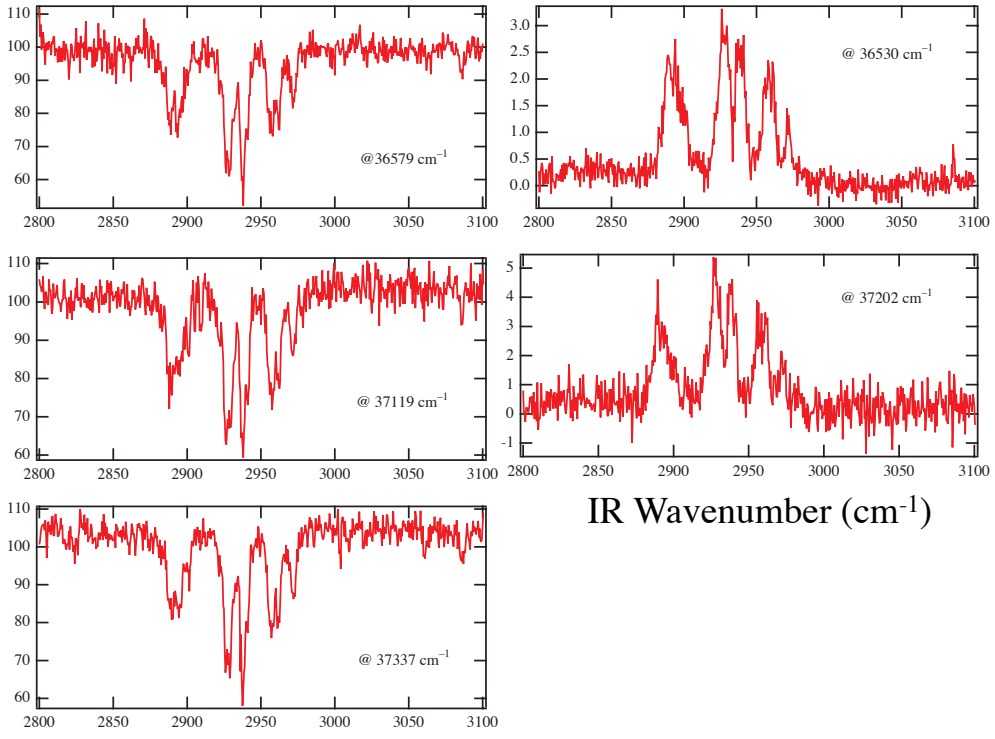


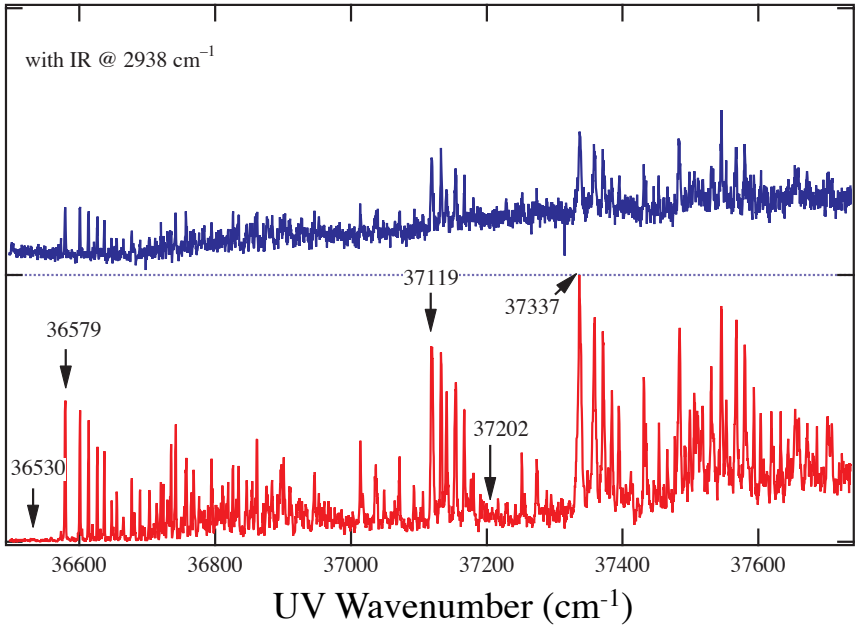
UV Spectra of $M^+ \cdot B15C5$

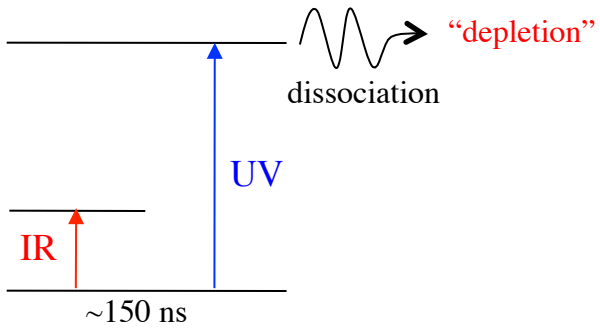


