68th OSU International Symposium on Molecular Spectroscopy

Electronic Transitions of Palladium Dimer (Pd_2)

Yue Qian, Y. W. Ng and A. S-C. Cheung

Department of Chemistry
The University of Hong Kong
June 2013

Challenges

- Experimentally challenging:
  preparation of the target species; interpretation of the congested spectrum.

- Theoretically challenging:
  appropriate treatment of the open d-shell structure; prediction of the energy orders of the many low-lying states.

Properties of the metal-metal bonding remains unclear for many transition metal dimers.

Why palladium dimer (Pd_2)?

Among these dimers, Pd_2 is the least understood.

IA		VIIIB	IB
K_2	…	Ni_2	Cu_2
Rb_2	…	Pd_2	Ag_2
Cs_2	…	Pt_2	Au_2
…	…	…	…

Spectroscopic perspective:

- Understand the molecular and electronic structure of Pd_2
  ---similarity and difference with its analogue, Ni_2 and Pt_2

- Evaluate the participation of 4*d* orbital in bonding
  --- the effect of the relative size of n*d* and (n+1)*s* orbitals
  --- reference for the theoretical calculations
  --- catalytic activities

Previous studies on Pd_2

G. A. Ozin et al., *Inorg. Chem.*, **19,** 3767 (1980);
recorded absorption spectrum in argon matrix
weak transition at 265 nm

M. D. Morse te al., *J. Chem. Phys.*. **92,** 2710 (1990);
attempted two-photo ionization spectroscopy in the visible and IR region
no transition was observed

W. C. Lineberger et al., *J. Chem. Phys.*, **95,** 4845 (1991);
photo-detachment spectroscopy
suggested ground state to be $^3\Sigma_u^+$, with vibrational frequency of 210 ± 10 cm^{-1} and second-order spin-orbit coupling at around 32 cm^{-1}

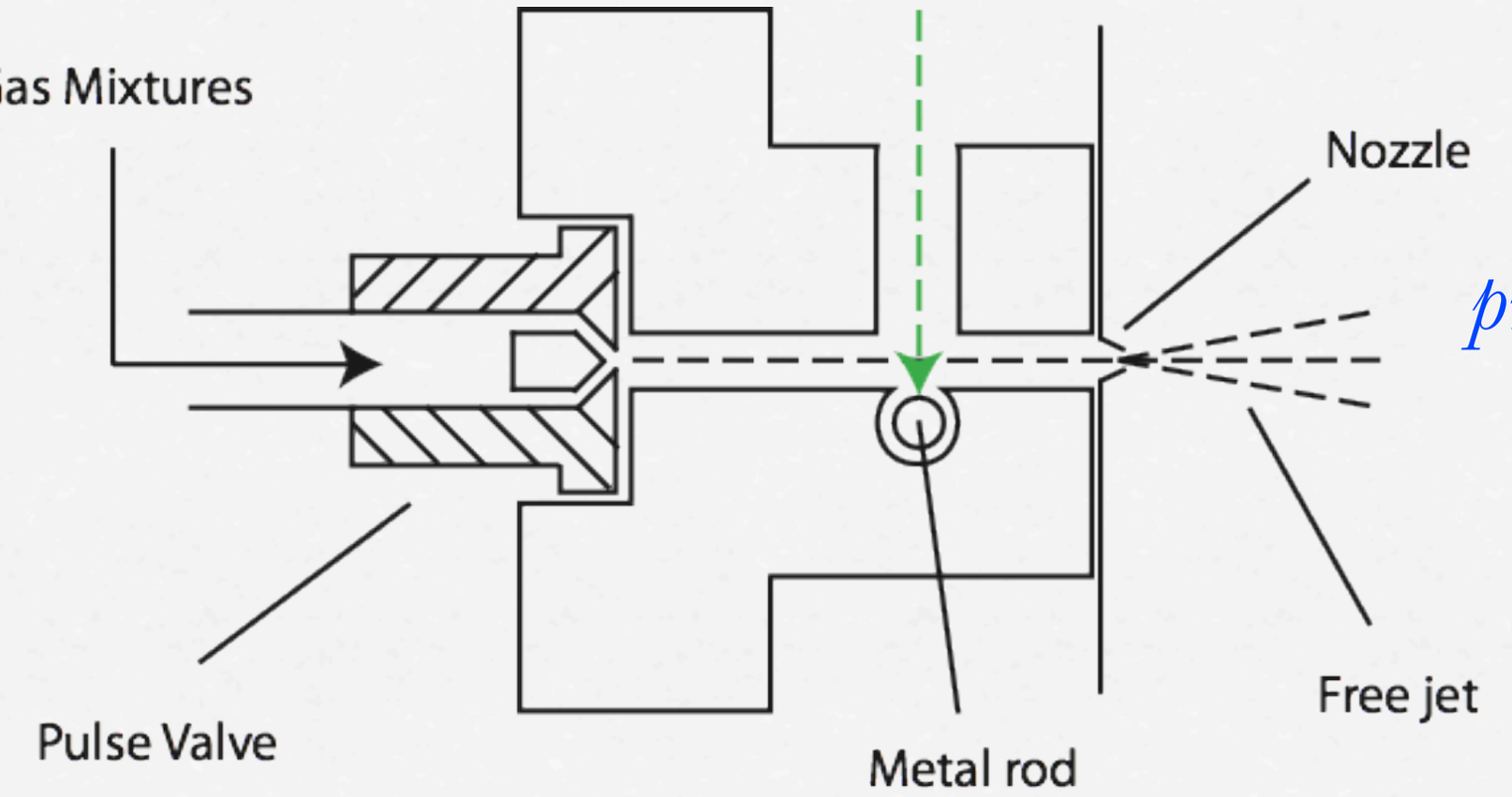
K. Balasubramanian, *J. Phys. Chem.*, **89,** 6310 (1988);
Complete active space MCSCF
found the ground $^3\Sigma_u^+$ state and predicted the second-order spin-orbit coupling effect (9 cm^{-1})

