Spectroscopy of Ultracold KRb Molecules

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- Supported by NSF, AFOSR(MURI), UConn Foundation

Ultracold Chemical Physics

- Cooling to below 1 mK
- Trapping (MOT, Optical, Magnetic, Electrostatic)
- Visible and Near-Visible Spectroscopy (e.g. Photoassociation(PA), Ultracold Molecule(UM), Raman Transfer)
- Elastic, Inelastic and Reactive Collisions
- Degenerate Bose and Fermi Gases (e.g. BEC)

ULTRACOLD KRb

PA: D. Wang et al. PRL**93**, 243005 (2004); Eur Phys J D**31**, 165 (2004); ICAP Proceedings, p. 315 (2009); J. Banerjee et al. PRA**86,** 043248 (2012); JCP, submitted

UM Detection: D. Wang et al., PRA **72**, 032502 (2005); J. Phys B **39**, S849 (2006); PRA **75**, 032511 (2007); New J Phys. **11**, 055020 (2009)

UM/MB: J. T. Kim et al., PCCP**13**, 18755(2011); PRA**84**, 062511 (2011); JCP**137**, 244301 (2012)

Ultracold Molecules Group

Professors Ed Eyler, Phil Gould and Bill Stwalley

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Supported by NSF and AFOSR(MURI)

Collaborators: D. Wang (Chinese U of Hong Kong), J. T. Kim (Chosun U), Y. Lee (Mokpo U), B.S. Kim (KAIST)

Inelastic/Reactive Collision
H2(v=1,J=0) + He Relaxation

300K

k= 3x10**-17 cm**3/molecules-sec

Falling exponentially to 100K

Extrapolation of 100-300K rates to

10mK	k= ~10**-29
1μK	k= ~10**-40
Actual T<10mK	k= 3x10**-17

Identical Bose/Fermi Symmetry (in atomic units)

Species	Scatt. Length	Cross Section(0 K)
H + H (2B)	1.335	44.8
H + D (B+F)	-0.448	2.52
H + T (2B)	-1.597	32.0
D + D (2F)	-6.907	0.
D + T (F+B)	-15.53	3031.
T + T (2B)	-81.55	167000.

Collision Dynamics of Near-Dissociation Levels (high v')

Cs + Cs2(v') -> Cs + Cs2(v"<v') P. Staanum et al.,

PRL **96**, 023201 (2006)

Cs + RbCs(v') -> Cs + RbCs(v"<v') or Rb + Cs2

Rb + RbCs(v')-> Rb + RbCs(v"<v') or Cs + Rb2

E. R. Hudson et al., PRL **100**, 203201 (2008)

All rates ~ 10**-10 cm**3/s

[theory for Li + Li2 (high v') similar G. Quemener et al. PRA **75**, 050701 (2007)]

Target States for Alkali Dimers

- Lowest rovibronic level X(0,0)
- Lowest metastable triplet level a(0,0)
- For homonuclear dimers X(0,1)
- Other possible homonuclear metastable levels

  e.g., a(0,1), b(0,0), b(0,1)
- For ions X+(0,0), A+(0,0) (+ other states for homonuclear ions)

FORMATION OF KRb X(0,0)

As T-> 0 K, no inelastic processes except hyperfine

Largest dipole moment in v”=0

All v”>0 and J”>0 levels have finite (>kilosecond) radiative lifetimes (see JCP **120**, 88 (2004))

Only X(0,0) with additional hyperfine selection appropriate for quantum degenerate gas

R- TRANSFER METHODS FOR FORMING X(0,0)

Direct Photoassociation of 2 atoms(PA)(large Δ)

Excitation of Ultracold Molecules (UM)

Resonant Coupling of X and a states (FOPA)

Resonant Coupling of Excited States

Stimulated Raman Transfer of 2 Atoms to X(0,0)

Stimulated Raman Transfer of UM to X(0,0)

More Complex Raman Transfer

EXAMPLE OF KRb X(0,0) AT JILA

40K87Rb Feshbach Molecules: PRL **100**, 143201 (2008); PRA **78**,013416 (2008)

Dense 40K87Rb X(0,0) Gas: Nature Physics **4**, 622 (2008); Science **322**, 231 (2008); PCCP **11**, 9626 (2009); Faraday Disc. **142**, 351 (2009)

Dense 40K87Rb X(0,0,mK=-4,mRb=3/2) Lowest Rovibronic Hyperfine Level PRL **104**, 030402 (2010); Science **327**, 853 (2010); Nature **464**, 1324 (2010); PRA **81**, 061404 (2010)

Collision Dynamics of KRb X(0,0,-4,3/2)

K + KRb ---> K2 + Rb 225 cm-1 exoergic

Rb + KRb –x-> K + Rb2 215 cm-1 endoergic

KRb + KRb ---> K2 + Rb2 9.7 cm-1 exoergic

Each exoergic reaction observed in accord with theory

Rovibronic Spectroscopy

Photoassociation (PA)

K + Rb + hγ -> KRb*(v’,J’)(many states)

Spontaneous Emission

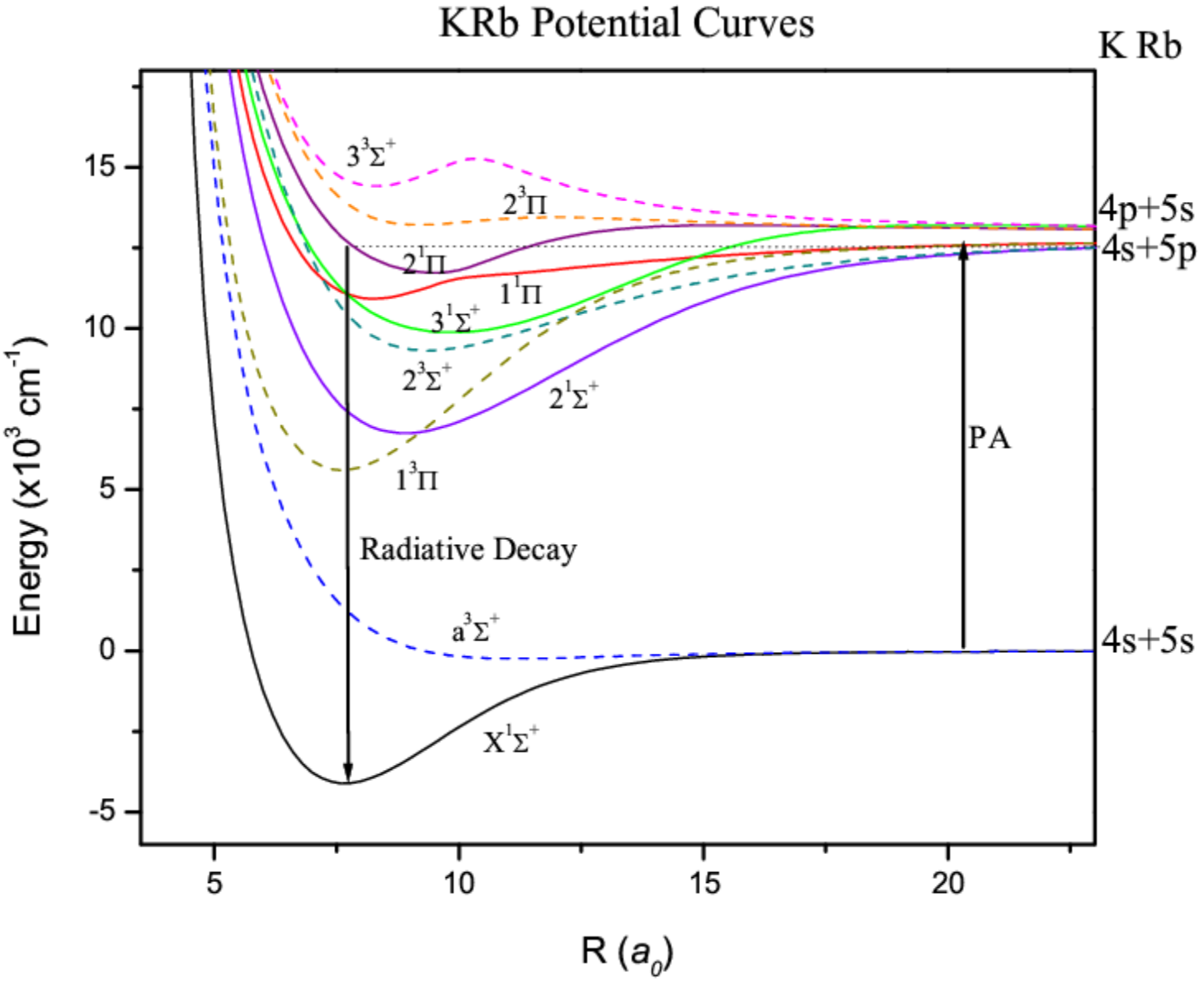
KRb*(v’,J’) -> {KRb(v”,J”)(X or a)

