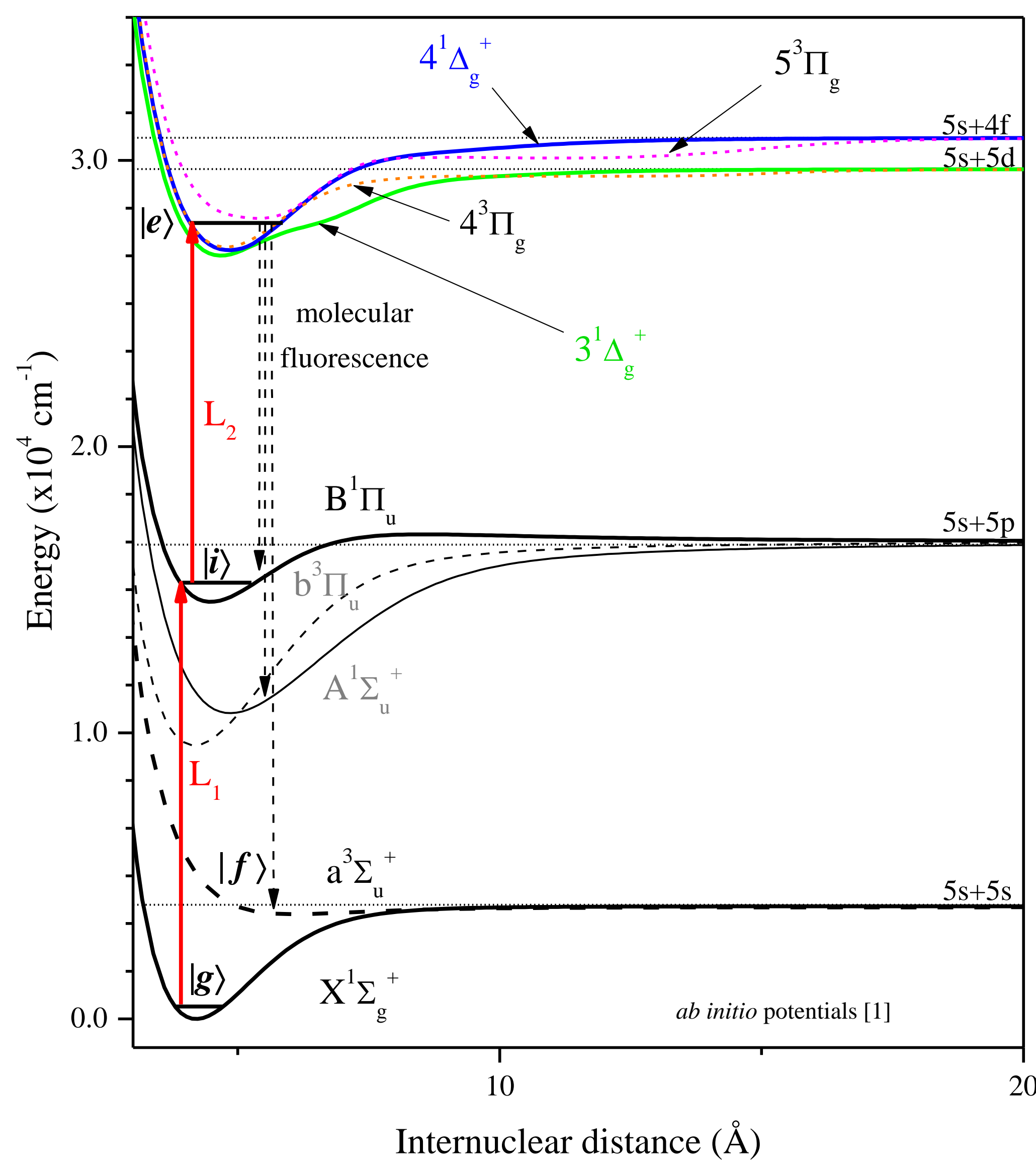