Molecule Generation

laser ablation/reaction free jet expansion

Ablation laser: Nd: YAG, 532 nm, ~5mJ

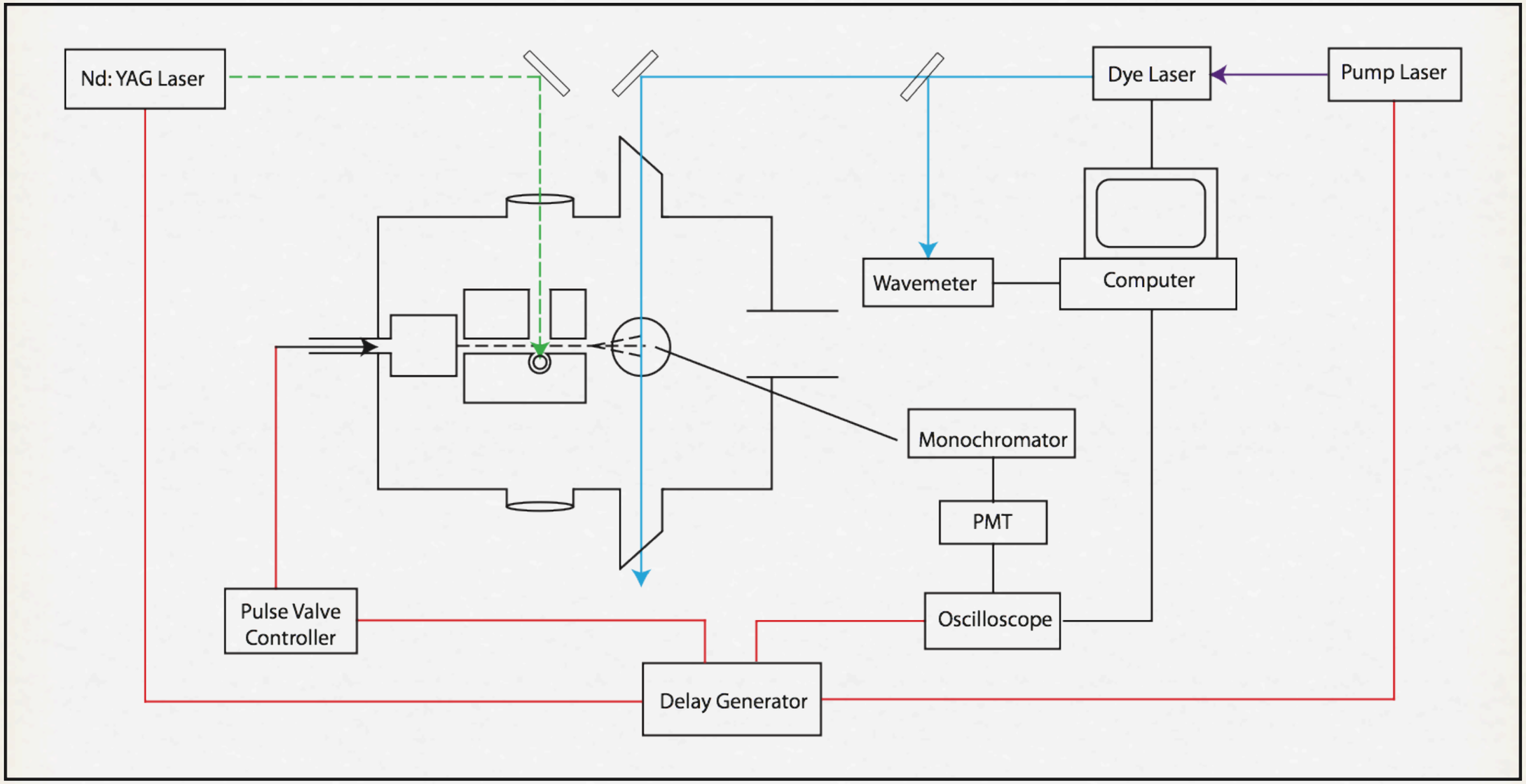
Backing pressure: 6 atm



Background pressure: 1x10^{-5} Torr

Metal rod: Palladium rod for Pd_2

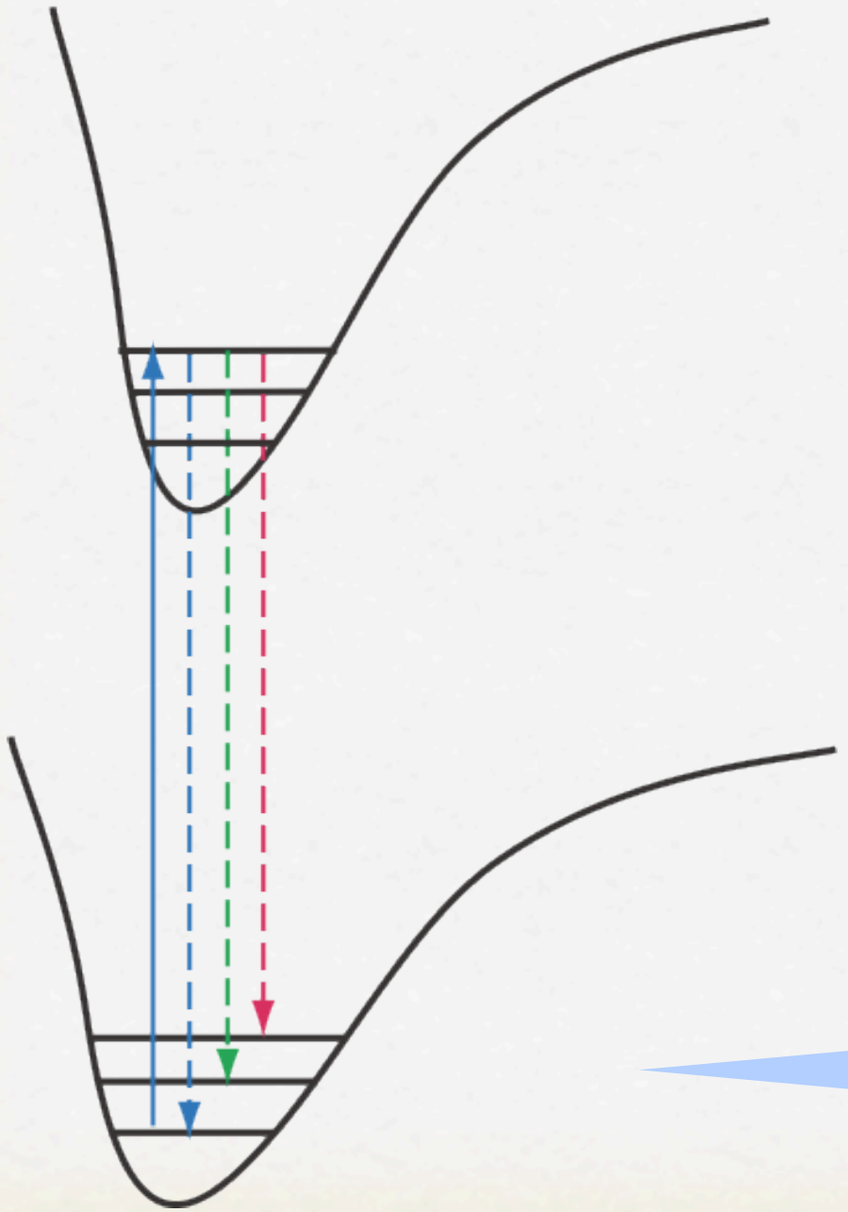
Experimental Setup