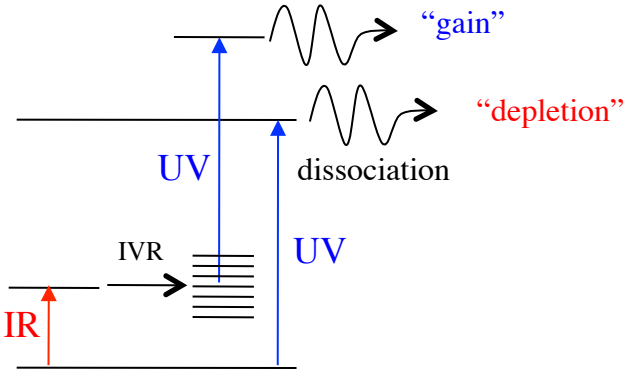
Na^+•B15C5 IR-UV

Only one isomer for Na^+•B15C5

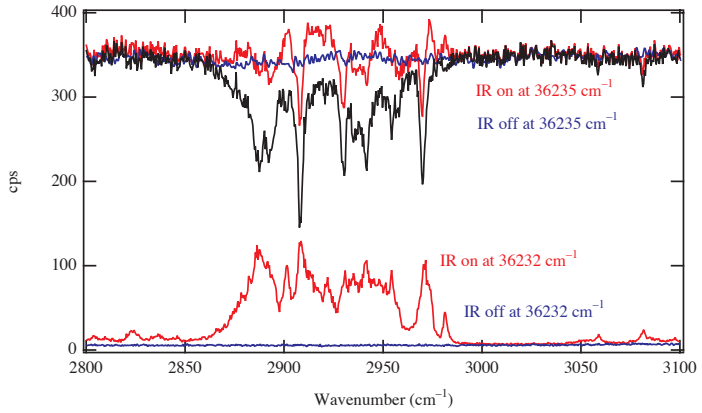