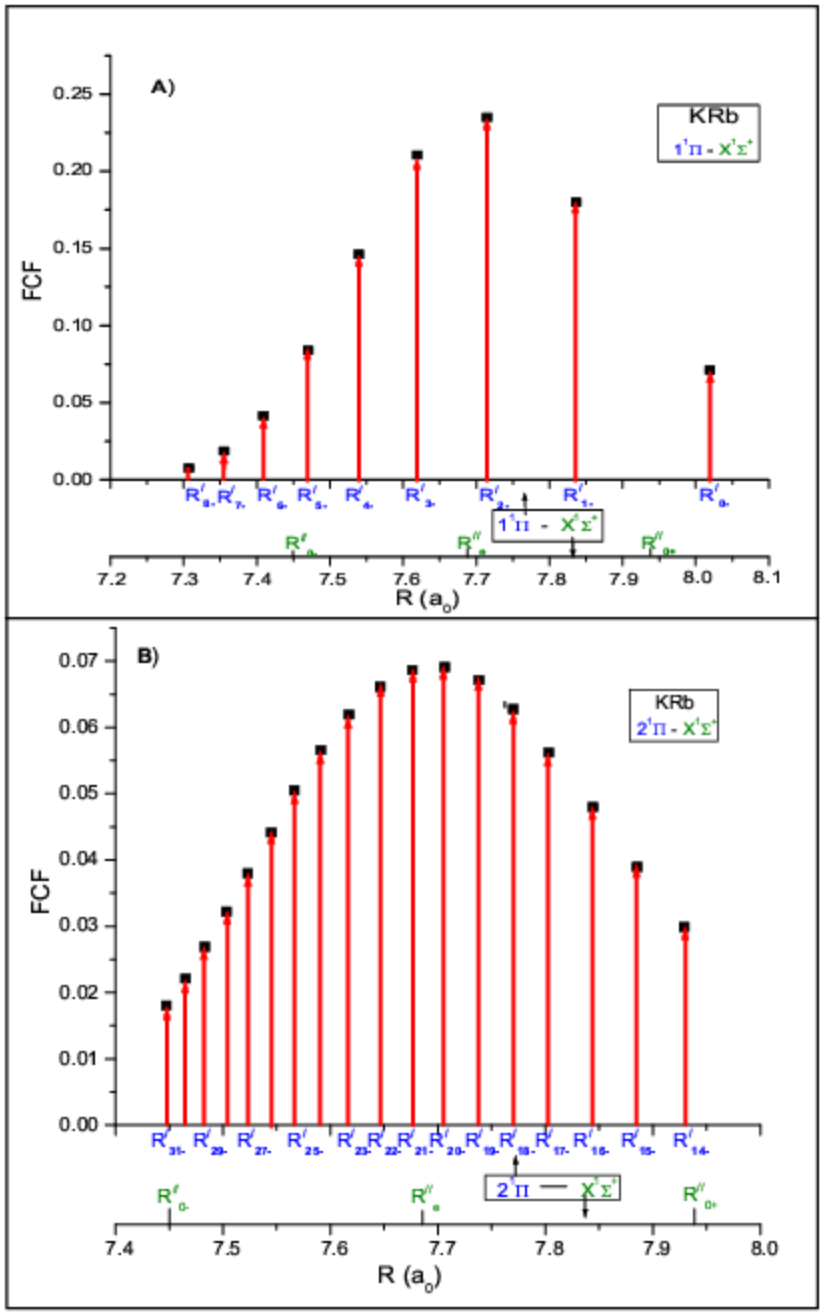
or K + Rb } + hγ”

Ultracold Molecule (UM)

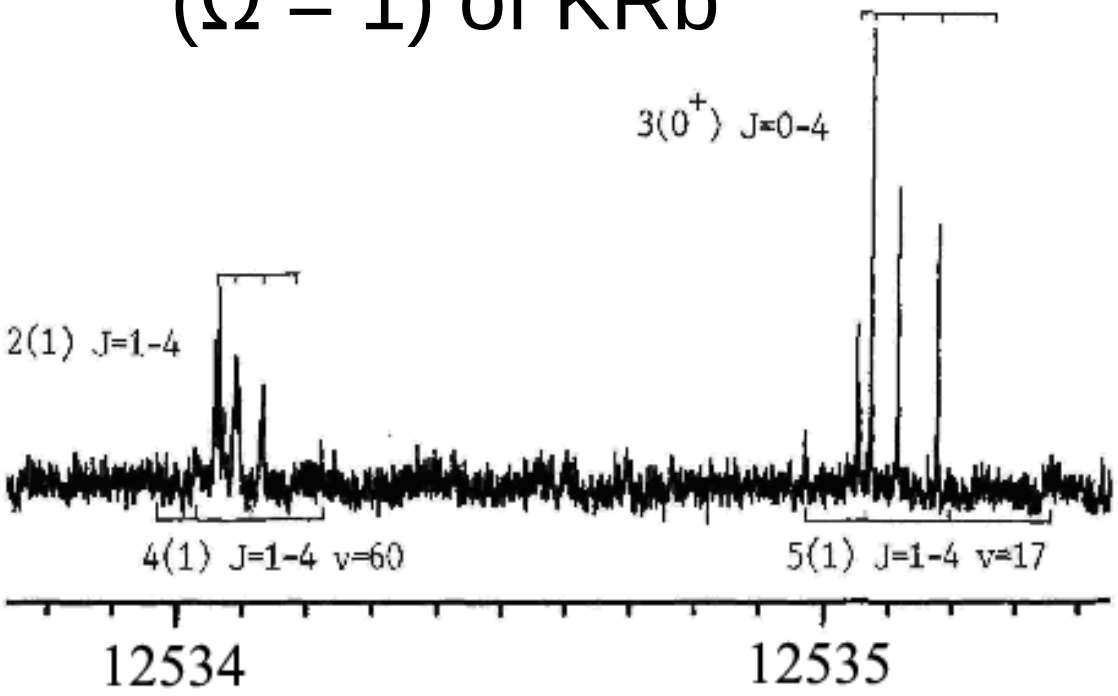
KRb(v”,J”)(X or a) -> KRb*(v’,J’)

All bound/quasibound states for K+Rb*,K*+Rb

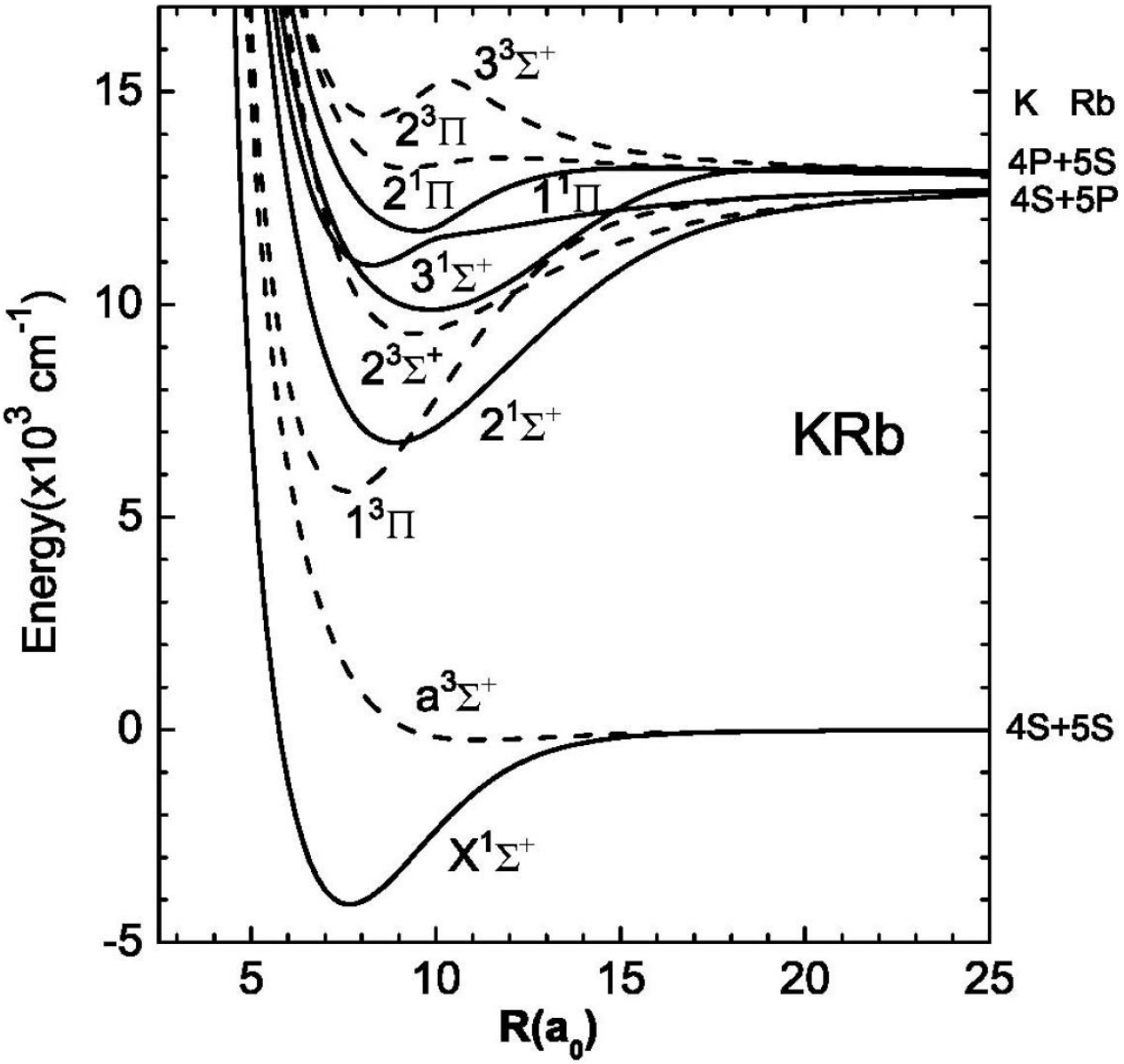

KRb Potential Curves
K Rb
4p+5s
4s+5p
4s+5s
$3^3\Sigma^+$
$2^3\Pi$
$2^1\Pi$
$1^1\Pi$
$3^1\Sigma^+$
$2^3\Sigma^+$
$2^1\Sigma^+$
$1^3\Pi$
$a^3\Sigma^+$
$X^1\Sigma^+$
Radiative Decay
PA
Energy (x10^3 cm^{-1})
R (a_0)
15
10
5
0
-5
5
10
15
20


A)
KRb
1¹Π - X¹Σ⁺
FCF
R (a0)
B)
KRb
2¹Π - X¹Σ⁺
FCF
R (a0)

Resonantly Coupled Levels of the First Two Singlet PI States ($\Omega = 1$) of KRb