Laser ablation/reaction with free jet expansion coupled with laser-induced fluorescence (LIF) spectroscopy

Solid line: Laser excitation

Dash line: Fluorescence signal



The LIF process:

1. Molecules are excited to a higher electronic state

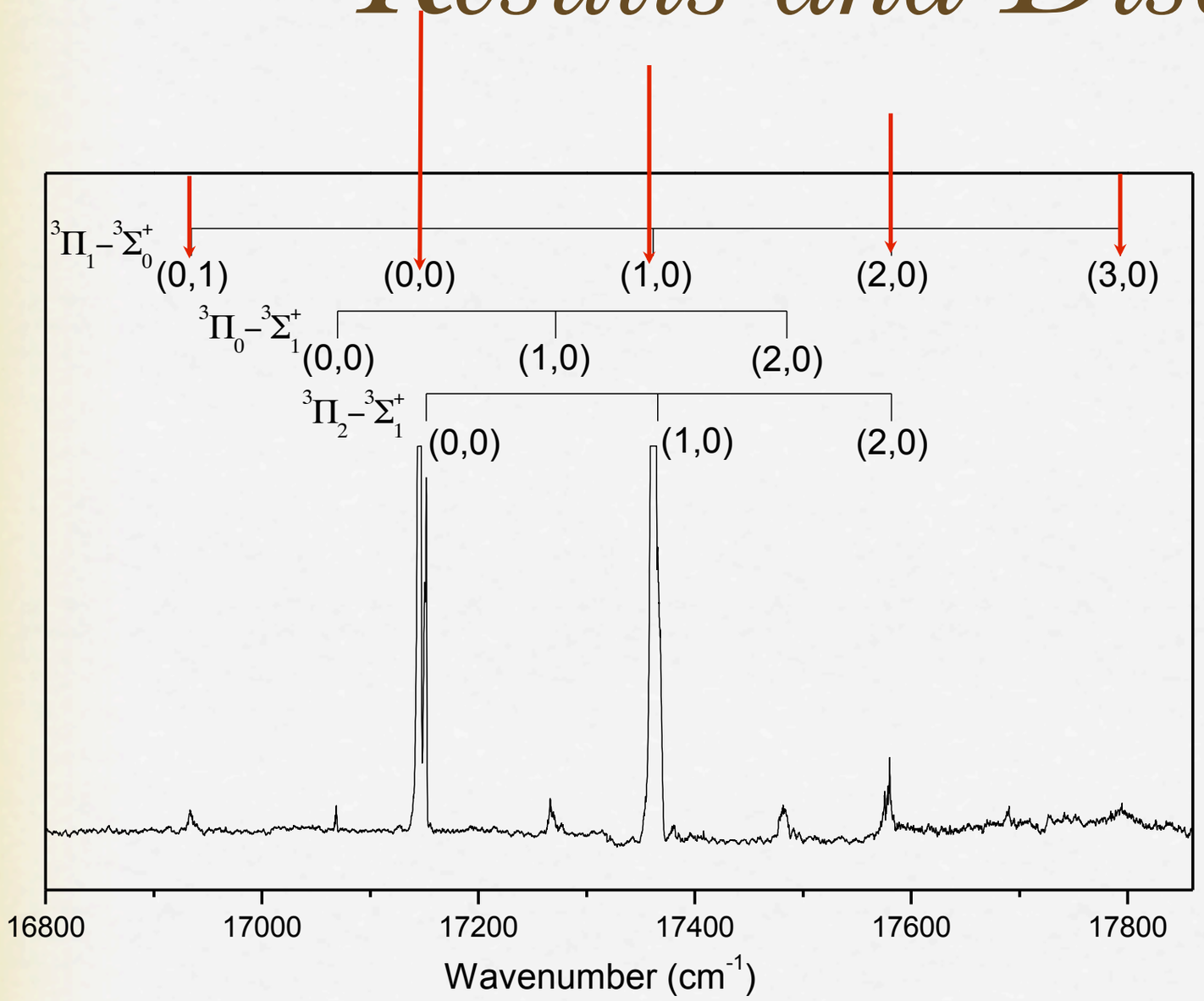
2. Molecules subsequently relax back to ground state releasing fluorescence photon