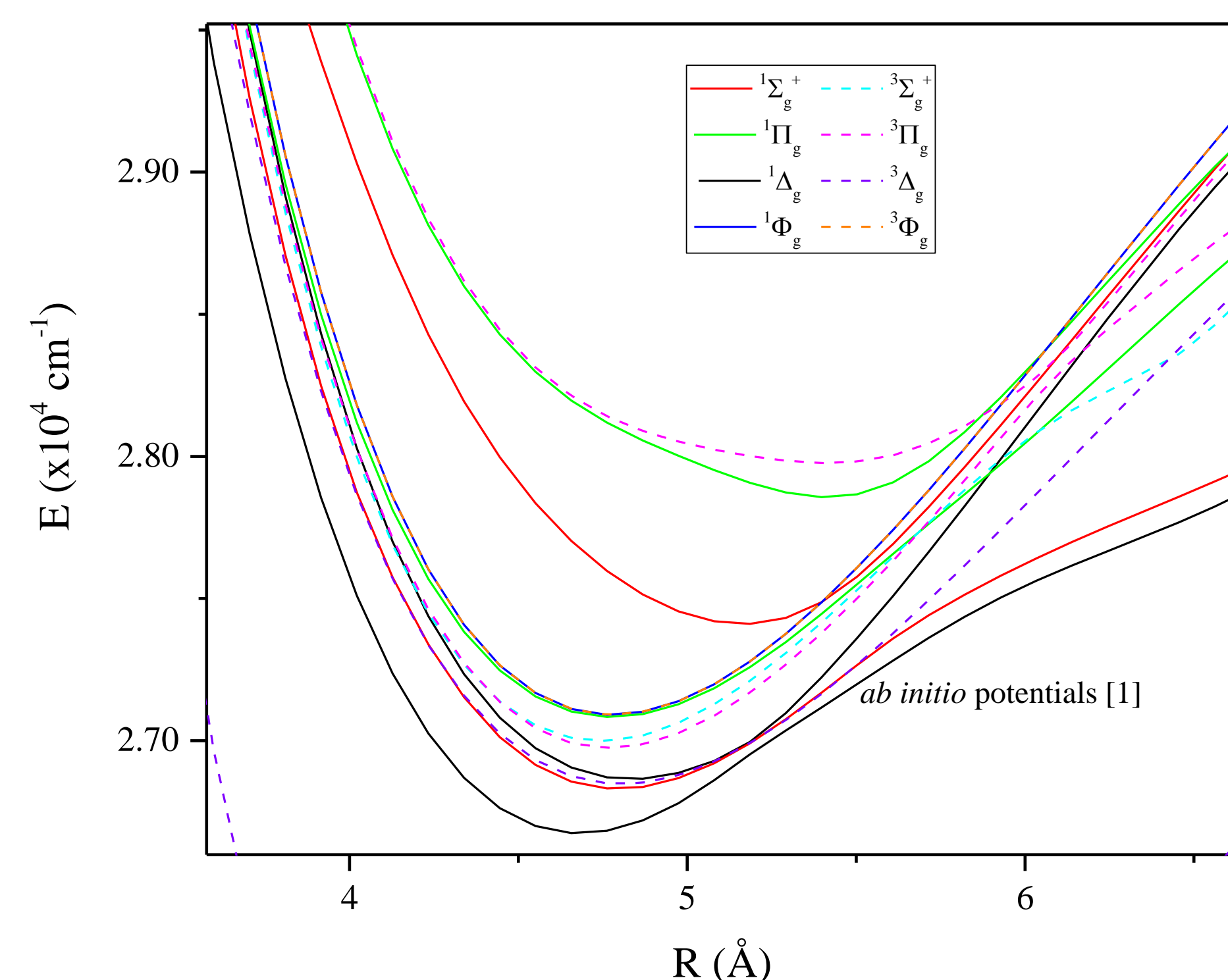
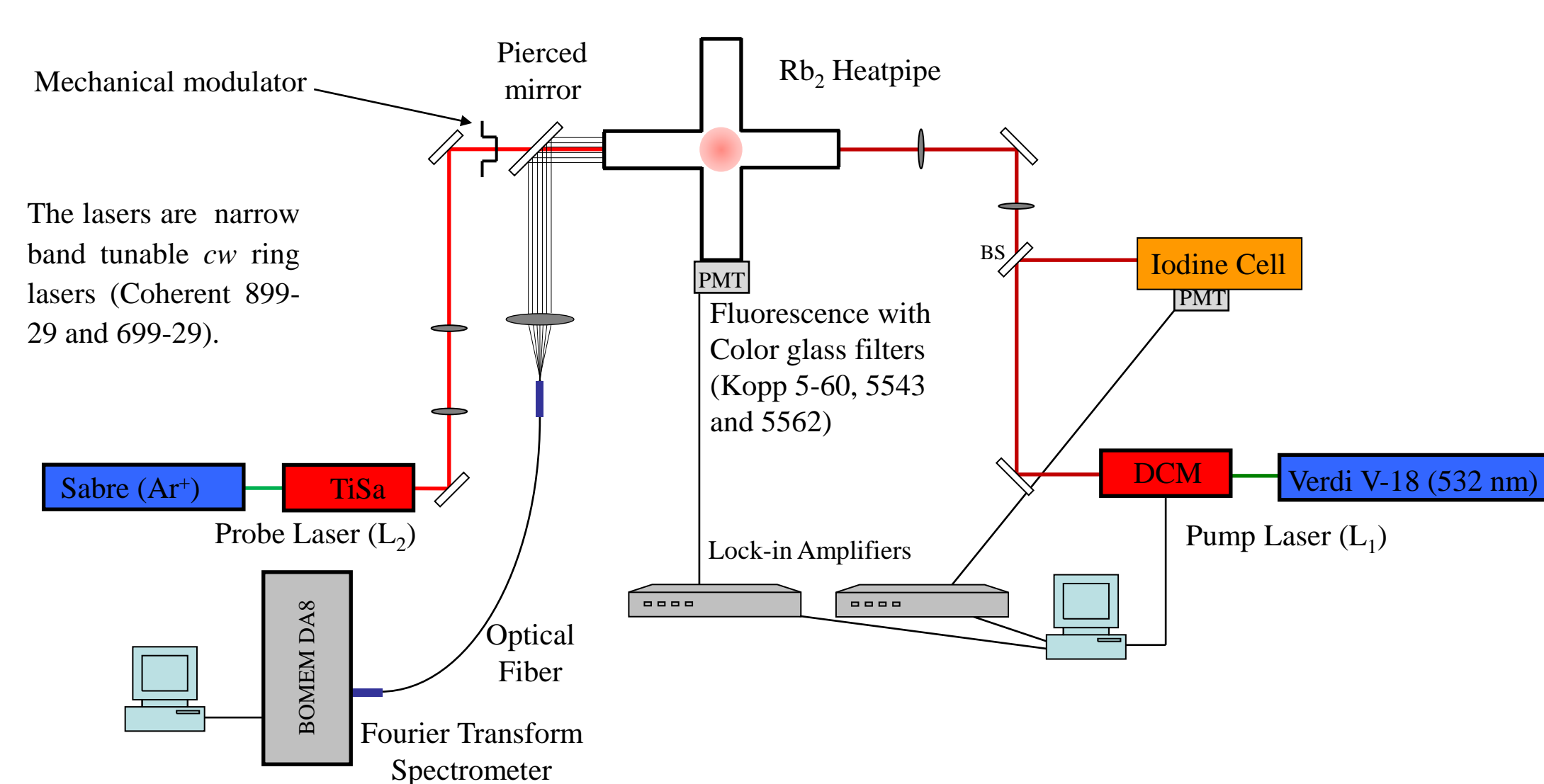