KRb Short-Range Potential Curves



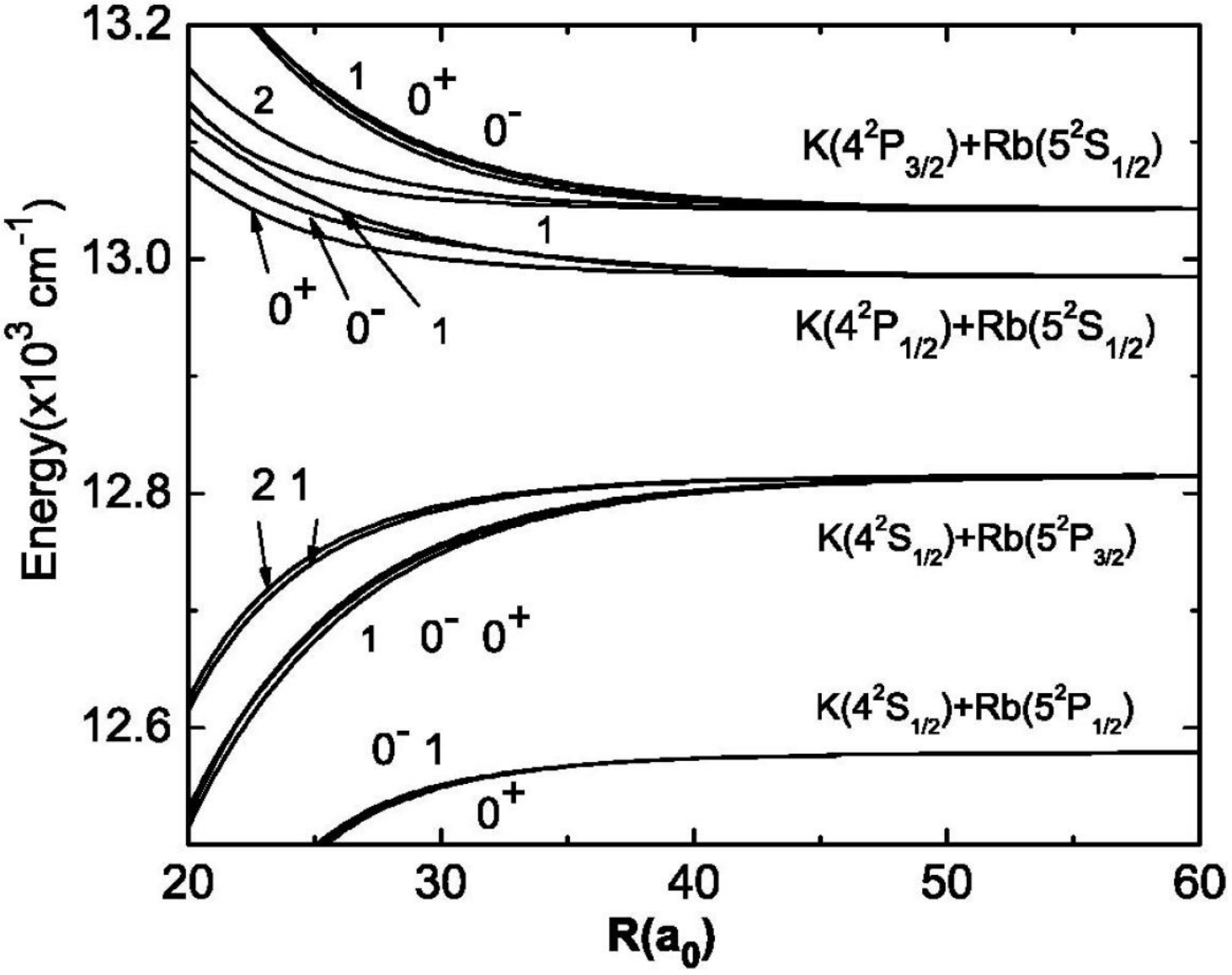
X & a State LR Selection Rules

X state $\Omega = 0+ \quad \leftrightarrow \Omega = 0+, 1$

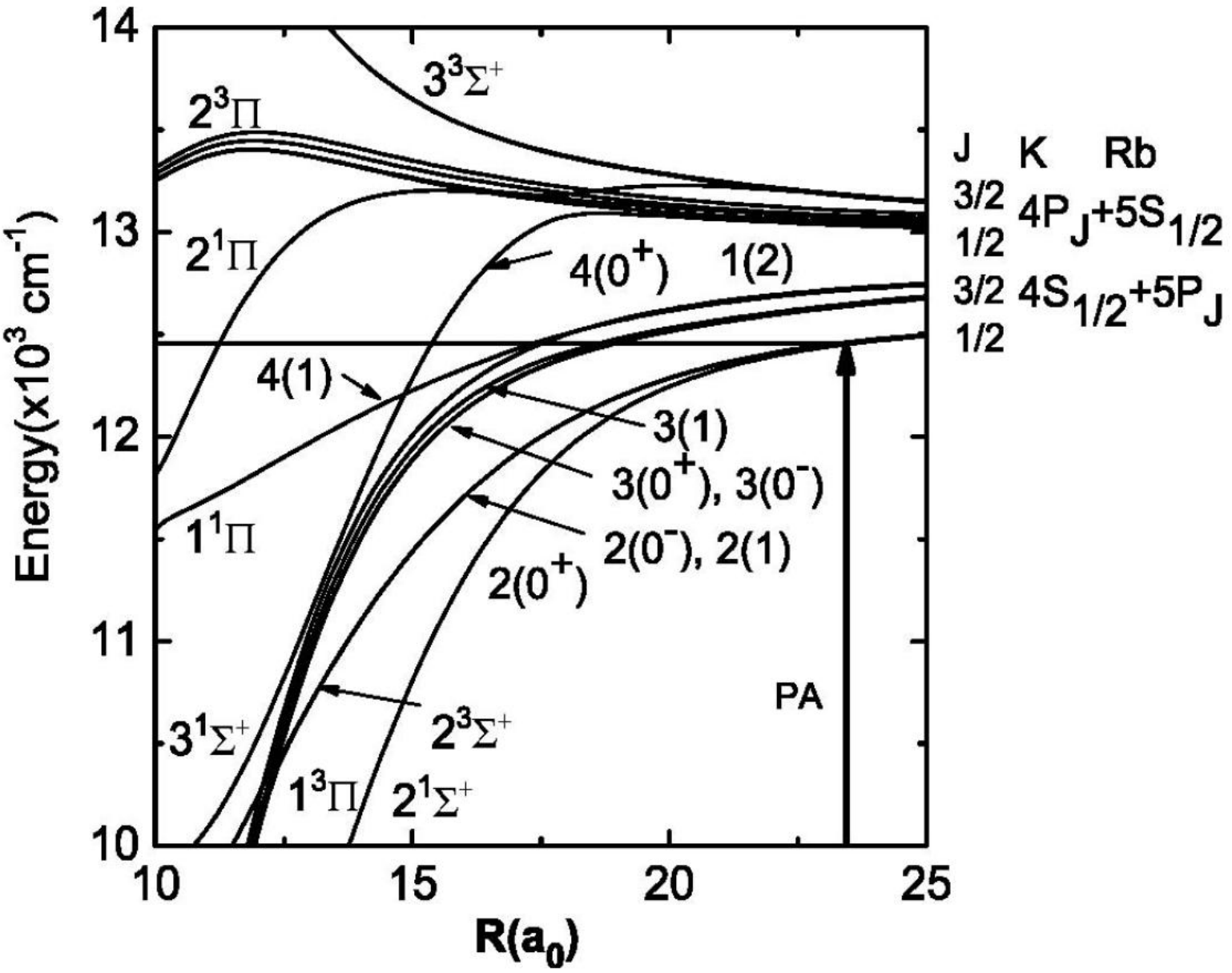
a state $\Omega = 0- \quad \leftrightarrow \Omega = 0-, 1$