Monochromator:

a). used to obtain wavelength resolved fluorescence spectrum

b). used as an optical filter in recording the LIF spectrum

Results and Discussion



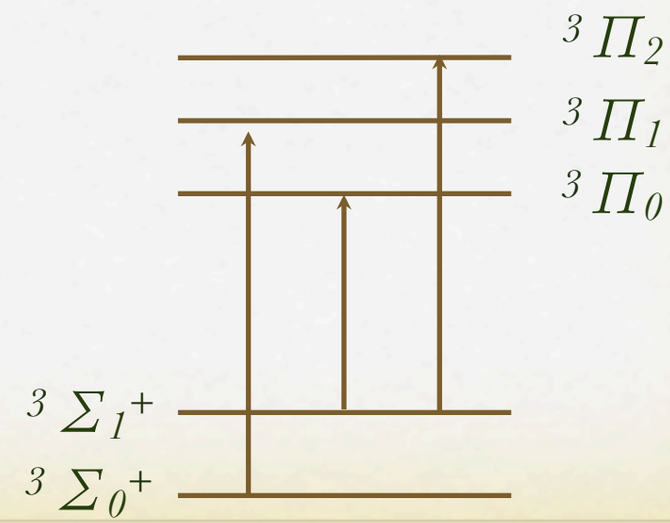
Broadband spectrum of Pd_2 [17.1]$^3\Pi_g$-$X^3\Sigma_u^+$ system

a). (0,0) band is of the largest intensity

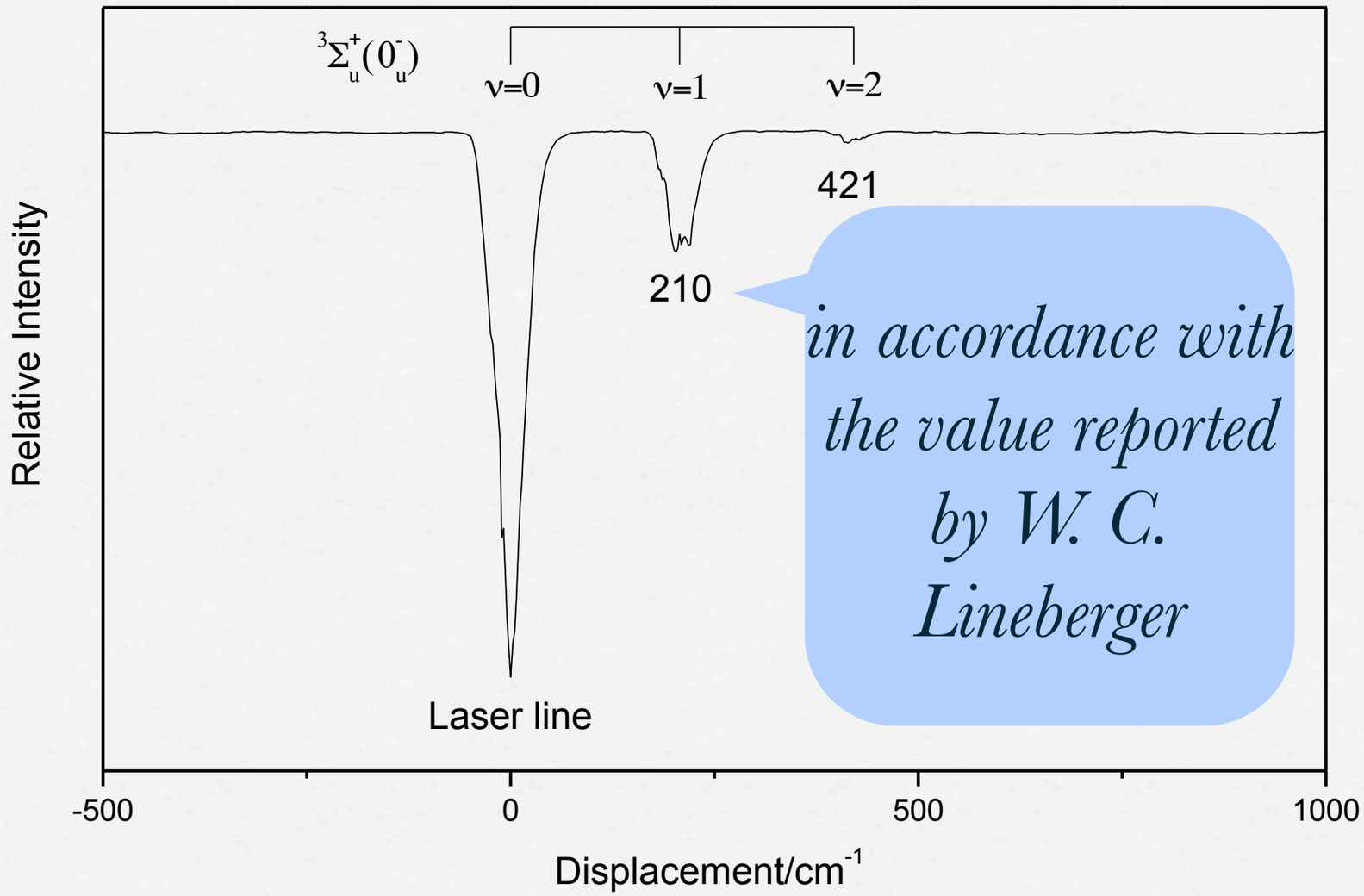
b). the $^3\Pi_1$-$^3\Sigma_0^+$ sub-band system is generally more intense than the rest two systems