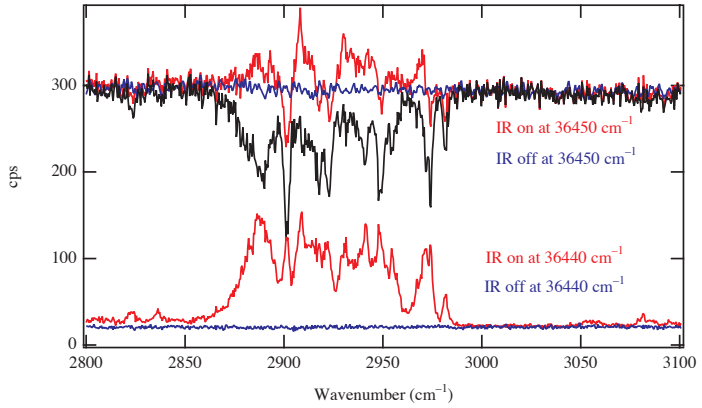


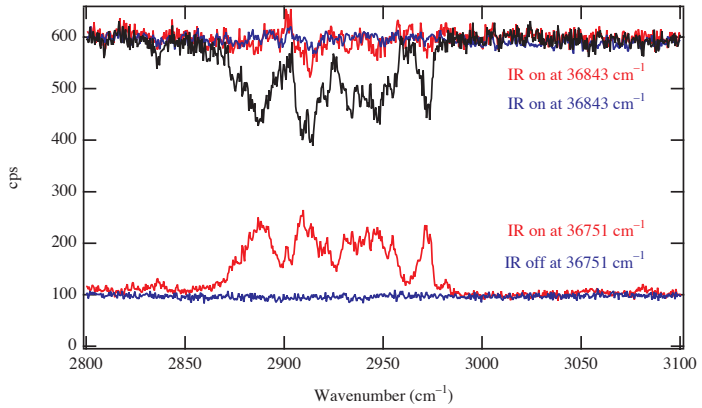


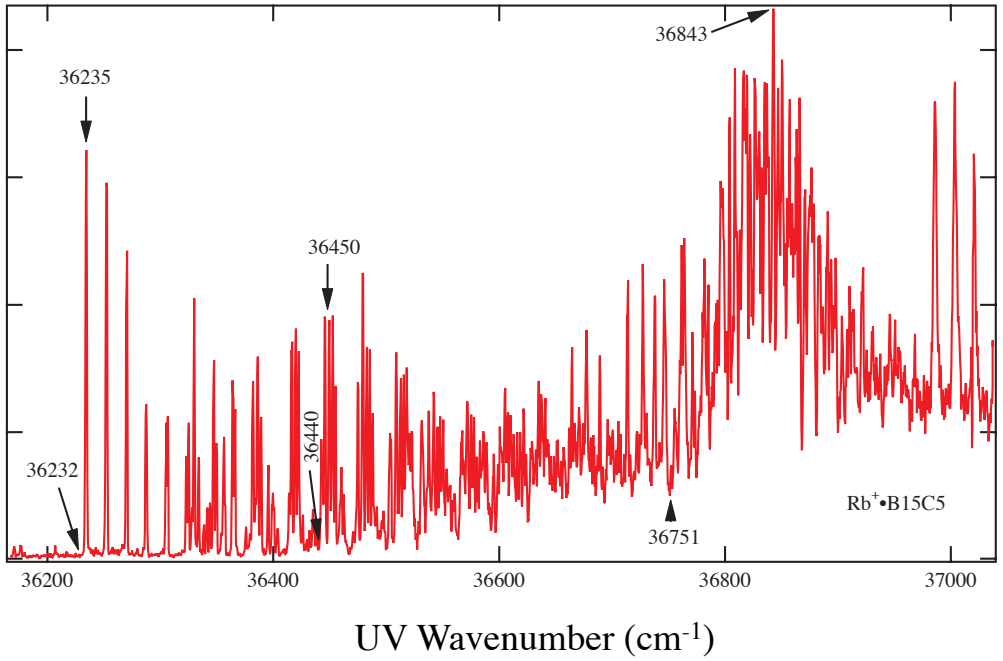


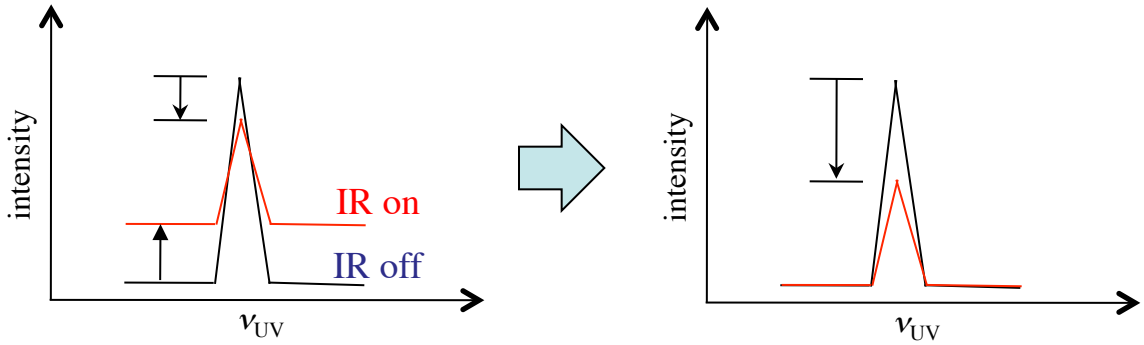