$\Omega = 1 \quad \leftrightarrow \Omega = 0+, 0-, 1, 2$

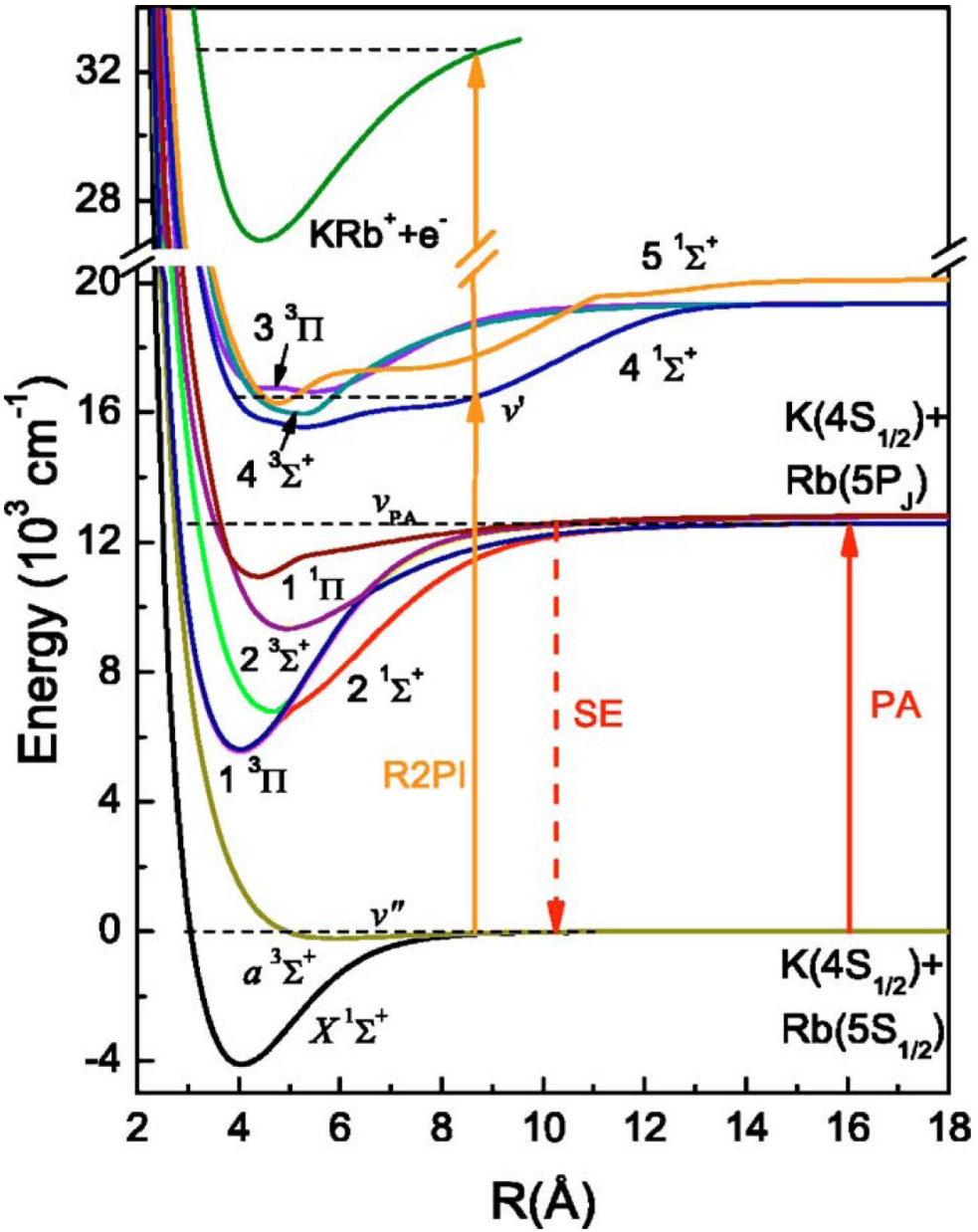
KRb Long-Range Potential Curves



KRb Intermediate-Range Potential Curves



Vibrational-State-Selective REMPI



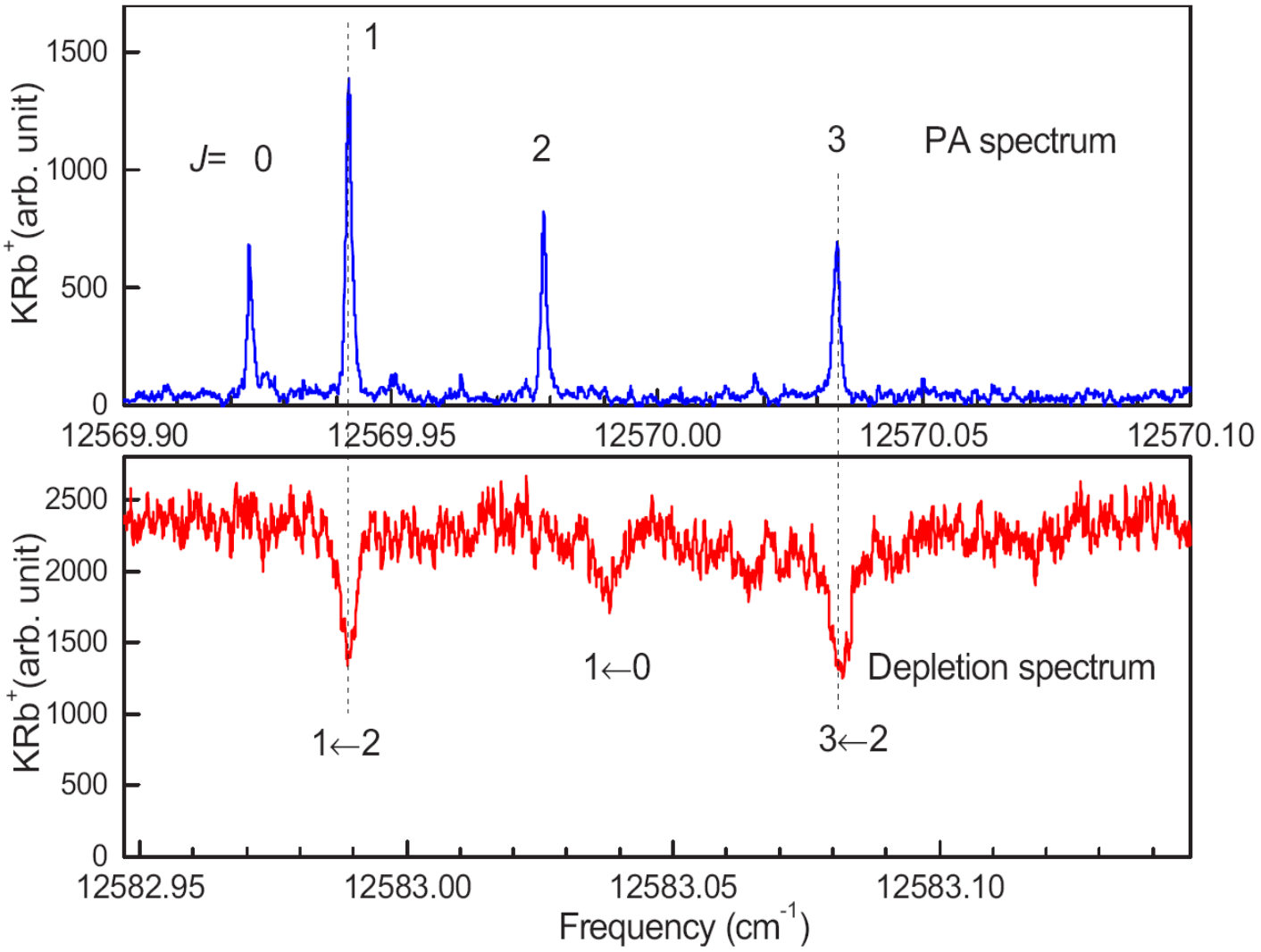
Upper level of PA and UM spectrum --------

Dissociation Limit of two atoms --------

binding energy

Near Dissociation Rovibrational Level --------

PA and Depletion Spectra for the Same Upper 0^+ level



Binding Energy of *X* state *(v=87, J=0)* and the *X* state Dissociation Energy

Binding Energy of $X_{(v=87, J=0)}$

$= (E_{(3\Sigma^+, v', J'=1)} - E_{(X, v''=87, J''=0)}) - (E_{(3\Sigma^+, v', J'=1)} - E_{(X, k''>0,\ J''=0)})$

$= 23.397 \pm 0.002\ \text{cm}^{-1}$

Dissociation Energy of *X*

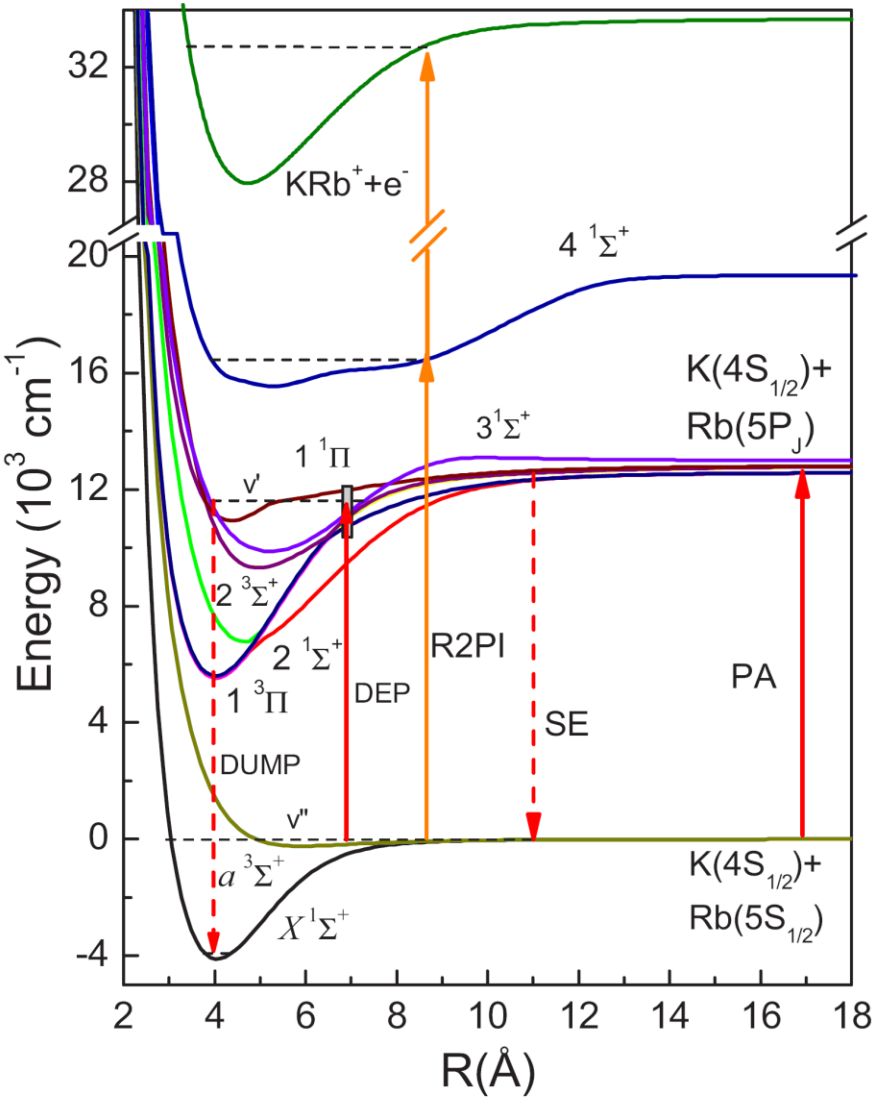
$= (E_{(X, v''=87, J''=0)} - E_{(X, v''=0, J''=0)})$ [Amiot] $- (E_{(X, v''=87, J''=0)} - E_{(X, k''>0, J''=0)})$