c). energy separation at around 210-220 cm^{-1}

Selection rules: $\Delta\Omega = 0, \pm 1$



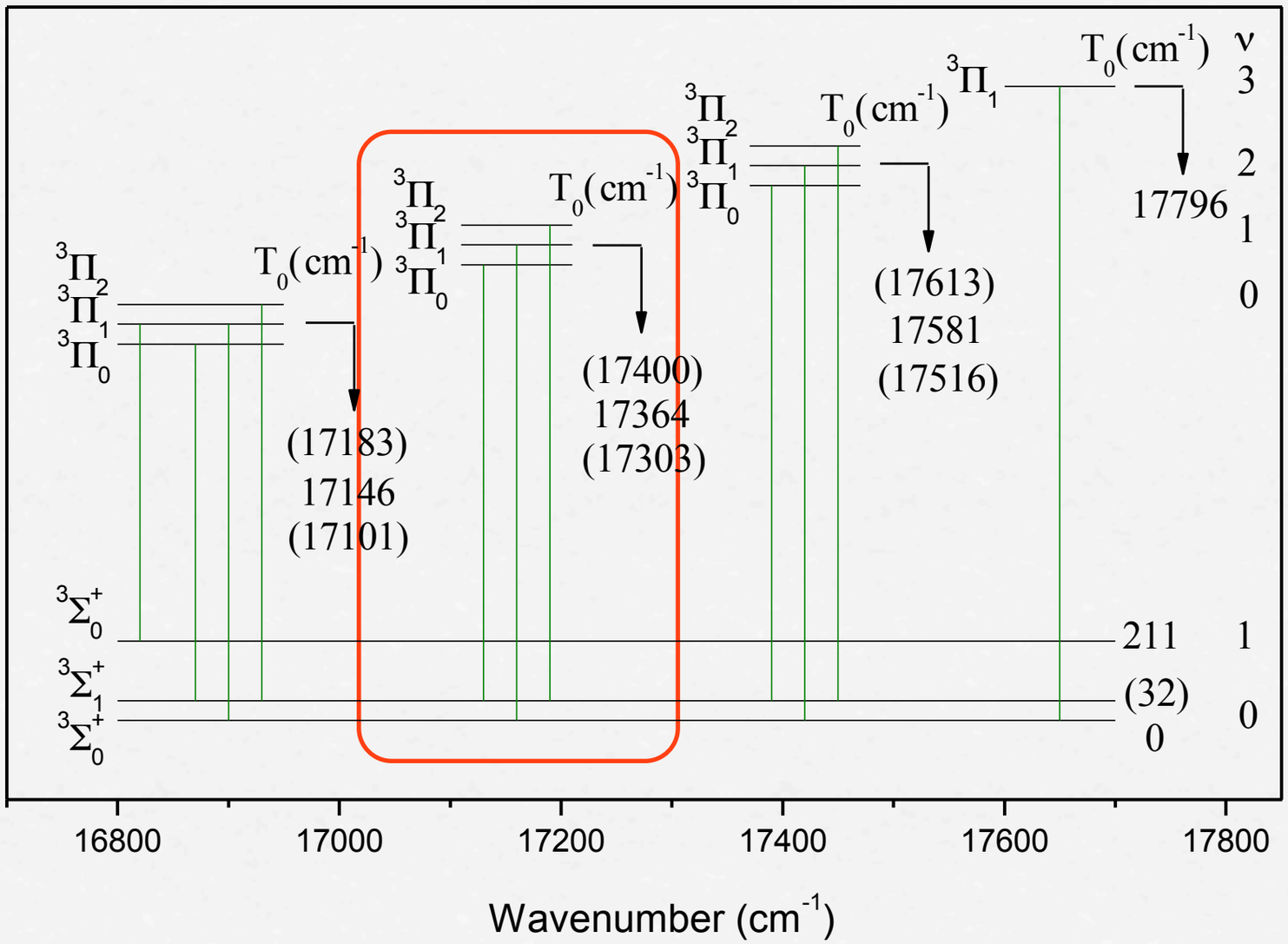
Wavelength resolved fluorescence spectra confirm that the observed bands arise from Pd_2 molecules.