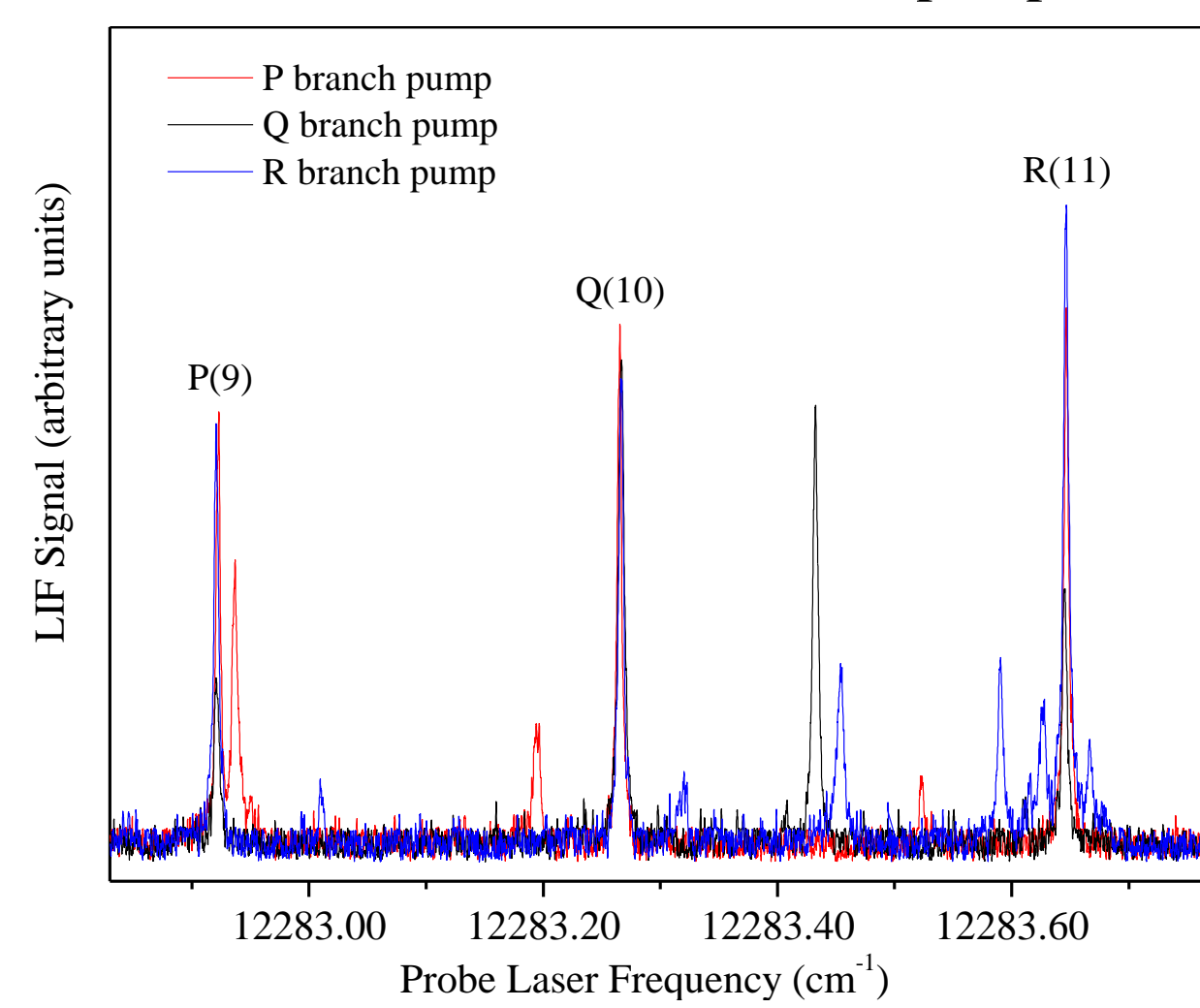