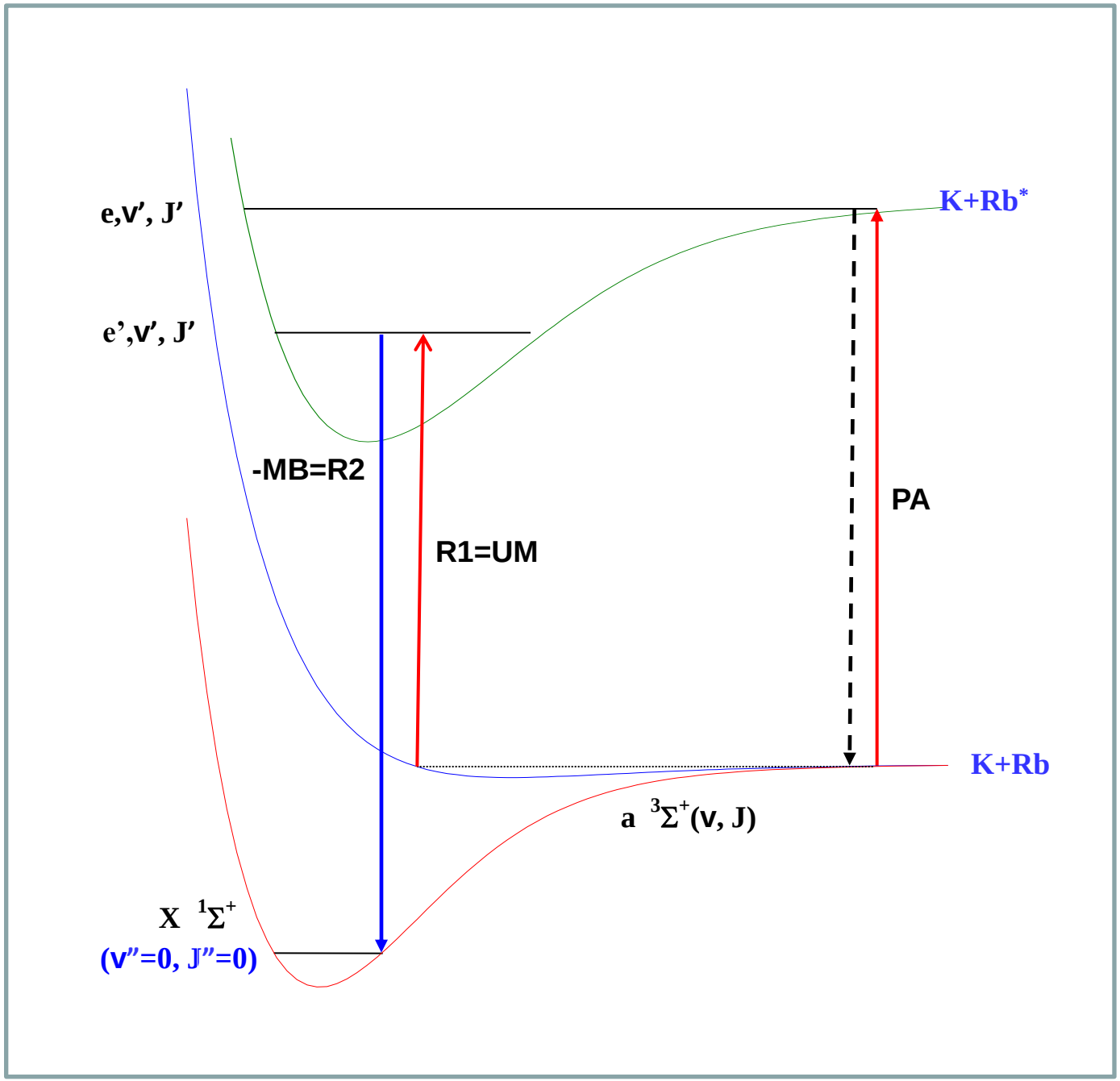
$= 4156.492 + 23.397 + 0.069$ [hyperfine]

$= 4179.958 \pm 0.003\ \text{cm}^{-1}$ [prior 4180.06 ± 0.42]

Tiemann et al. value for $X = 4179.916 \pm 0.006\ \text{cm}^{-1}$ [question Amiot's *v*=87 assignments]

REMPI from X and a Levels Near Dissociation with PUMP (Depletion) and DUMP lasers added to produce $X(0,0)$




e,v', J'
e',v', J'
K+Rb*
-MB=R2
R1=UM
PA
K+Rb
a $^3\Sigma^+$(v, J)
X $^1\Sigma^+$
(v"=0, J"=0)

Upper level with Ω = 0+, 1 ----------

(~15000-16000 cm-1)

a state level with Ω = 0-, 1 ----------UM

(~4400 cm-1)

X(0,0) level with Ω = 0+ MB----------

(0 cm-1)

I(Stimulated Raman) ~

|<a, v, J| d(a/e) | e, v', J'>| **2 x

|<e, v', J'| d(e/X) | X, v"=0, J"=0>|**2/ΔE

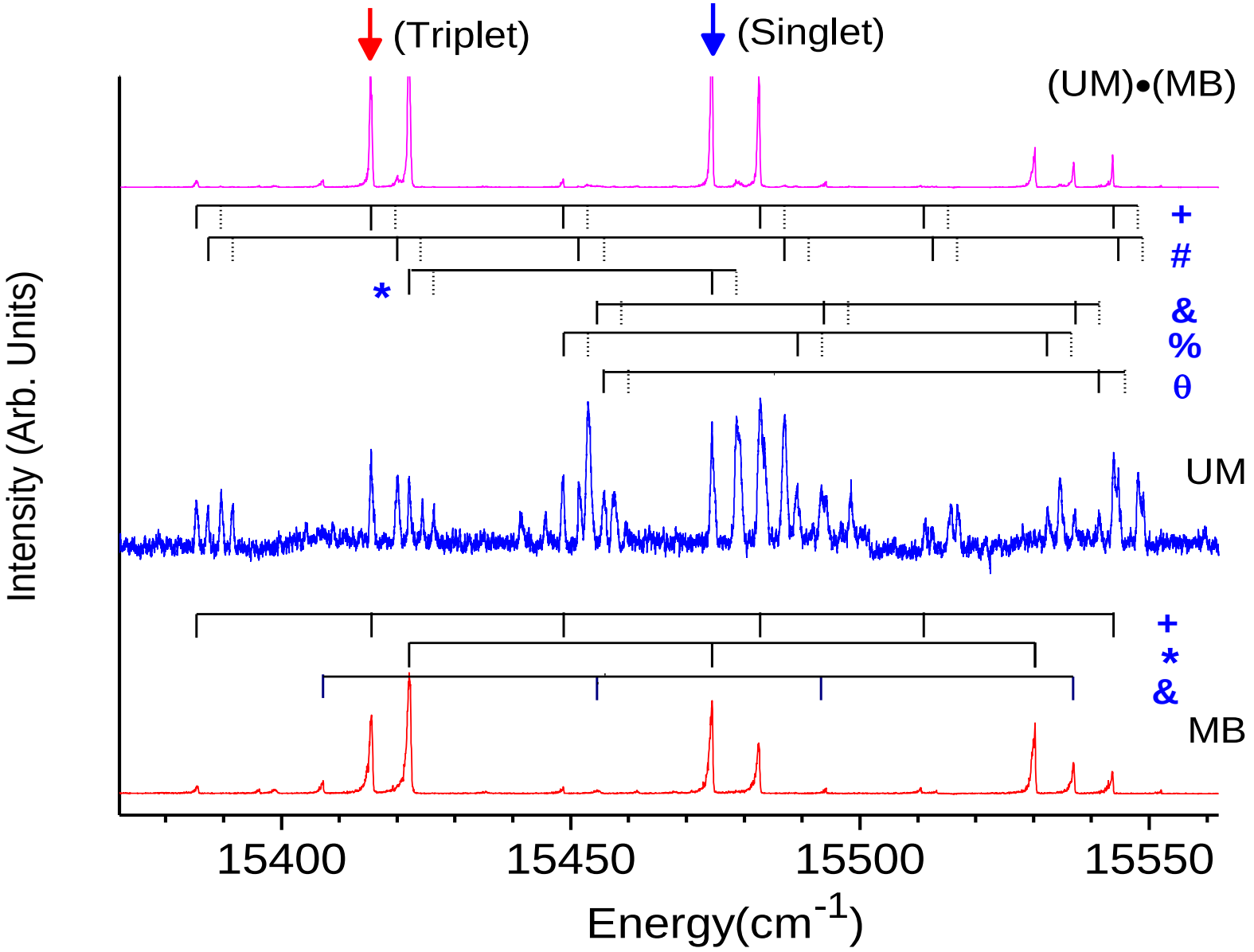
I(Molecular Beam) ~

|<X,v"= 0,J"= 0|d(X/e)|e,v',J'>|**2

I(Ultracold Molecule) ~

|<a,v,J|d(a/e)|e,v',J'>|**2

I(SR) ~ I(MB) x I(UM)


(Triplet)
(Singlet)
(UM)•(MB)
+
#
*
&
%
θ
UM
+
*
&
MB
Intensity (Arb. Units)
15400
15450
15500
15550
Energy(cm-1)

MBxUM Product Spectra-1

- Optimal products without assignment of the intermediate rovibronic state (which is seriously perturbed in many alkali dimer spectra under consideration for stimulated Raman transfer (SR)).
- The same MB spectra can be used with

  UM spectra from any given X or a state vibrational level.

MBxUM Product Spectra-2

- The MB spectra can be replaced by depletion spectra from the X(0,0) level obtained in other ways.
- The shift of the UM spectra by the energy of the UM level minus the energy of the X(0,0) level can also be used to determine one of those two quantities if the other is unknown.

Other Paths to X(0,0)

- STIRAP from PA-formed X state UM near dissociation via 3 singlet SIGMA+ (Aikawa et al., PRL **105**, 203001 (2010))
- Spontaneous emission from PA-formed resonantly-coupled levels (2(1), v’ = 165 LR level + 4(1), v’ = 61 SR level) (Banerjee et al., Phys. Rev. A **86**, 053428 (2012))
- Other molecules (K2, RbCs, LiCs, NaCs)

Other Target States in Alkali Dimers-1

- Lowest rovibronic metastable triplet a(0,0) by spontaneous emission of 2 triplet PI formed by blue-detuned PA (See Kim et al., New J. Phys. **11**, 055020 (2009); also Bellos et al., PCCP, **13**, 18880 (2011) for the analogous Rb2 case where the v”=0 level of the a state is observed)

Other Target States in Alkali Dimers-2

- Lowest rovibronic level of KRb+ (X+(0,0)) by autoionization from low vibrational levels of the 2 triplet PI or 3 triplet SIGMA+ states formed by blue-detuned PA (See Kim et al., New J. Phys. **11**, 055020 (2009); Lee et al., J. Chem. Phys., **120**, 6551 (2004))

Such autoionization was observed at high T in Na2 (C.-C. Tsai et al., Chem. Phys. Lett., **236**, 553 (1995))

Other Target States in Alkali Dimers-3

- Lowest rovibronic level of lowest antibonding state of KRb+ (Re ~ 18 ao) by autoionization from the outer well of the 0+ component of the 2 triplet PI state formed by PA.
- This outer well (Re ~ 18 ao) is predicted to have 4 vibrational levels, 3 of which we have observed (New J. Phys. **11**, 055020 (2009)

Summary

Ultracold Chemical Physics is an exciting field involving the quantum behavior of molecules at T< 1mK.