in accordance with the value reported by W. C. Lineberger

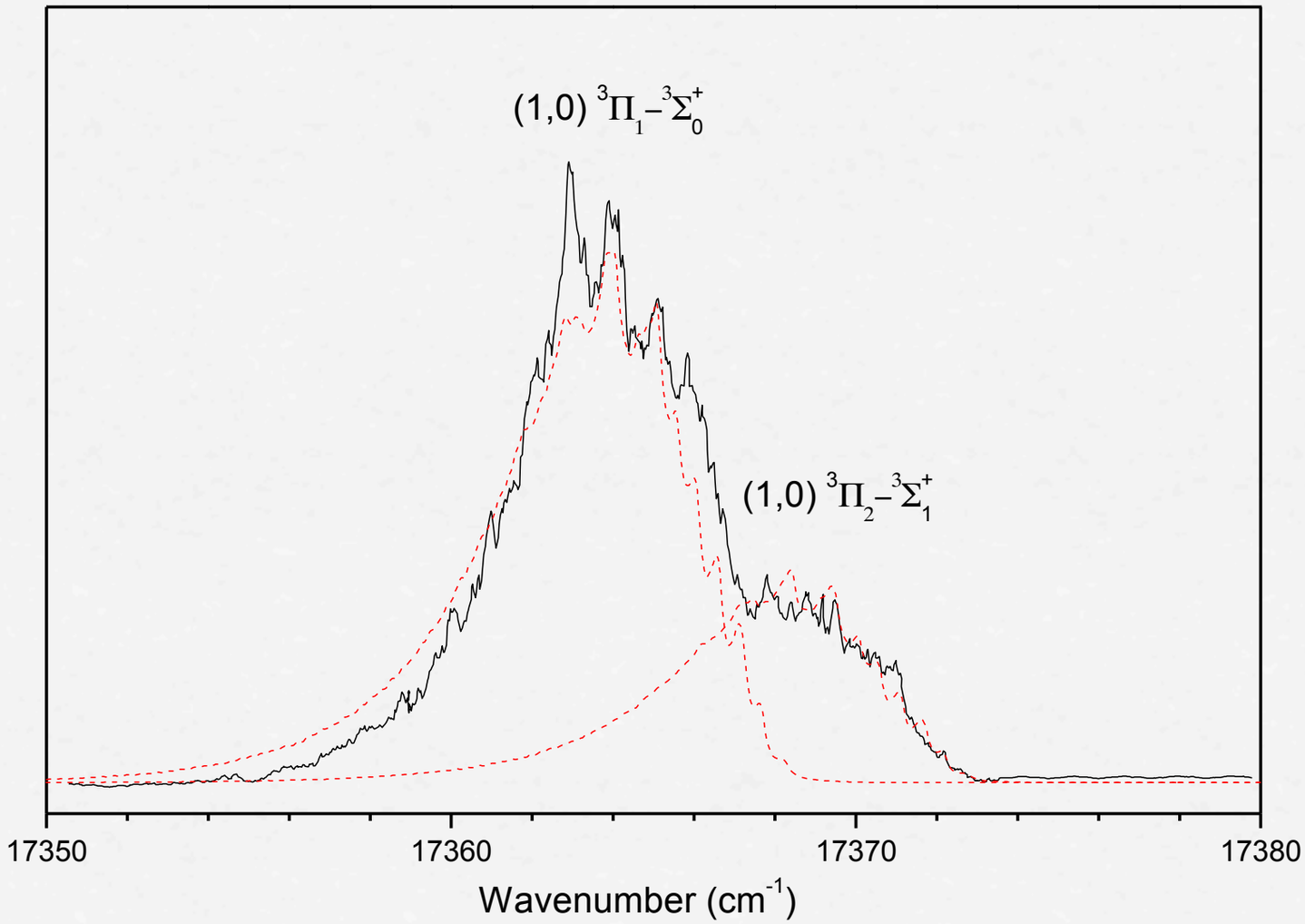
Wavelength resolved fluorescence spectrum of the (0,0) band of the $^3\Pi_1$-$^3\Sigma_0^+$ transition of Pd_2

11 bands have been identified and assigned to the $[17.1]^3\Pi_g$-$X^3\Sigma_u^+$ system