**Abstract**

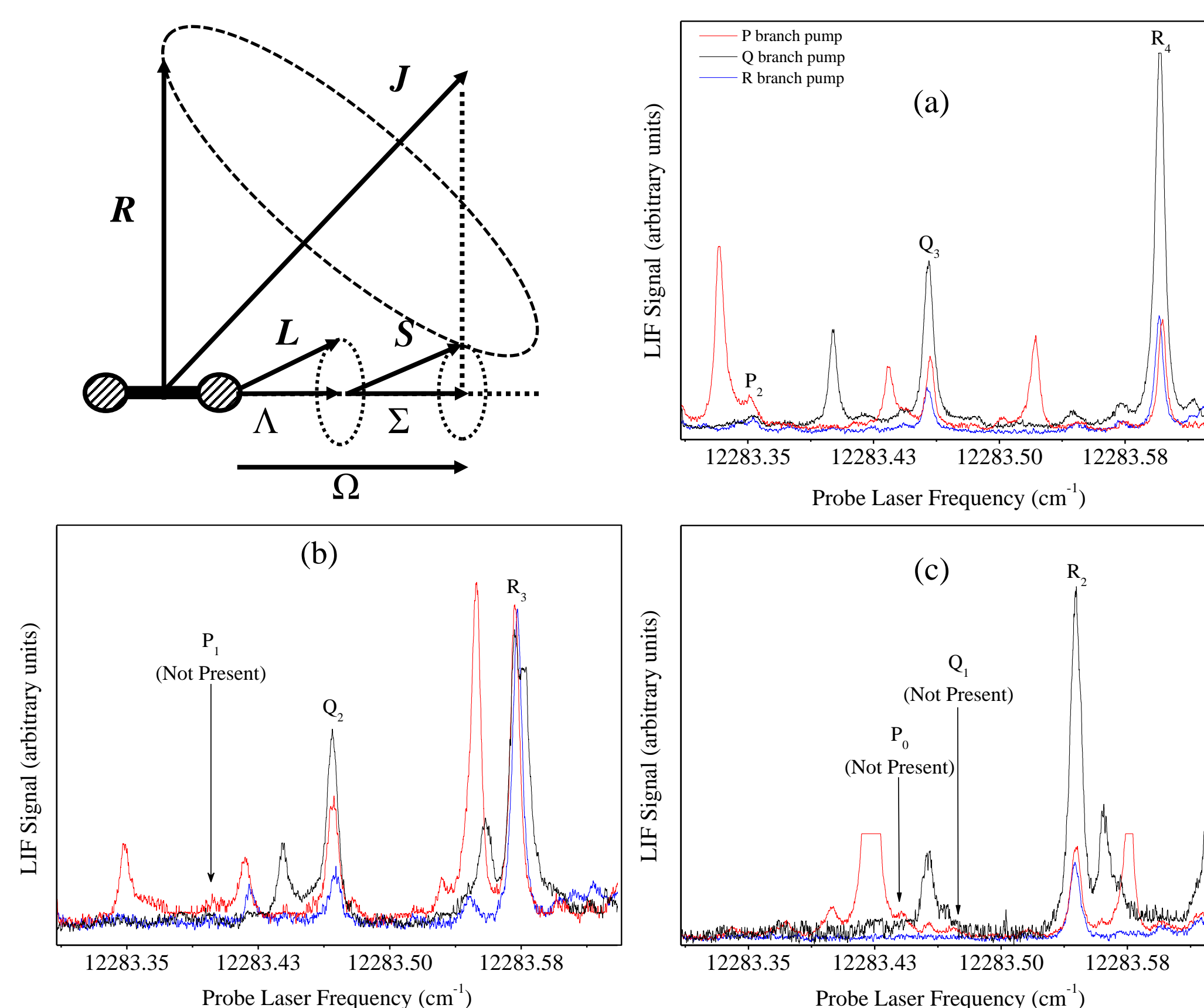
We report a high-resolution experimental study of the highly excited  $3^1\Delta_g$  and  $4^1\Delta_g$  electronic states of the  $^{85}\text{Rb}_2$  dimer. Rovibrational levels of the two electronic states were probed using the optical-optical double resonance (OODR) technique by exciting  $^{85}\text{Rb}_2$  molecules from thermally populated levels of the  $X^1\Sigma_g^+$  ground state through intermediate levels of the  $B^1\Pi_u$  electronic state. The  $^1\Delta_g$  resonances induced by the probe laser were observed by detecting laser induced fluorescence (LIF) from nearby, collisionally populated triplet states down to the  $a^3\Sigma_u^+$  triplet ground state. The  $^1\Delta_g$  character of the two electronic states was confirmed by showing that the transitions to these states abide by  $^1\Pi - ^1\Delta$  dipole selection rules and by observing that their lowest rotational level is  $J = 2$ . Preliminary molecular constants and Rydberg-Klein-Rees (RKR) potential energy curves from the observed term values were calculated for each electronic state and compared with *ab initio* calculations.