A variety of target states are of special interest because of their stability/metastability.

The spectroscopy and dynamics of molecules at low T is now available for study and possible applications to ultracold chemistry, quantum information, new phases of matter, etc.

Short Range Photoassociation to form *a*(0,0)

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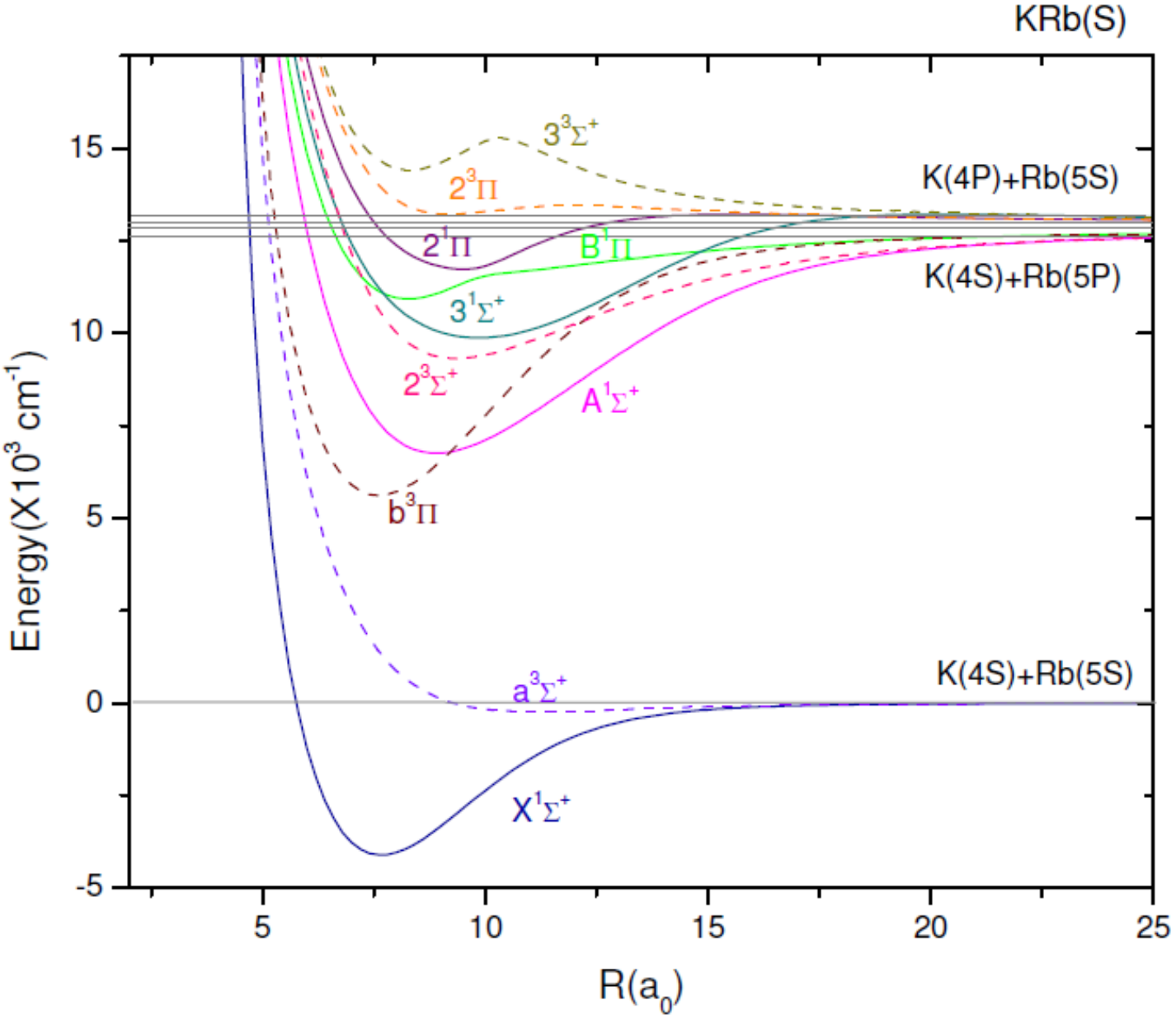
- *Department of Physics*
- *University of Connecticut*