Rb^+•B15C5 IR-UV



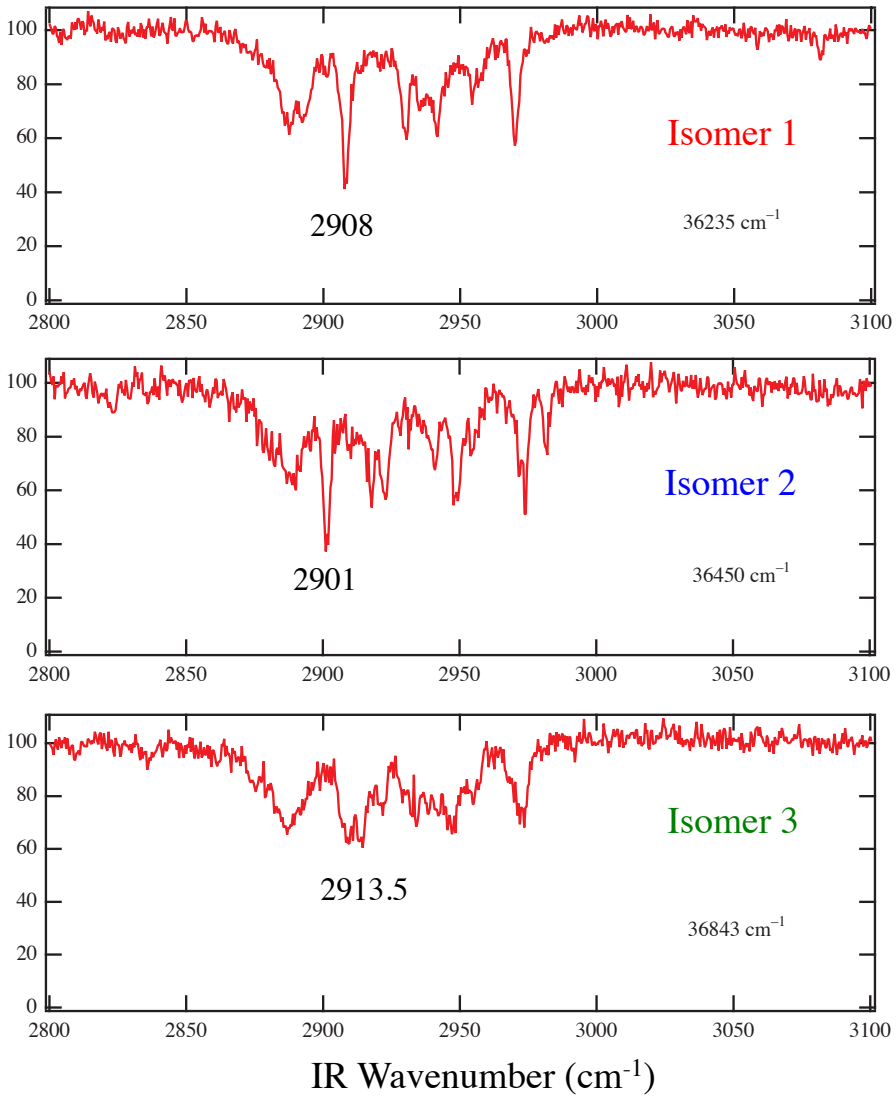


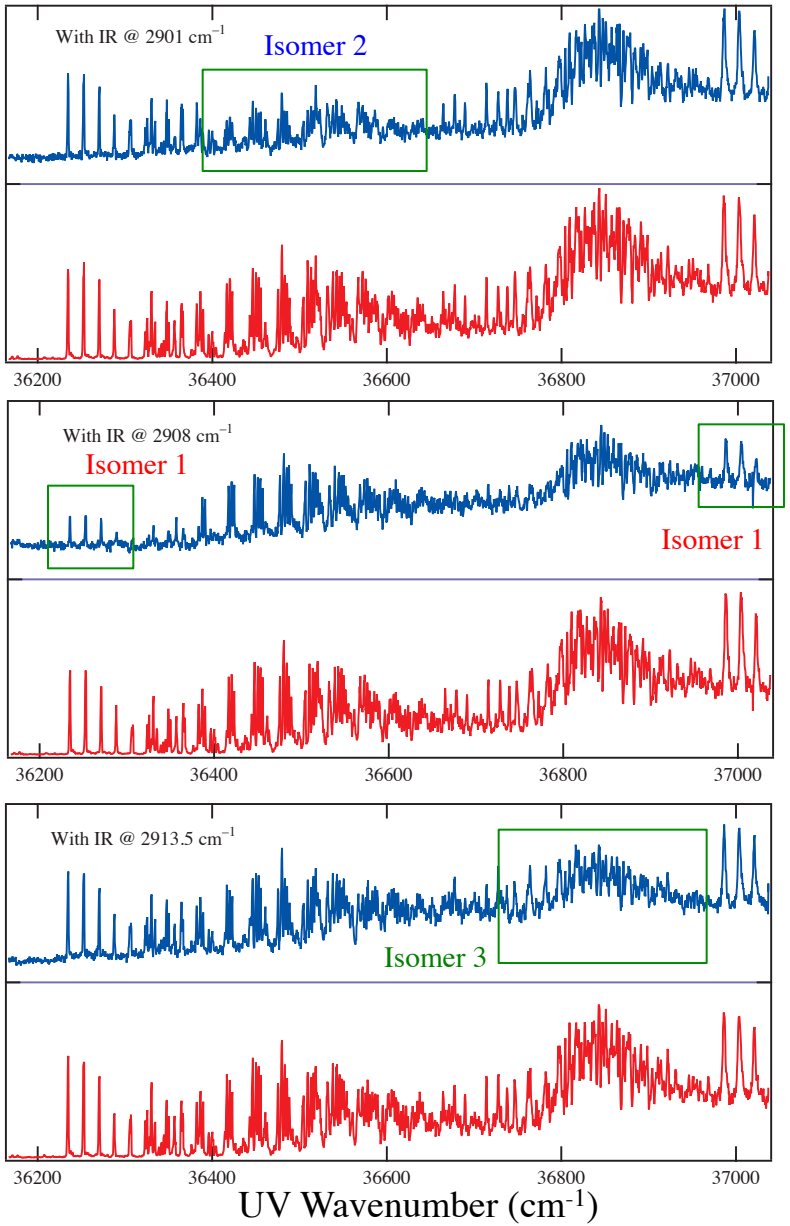




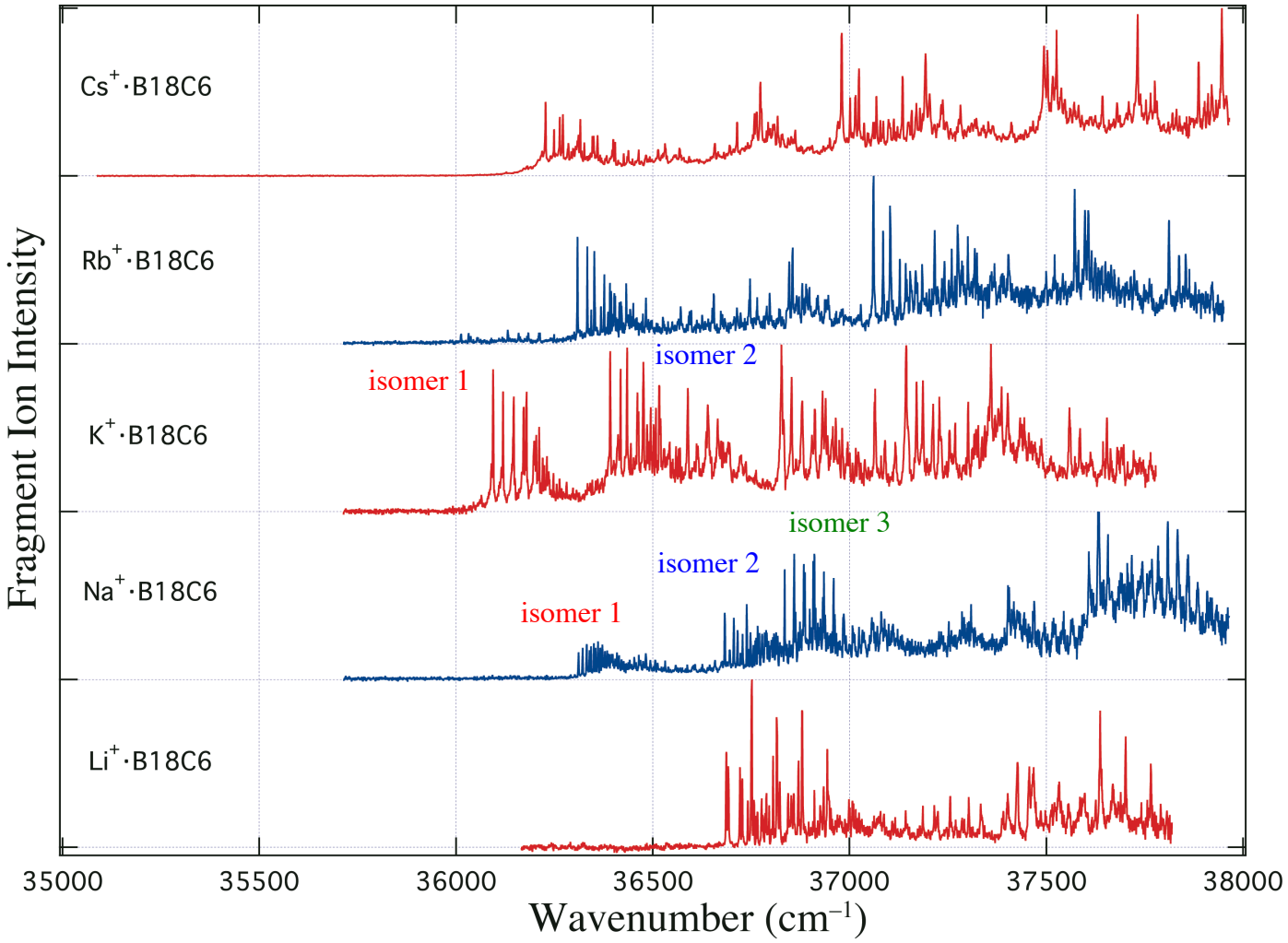