**Excitation scheme and relevant electronic states of  $^{85}\text{Rb}_2$** 

**Zoomed in view of electronic states arising from the  $^{85}\text{Rb}(5s) + ^{85}\text{Rb}(5d)$  and  $^{85}\text{Rb}(5s) + ^{85}\text{Rb}(4f)$  dissociation limits**

**Experimental setup**

**Example OODR excitation spectra**

Observed LIF from  $4^1\Delta_g(v=7, J=9, 10, 11) \leftarrow B^1\Pi_u(v'=5, J'=10)$  for P (red), Q (black) and R branch (blue) pump excitations.


**Identifying the  $\Lambda$  quantum number of the observed electronic states**
**Angular Momenta:**

- $L$ : electron orbital angular momentum
- $\Lambda$ : magnitude of projection of  $L$  onto internuclear axis
- $R$ : nuclear rotational angular momentum
- $S$ : electron spin
- $\Sigma$ : magnitude of projection of  $S$  onto internuclear axis
- $\Omega = |\Lambda + \Sigma|$ : total angular momentum projection onto internuclear axis
- $J = R + L + S$ : total angular momentum excluding nuclear spin



LIF from: (a)  $4^1\Delta_g(v=7, J=2, 3, 4) - B^1\Pi_u(v'=5, J'=3)$  showing P, Q, and R branches; (b)  $4^1\Delta_g(v=7, J=2, 3) - B^1\Pi_u(v'=5, J'=2)$  showing missing P branch; & (c)  $4^1\Delta_g(v=7, J=2) - B^1\Pi_u(v'=5, J'=1)$  showing missing P and Q branches. All above probe spectra were recorded three times: pumping from a P branch (red), Q branch (black) and R branch (blue).

The above spectra show that  $\Lambda = 2$  ( $\Rightarrow ^1\Delta$ ) for the observed state.

\*This pattern was observed for both states. (not shown here)

**Orientation Factors for  $\Delta\Omega = +1, \Delta M = 0$  (e.g.  $^1\Delta \leftarrow ^1\Pi, ^1\Pi \leftarrow ^1\Sigma$ ) transitions**

- These are independent of  $v$  and proportional to the overall signal, but derived for single laser excitations.

$$\langle \Omega J M | \alpha \bar{z} | \Omega' J' M' \rangle = \langle \Omega = \Omega' + 1, J, M = M' | \alpha \bar{z} | \Omega' J' M' \rangle = f(J, J') (g_x - i g_y) h_z$$

$$= -\frac{\sqrt{(J'+\Omega'+1)(J'+\Omega'+2)}\sqrt{(J+1)^2-M^2}}{(J+1)\sqrt{(2J'+1)(2J+3)}} \quad \text{for } J = J' + 1$$

$$= \frac{\sqrt{(J'-\Omega')(J'+\Omega'+1)M}}{J'(J+1)} \quad \text{for } J = J'$$

$$= \frac{\sqrt{(J'-\Omega')(J'-\Omega'-1)}\sqrt{J^2-M^2}}{J'\sqrt{(2J'+1)(2J-1)}} \quad \text{for } J = J' - 1$$