- *Supported by AFOSR(MURI), NSF, UConn Foundation*

KRb Short-Range Potential Curves



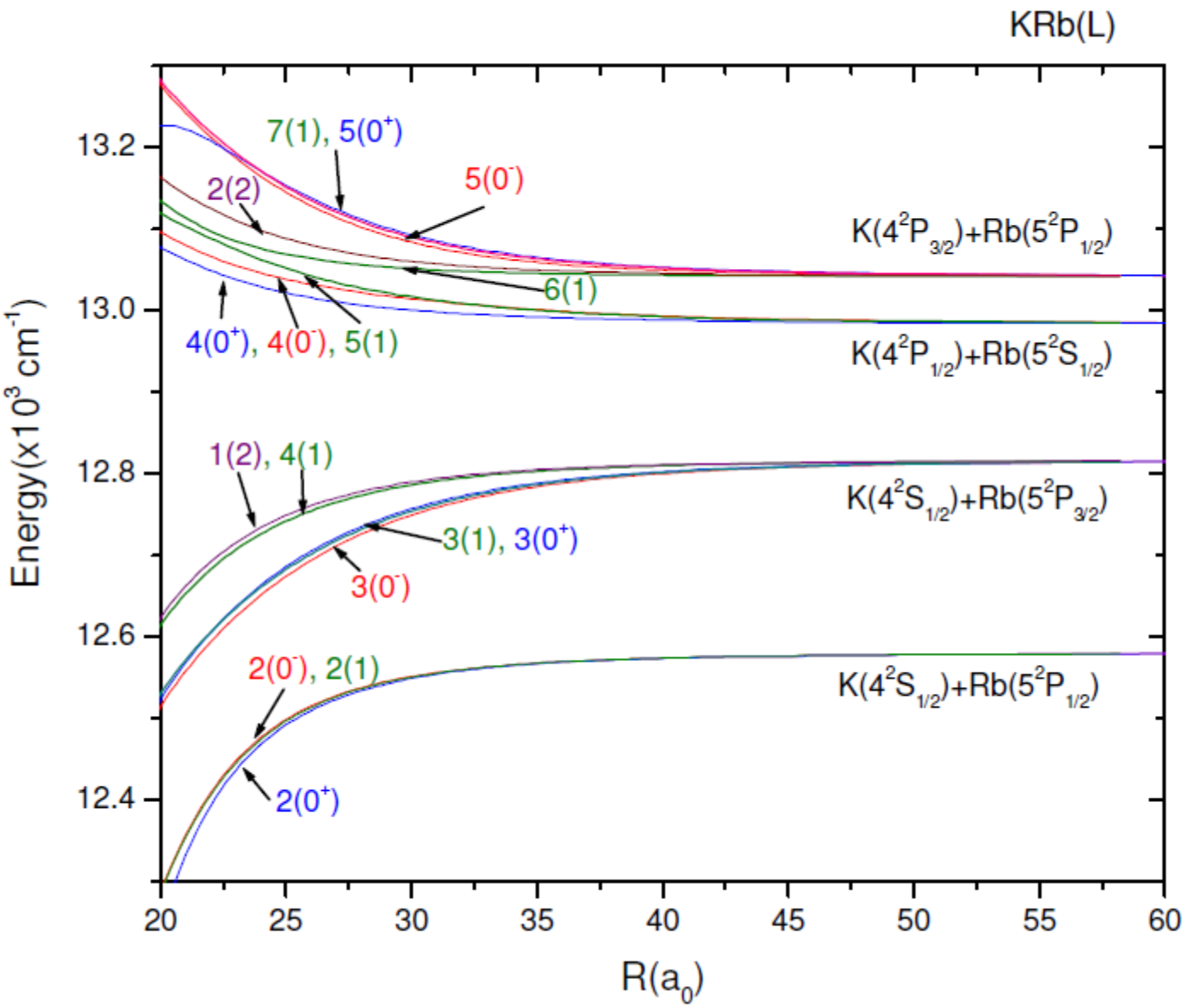
X & a State LR Selection Rules

X state $\Omega = 0+ \leftrightarrow \Omega = 0+, 1$

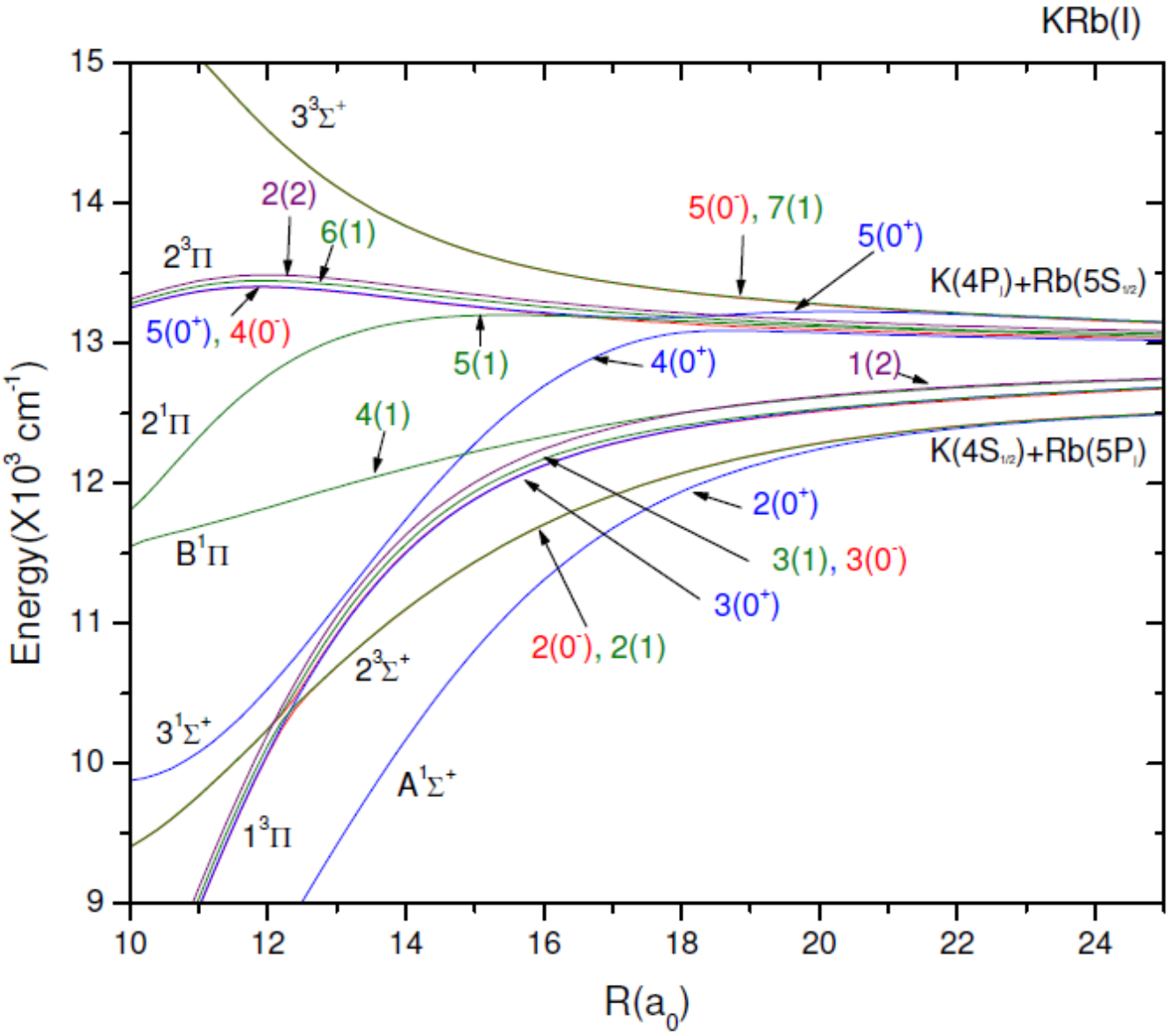
a state $\Omega = 0- \leftrightarrow \Omega = 0-, 1$