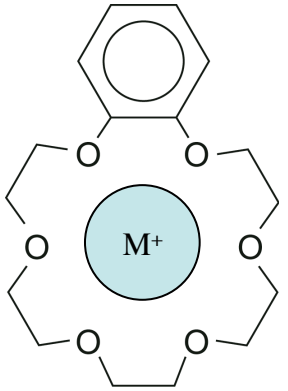
Rb^+•B15C5 IR-UV



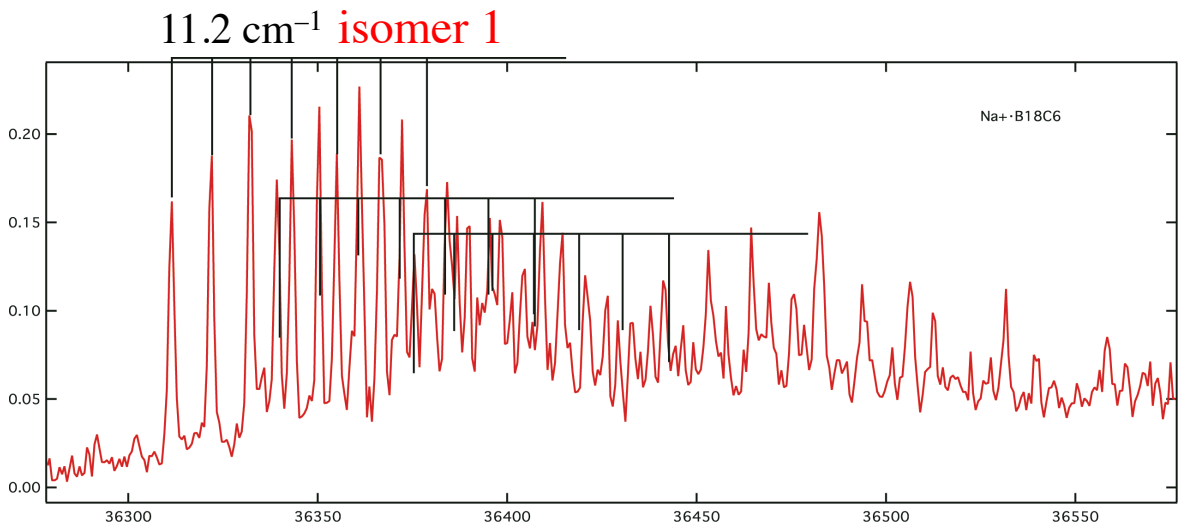


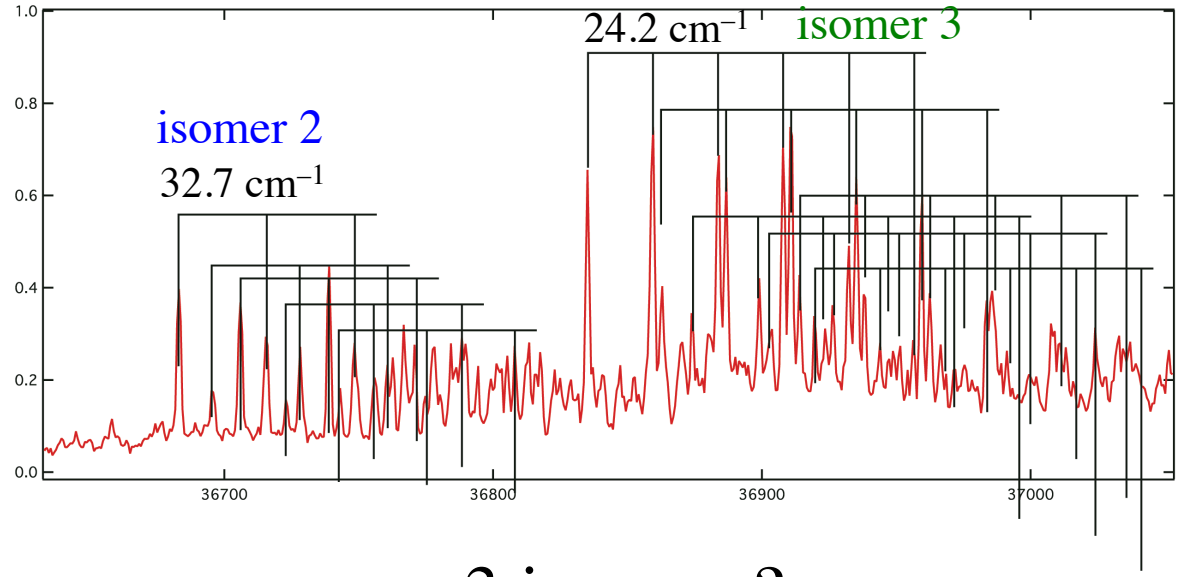