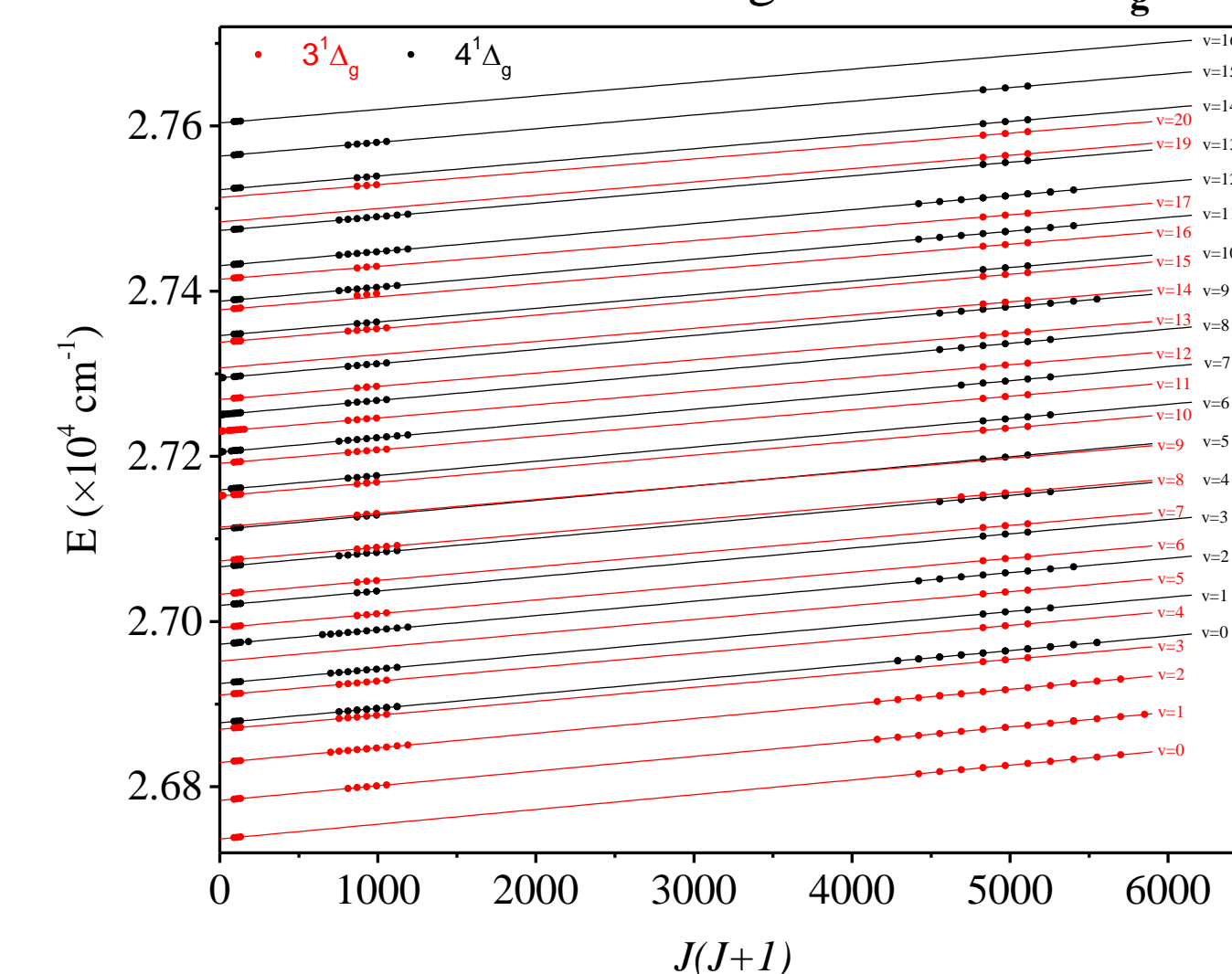
- Predicted vs. observed excitation-dependent rotational-branch signal-strength ratios for  $4^1\Delta_g \leftarrow ^1\Pi_u \leftarrow ^1\Sigma_g^+$  (two laser) excitations:

$J'$	Pump	Predicted	Observed
10	R	0.54 : 0.65 : 1	0.65 : 0.73 : 1
	Q	0.11 : 1 : 0.25	0.34 : 1 : 0.52
	P	0.53 : 0.83 : 1	0.80 : 0.97 : 1
3	R	0.11 : 0.26 : 1	0.09 : 0.36 : 1
	Q	0.03 : 1 : 0.55	0.03 : (0.45 : 1) <sup>†</sup>
	P	0.10 : 0.54 : 1	0.30 : 0.66 : 1
2	R	0 : 0.13 : 1	0 : 0.18 : 1
	Q	0 : 1 : 0.94	0 : (0.66 : 1) <sup>†</sup>
	P	0 : 0.38 : 1	0 : 0.40 : 1
1	R	0 : 0 : 1	0 : 0 : 1
	Q	0 : 0 : 1	0 : 0 : 1
	P	0 : 0 : 1	0 : 0 : 1

<sup>†</sup> Off from prediction – potentially due to additional resonances at the same energy as the R branches, or a perturbed (*e* parity) Q branch, or both.

**Observed ro-vibrational levels**

Assigned rovibrational levels of the  $3^1\Delta_g$  (red) and  $4^1\Delta_g$  (black) electronic states. 480 rovibrational levels spanning from  $v=0$  to  $v=20$  and  $J=2$  to  $J=74$  were assigned for the  $3^1\Delta_g$  state, and 543 rovibrational levels spanning from  $v=0$  to  $v=16$  and  $J=2$  to  $J=76$  were assigned for the  $4^1\Delta_g$  state.