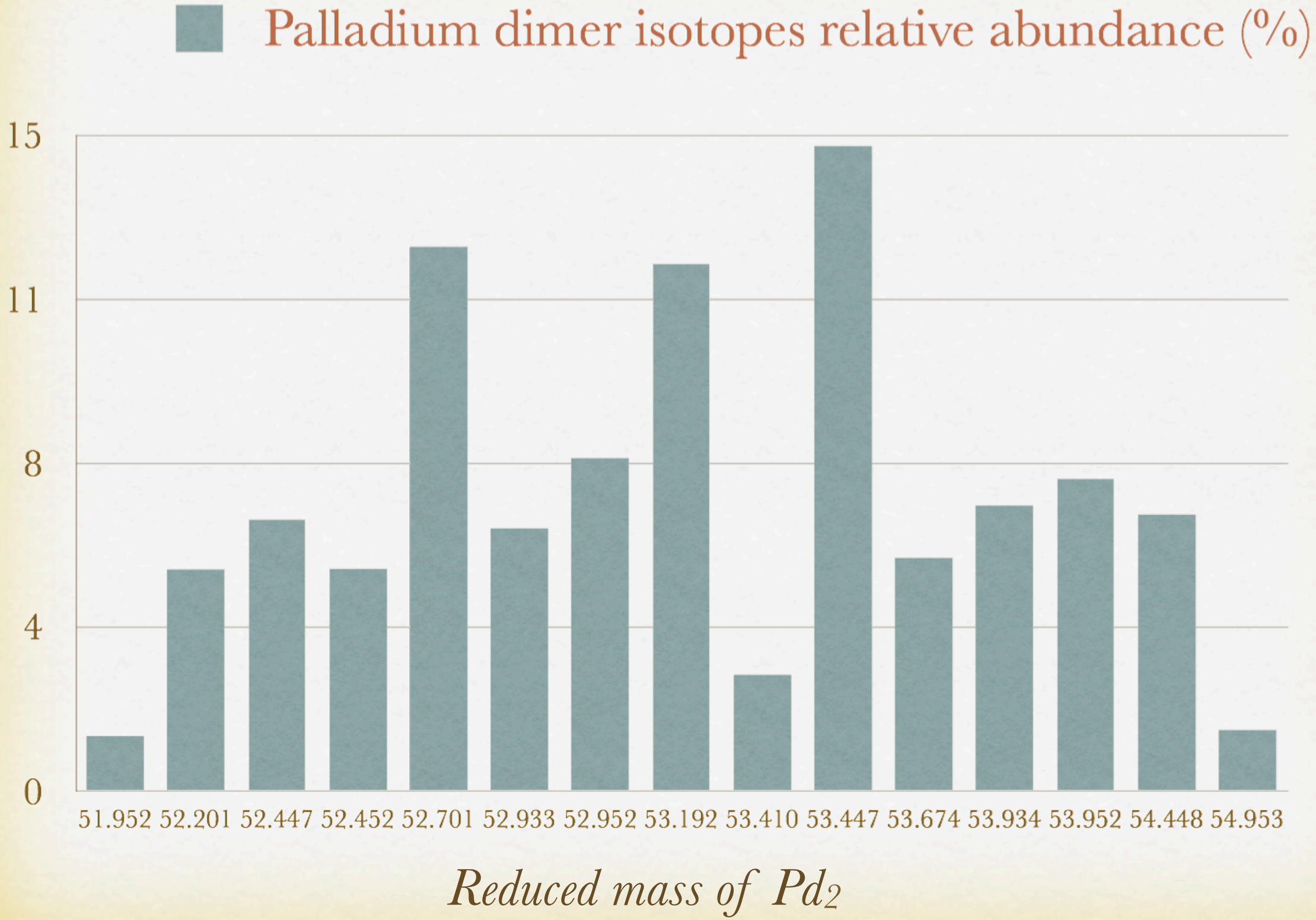


The energy level diagram of the $[17.1]^3\Pi_g$-$X^3\Sigma_u^+$

Simulated spectrum taking account of the isotopic displacement agree with the observed contour very well.



Simulated (red dash line) and experimental band contour (black solid line) fit of the (1,0) band of the $^3\Pi_1$-$^3\Sigma_0^+$ and $^3\Pi_2$-$^3\Sigma_1^+$ sub-band transitions


Palladium dimer isotopes relative abundance (%)
15
11
8
4
0
51.952
52.201
52.447
52.452
52.701
52.933
52.952
53.192
53.410
53.447
53.674
53.934
53.952
54.448
54.953
Reduced mass of Pd_2

Molecular constants used to obtain the band contour of the [17.1]$^3\Pi_g$-$X^3\Sigma_u^+$ transition system (cm^{-1})

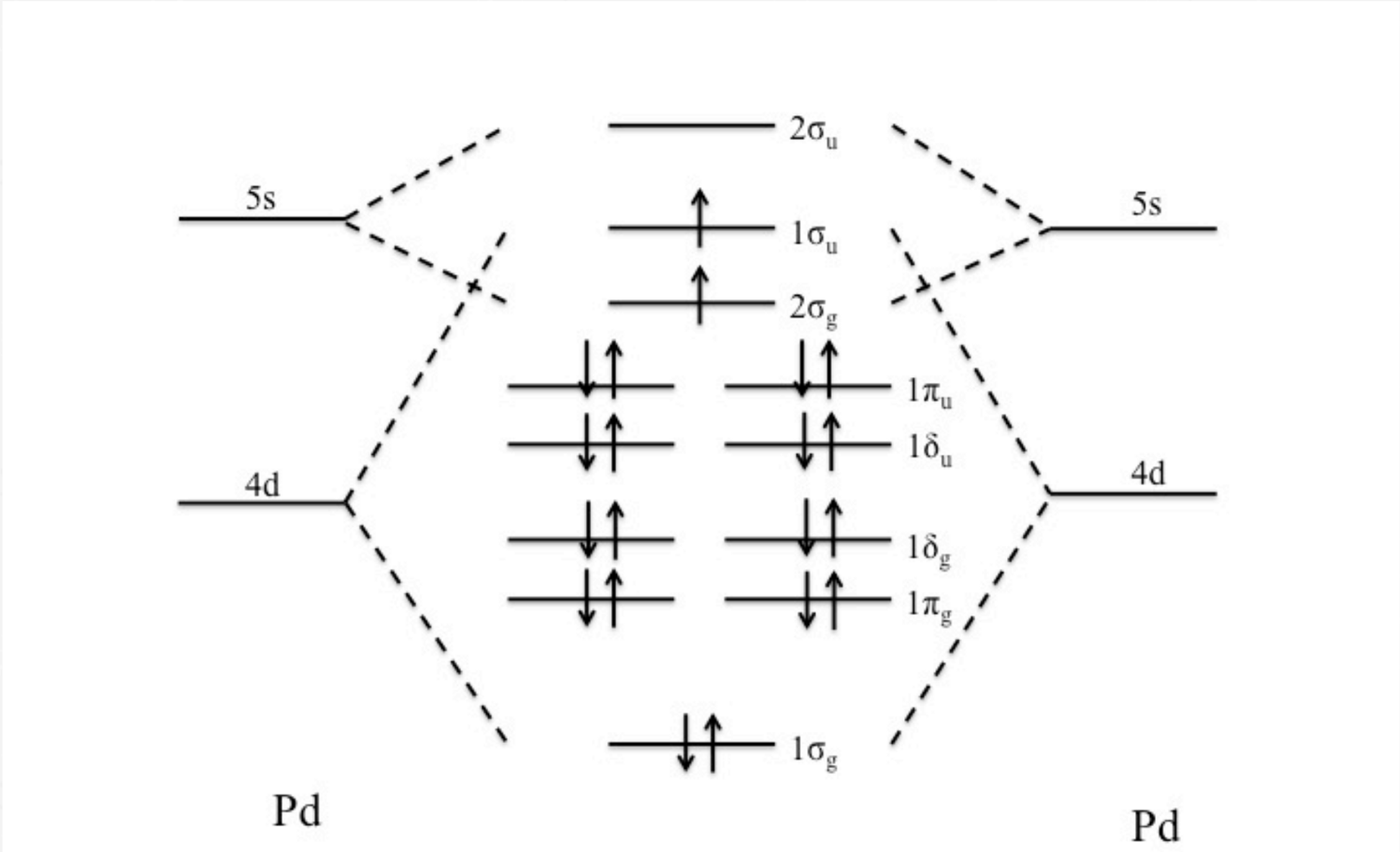
State	v	T_0 (cm^{-1})	B_{eff} (cm^{-1})
$^3\Pi_g$	3	17796.4(7)	0.0490(5)
	2	17581.5(8)	0.0492(5)
	1	17364.4(7)	0.0494(5)
	0	17146.3(6)	0.0496(5)
$X^3\Sigma_u^+$	1	211.4(5)	0.0500(3)
	0	0	0.0515(3)