UV Spectra of $M^+ \cdot B18C6$





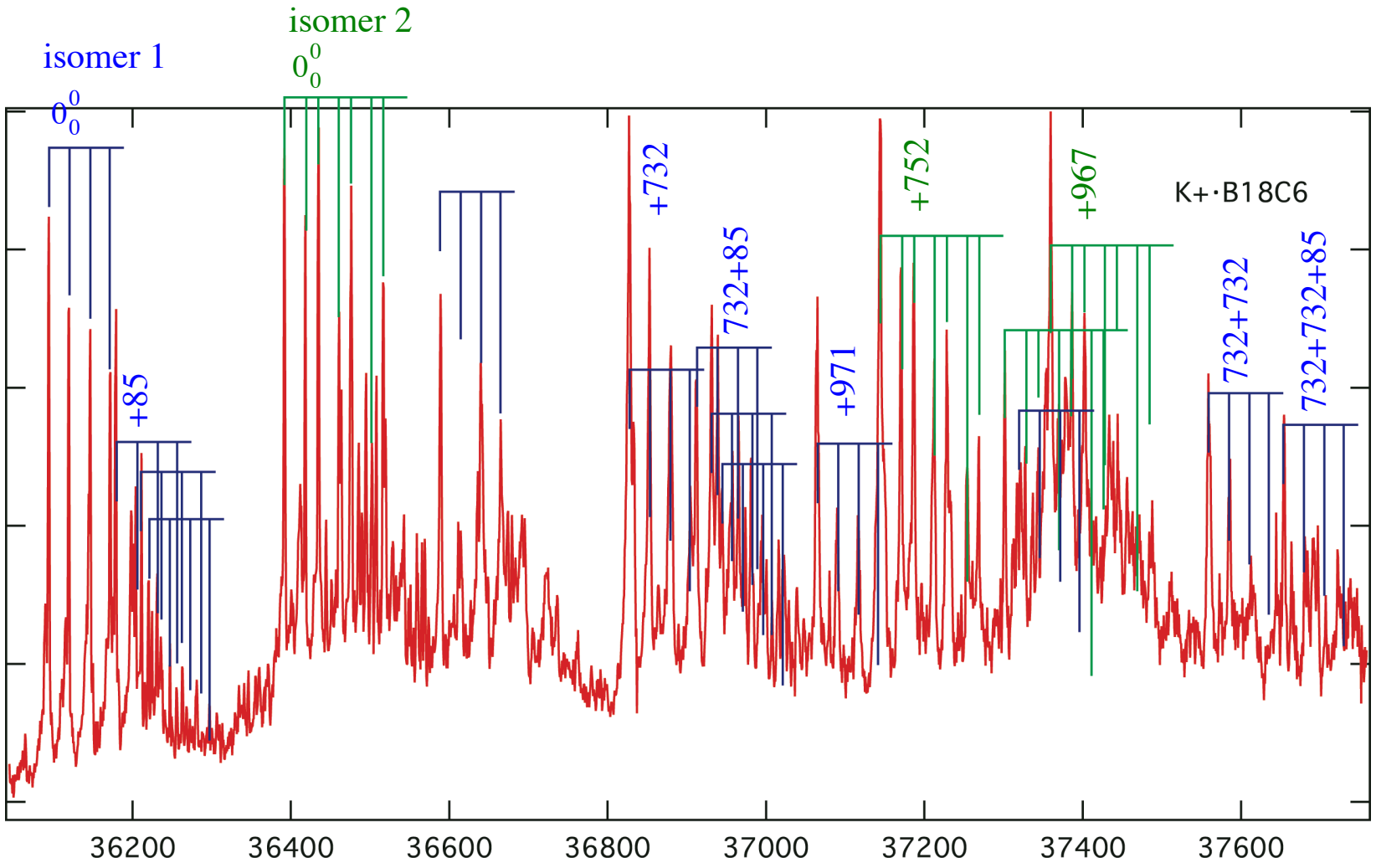
UV Spectrum of $Na^+ \cdot B18C6$





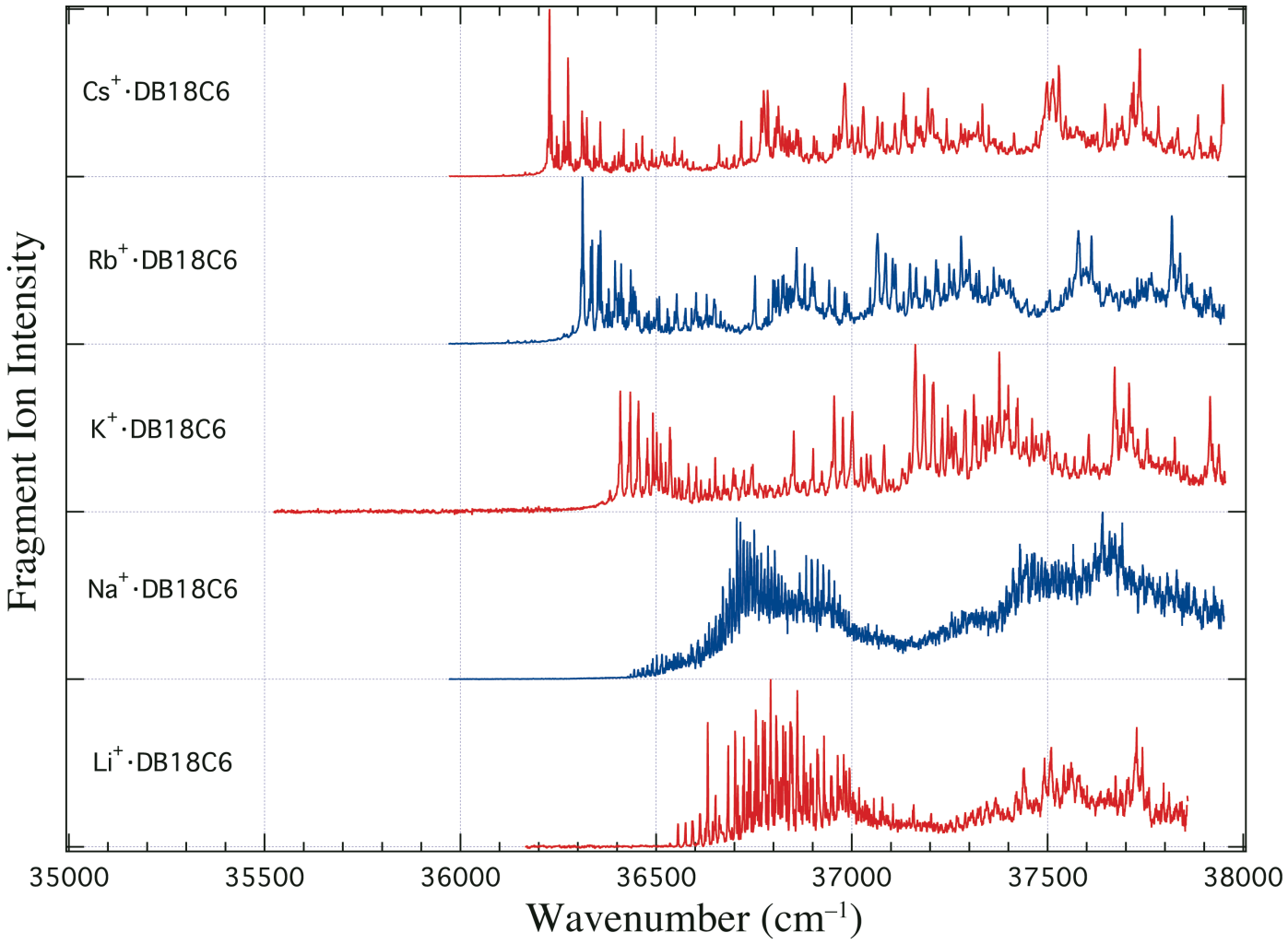
3 isomers?