**Analysis and potential curves**
**Dunham Expansion [1]**

The energy levels of a vibrating rotor in the framework of first order semiclassical quantization is given by:

$$T_{v,J} = \sum_{k,l} Y_{k,l} \left( v + \frac{1}{2} \right)^k [J(J+1) - \Omega^2]^l$$

The  $Y_{k,l}$  coefficients are related to the molecular potential parameters by a set of power series equations in  $v$  and  $J$  and given as follows:

$$G_v = \sum_{k=1} Y_{k0} \left( v + \frac{1}{2} \right)^k = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \dots$$

$$F_J = \sum_{l=0} Y_{0l} [J(J+1)]^l = B_v J(J+1) - D_v [J(J+1)]^2 + \dots$$

$$B_v = B_e - \alpha_e \left( v + \frac{1}{2} \right) + \gamma_e \left( v + \frac{1}{2} \right)^2 + \dots$$

$3^1\Delta_g$	$T_0(Y_{00})$	$\omega_e(Y_{10})$	$-\omega_e x_e(Y_{20})$	$\omega_e y_e(Y_{30})$	$B_e(Y_{01})$
This work	26710.370	51.9815	-0.09021913857	-0.002996955245	0.018255
<i>ab initio</i> [2]	26697.7	47.4			0.01809
<i>ab initio</i> [3]	27212	56.5			0.01668
$4^1\Delta_g$	$T_0(Y_{00})$	$\omega_e(Y_{10})$	$-\omega_e x_e(Y_{20})$	$\omega_e y_e(Y_{30})$	$B_e(Y_{01})$
This work	26853.648	47.7014	-2.52581	0.259762	0.017503