$\Omega = 1 \leftrightarrow \Omega = 0+, 0-, 1, 2$

KRb Long-Range Potential Curves

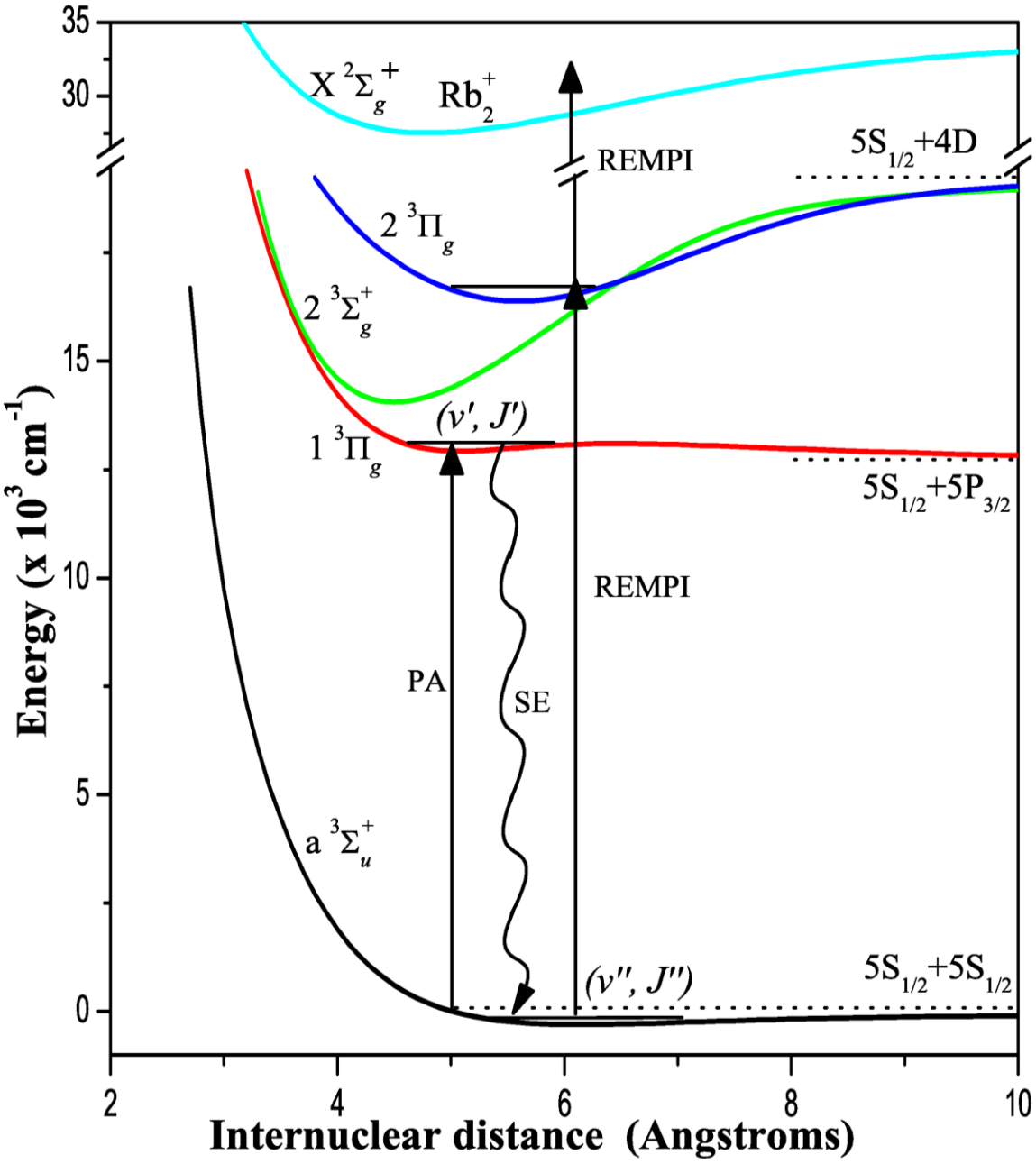


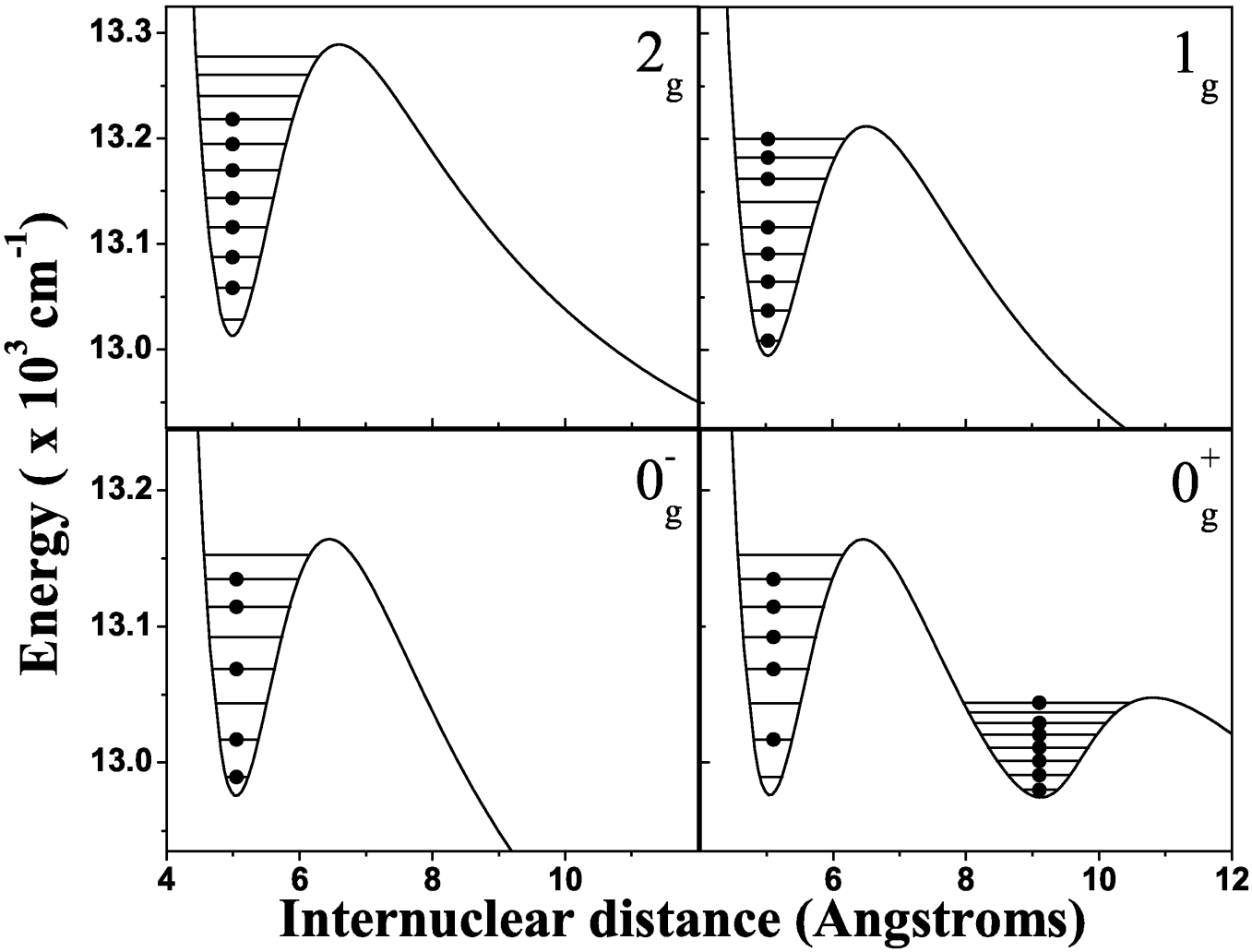
KRb Intermediate-Range Potential Curves

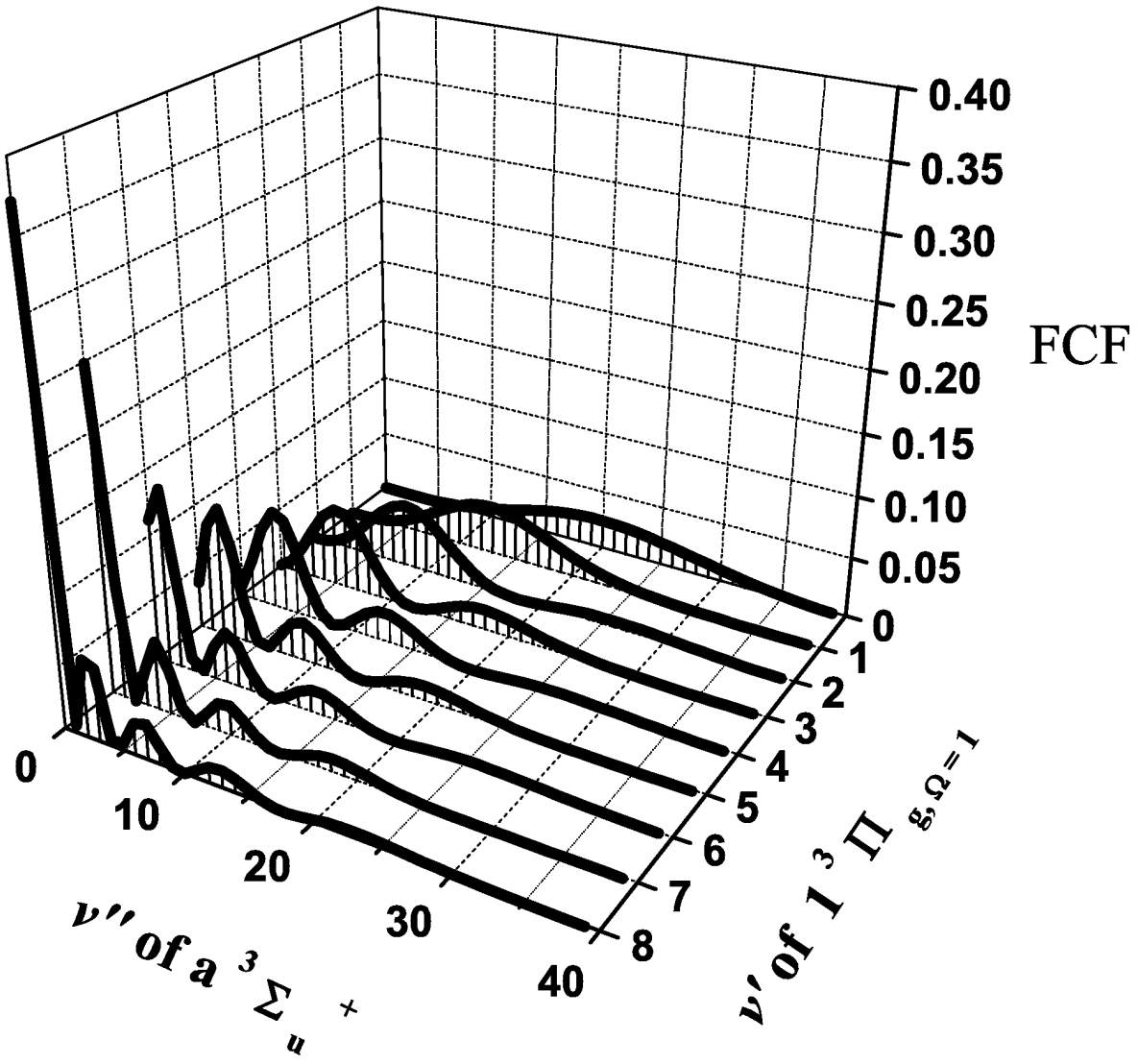


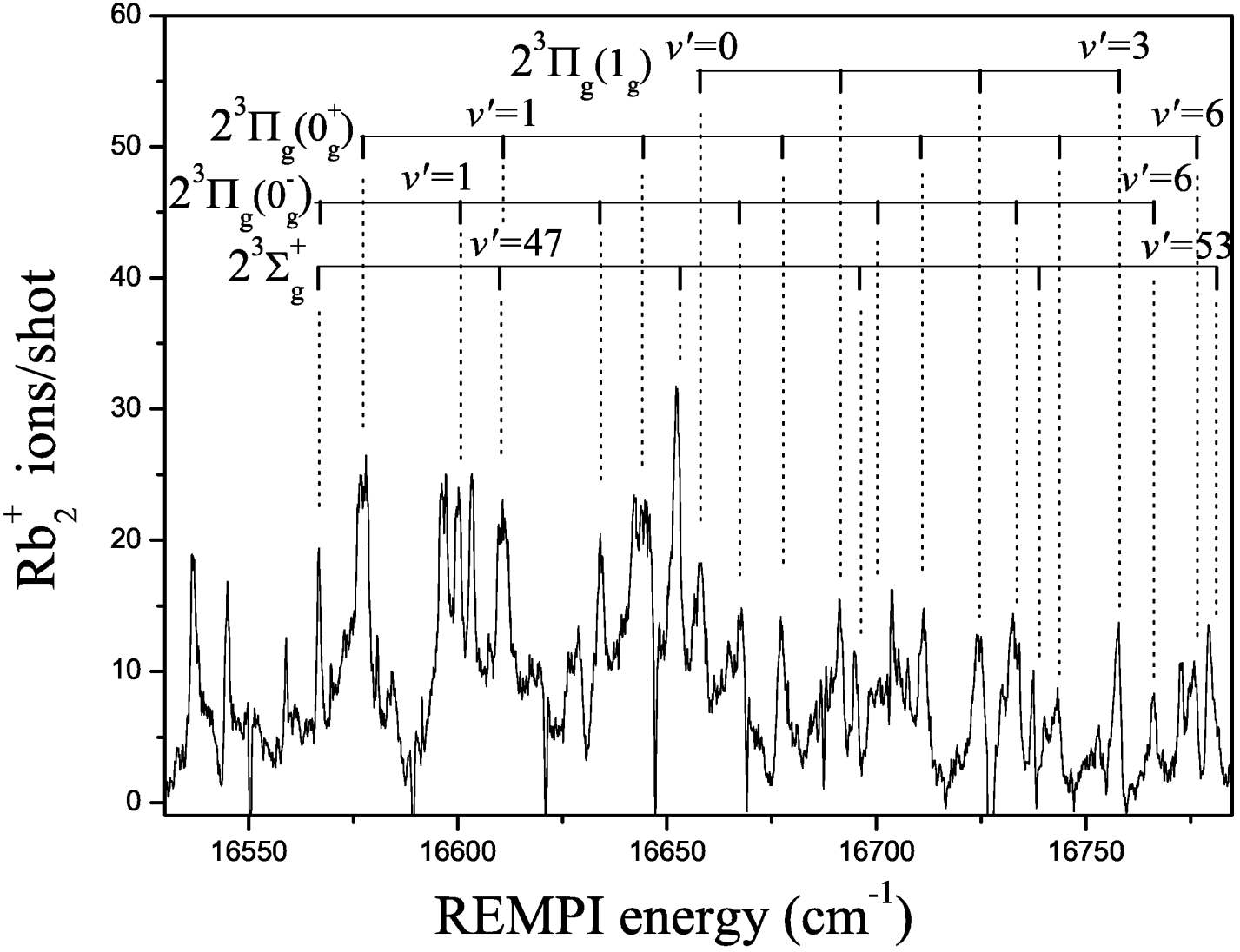
SHORT RANGE PHOTOASSOCIATION: Franck-Condon Factors for formation of *a*(0,0)

Ω	$1^3\Pi_g$ $^{85}Rb_2$	$2^3\Pi$ $^{39}K^{85}Rb$
0^+	0.40, v' = 7	0.42, v' = 6
0^-	0.40, v' = 7	0.42, v' = 6
1	0.37, v' = 8	0.36, v' = 6
2	0.30, v' = 9	0.34, v' = 7


35
30
15
10
5
0
2
4
6
8
10
Energy (x 10^3 cm^-1)
Internuclear distance (Angstroms)
X ²Σg+ Rb2+
REMPI
5S1/2+4D
2 ³Πg
2 ³Σg+
(v', J')
1 ³Πg
5S1/2+5P3/2
REMPI
PA
SE
a ³Σu+
(v'', J'')
5S1/2+5S1/2


Energy (x 10^3 cm^-1)
13.3
13.2
13.1
13.0
2g
1g
0g-
0g+
13.2
13.1
13.0
4
6
8
10
6
8
10
12
Internuclear distance (Angstroms)


0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
FCF
0
10
20
30
40
v'' of a 3Σu+
0
1
2
3
4
5
6
7
8
v' of 1 3 Π g,Ω=1


60
50
40
30
20
10
0
Rb_2^+ ions/shot
16550
16600
16650
16700
16750
REMPI energy (cm^{-1})
$2^3\Pi_g(1_g)$ v'=0
v'=3
$2^3\Pi_g(0_g^+)$
v'=1
v'=6
$2^3\Pi_g(0_g^-)$
v'=1
v'=6
$2^3\Sigma_g^+$
v'=47
v'=53