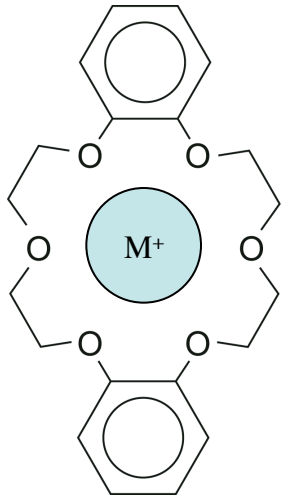
UV Spectrum of $K^+ \cdot B18C6$



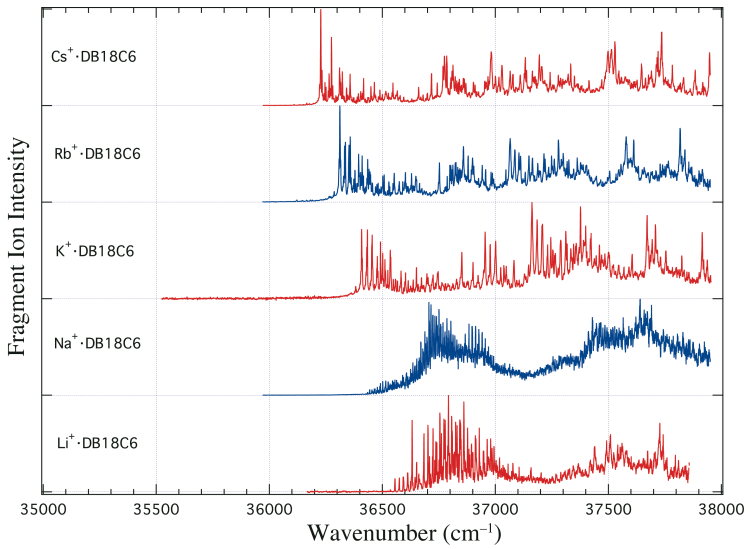
2 isomers?