<i>ab initio</i> [2]	26886.7	43.2			0.01696

All above values are given in units of  $\text{cm}^{-1}$ .

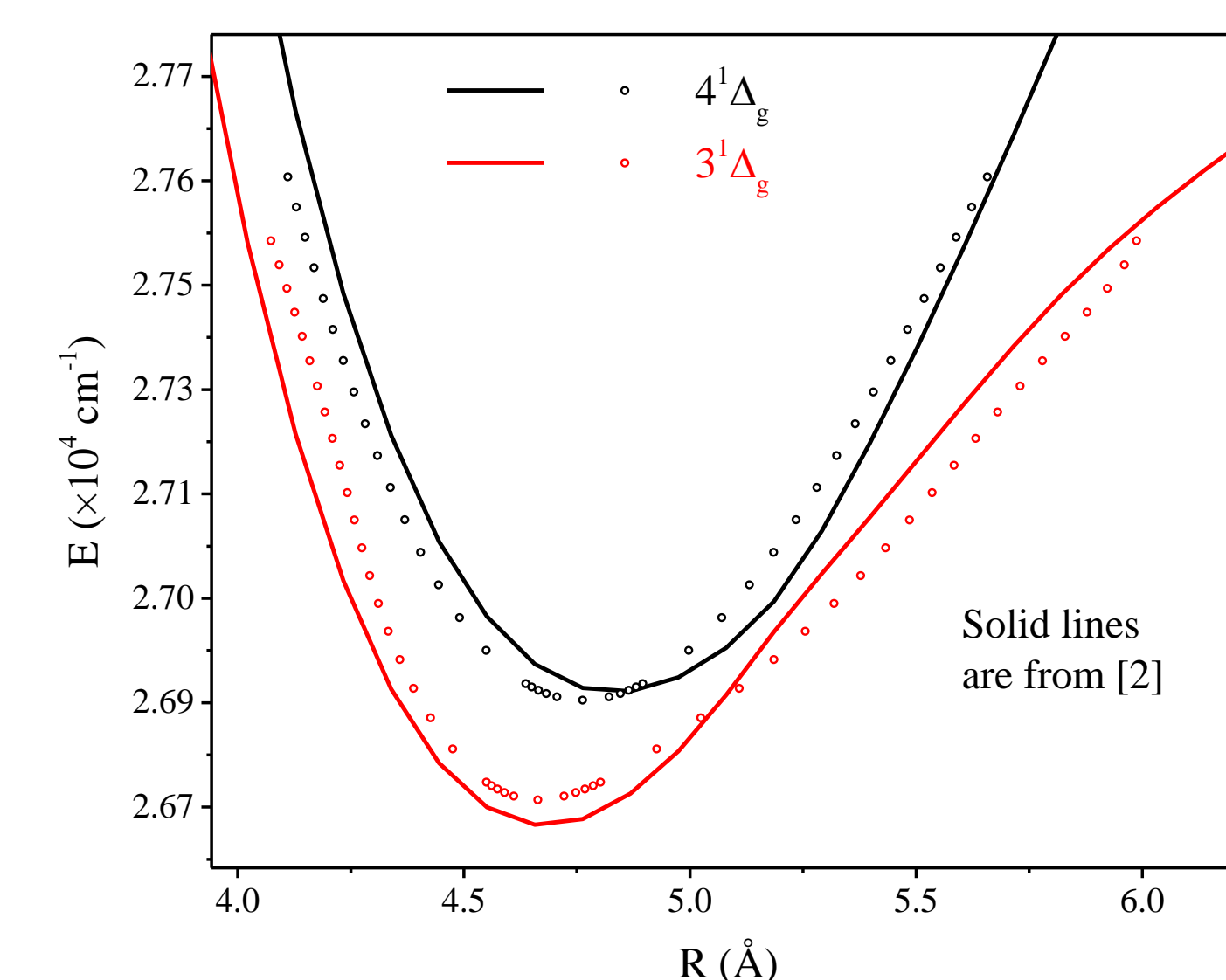
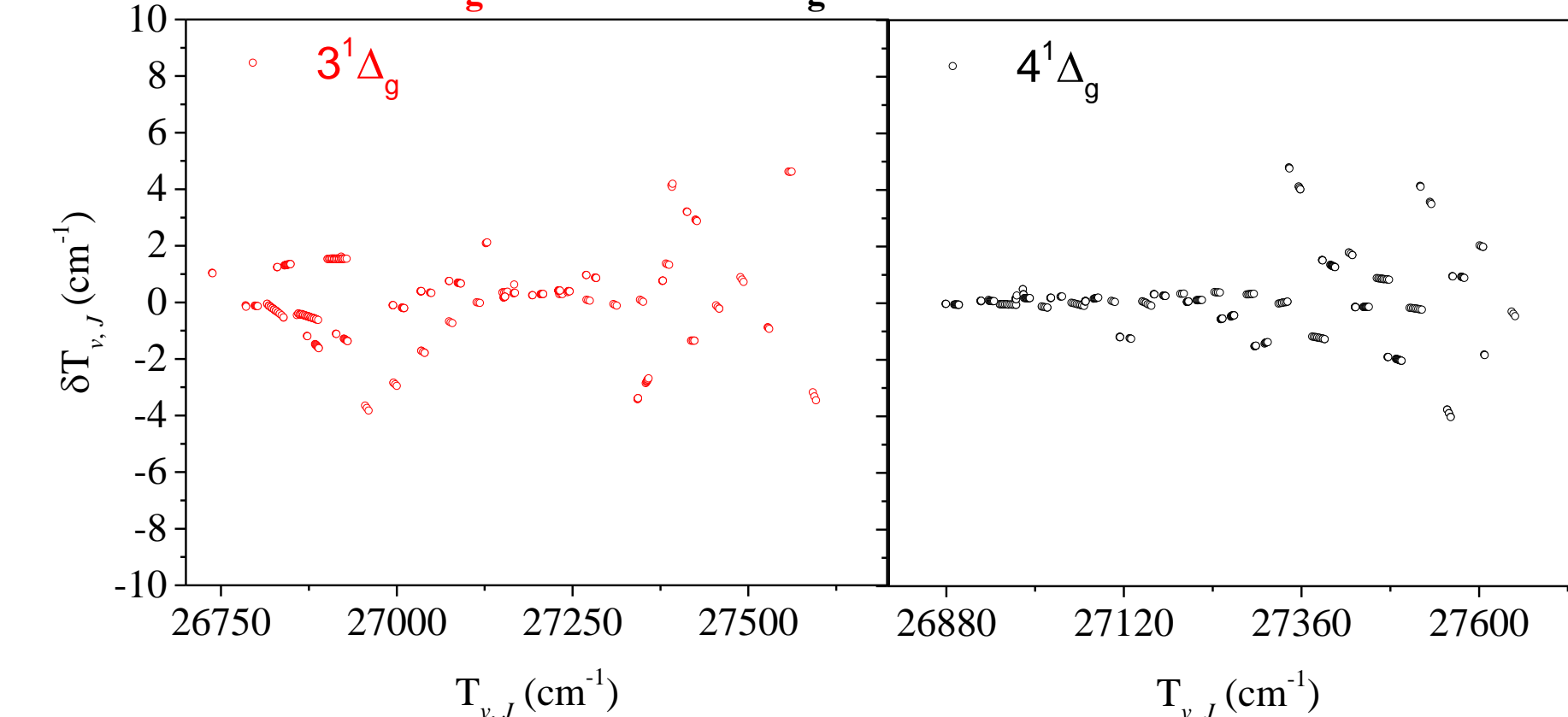
**RKR Potential Energy Curves [4]**

The fitted  $G_v$  and  $B_v$  constants from the Dunham expansion are related to the potential energy curve turning points via the Klein integrals:

$$r_2(v) - r_1(v) = C \int_{v_{\min}}^v \frac{dv'}{[G_v - G_{v'}]^{1/2}} \quad \text{and}$$

$$\frac{1}{r_1(v)} - \frac{1}{r_2(v)} = C \int_{v_{\min}}^v \frac{B_{v'} dv'}{[G_v - G_{v'}]^{3/2}}$$

where  $C = (2h^2/\mu)^{1/2}$ . The unique set of turning points for each vibrational level is solved for using numerical integration. The results of this analysis is plotted against *ab initio* curves.


**Residuals for the  $3^1\Delta_g$  (red) and  $4^1\Delta_g$  (black) electronic states**

**References and support**

1. J.L. Dunham, Phys. Rev. **41**, 721 (1932).
2. W. Jastrzebski et al., J. Chem. Phys. **143**, 044308 (2015).
3. M. Tomza et al., Mol. Phys. **111**, 1781 (2013).
4. R. Rydberg, Z. Physik **73**, 376 (1931).



We gratefully  
Acknowledge  
support from  
NSF Grants PHY 2207665  
and PHY 1912269.