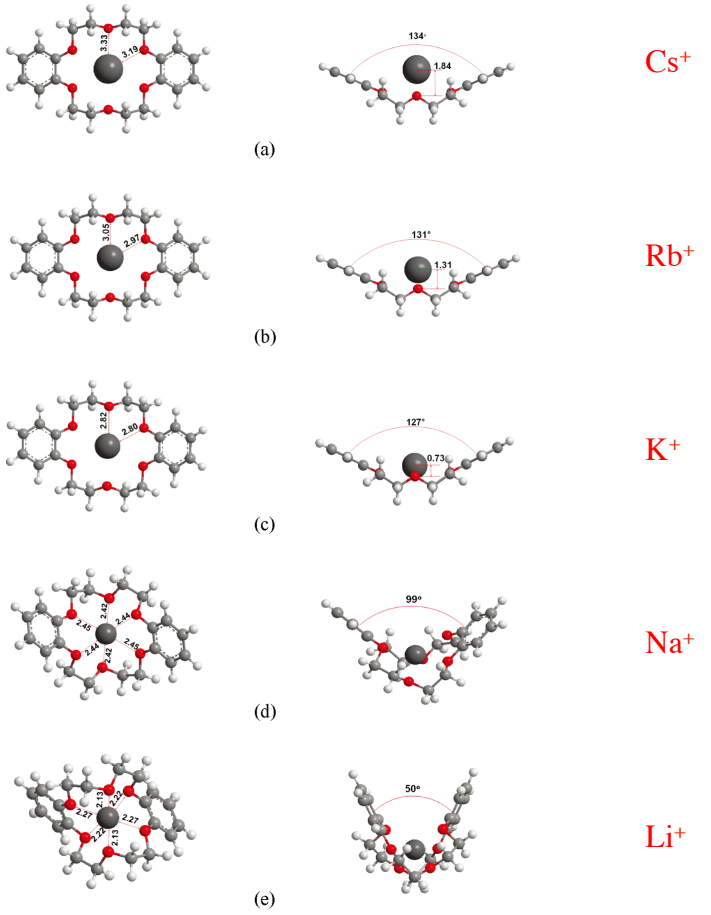
UV Spectra of $M^+ \cdot DB18C6$



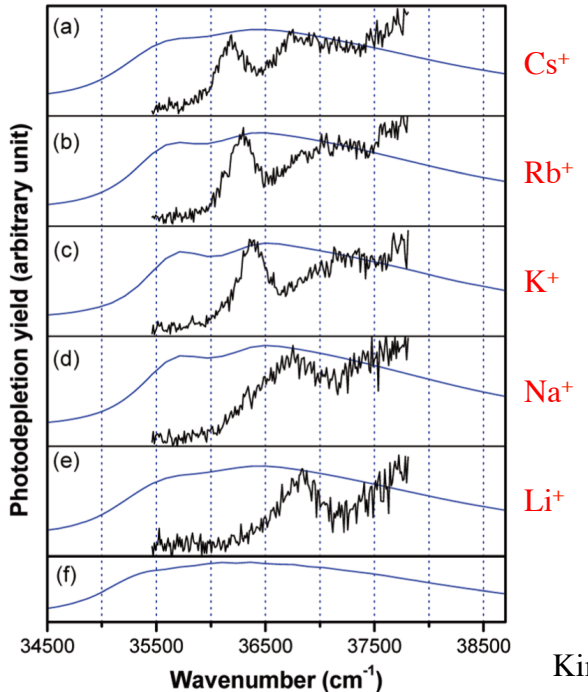


UV Spectra of $M^+ \cdot DB18C6$





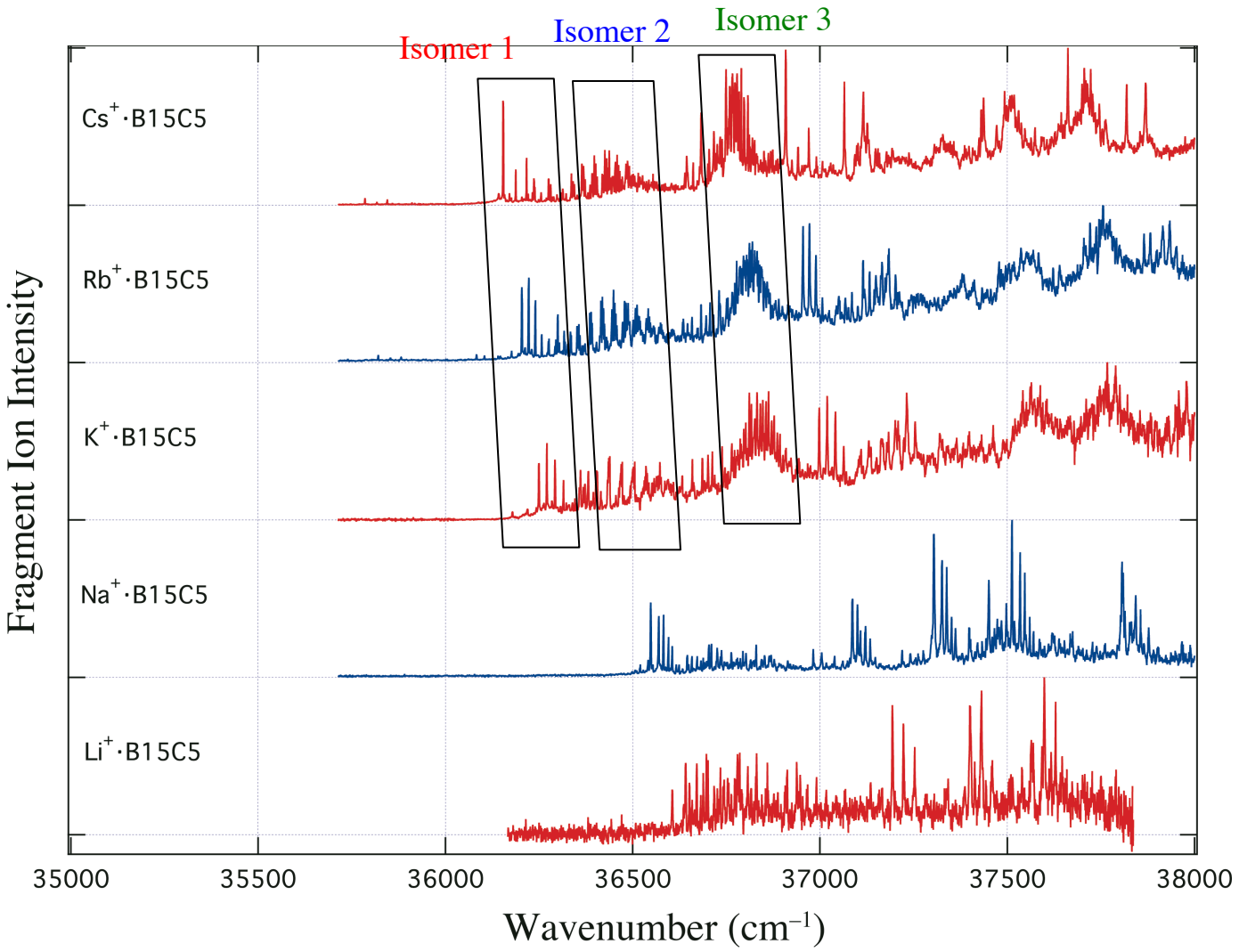
(at 150 K)



More "buckled" structure gives more active low-frequency vibronic structure. (Zwier, 2010)

Kim et al., *JPCA*, **2009**, *113*, 8343.

UV Spectra of $M^+ \cdot B15C5$



Future Work

- Quantum chemical calculations
  - Geometric structures, vibrational analysis, calculation of electronic transitions
- IR-UV and UV-UV double resonance spectroscopy
- Transition metal ions
  - anisotropic electronic structures
- Recognition of chiral molecules with crown ethers