Values obtained via PGOPHER simulation program

M. E. Green, and C. M. Western, J. Chem. Phys. 104, 848 (1996).

Ground state electronic configuration:

$$4d\sigma_g^2 4d\pi_g^4 4d\delta_g^4 4d\delta_u^4 4d\pi_u^4 5s\sigma_g^1 4d\sigma_u^1 \rightarrow X^3\,\Sigma_u^+$$

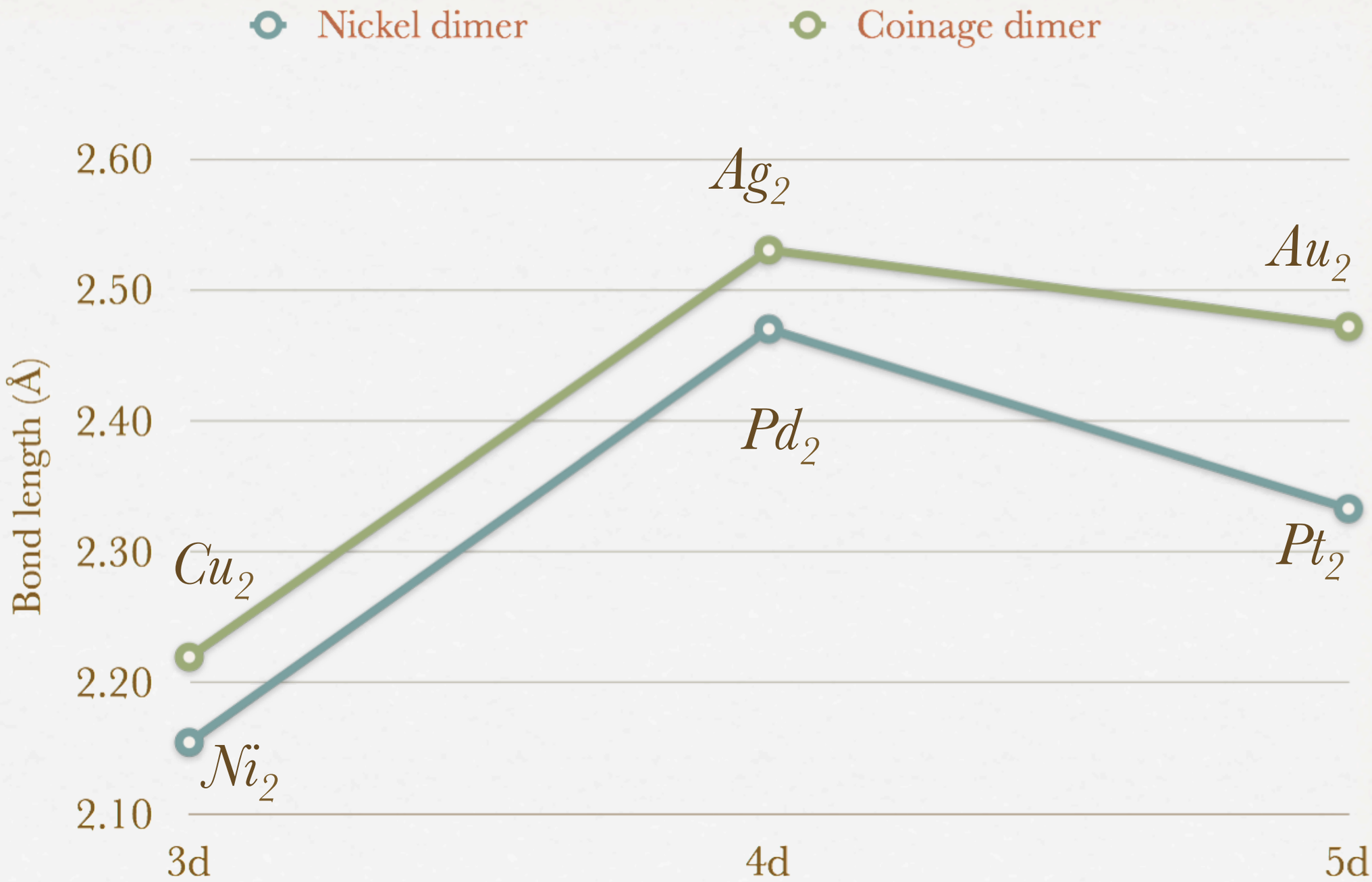


Molecular orbital energy level diagram of Pd_2

Pd_2 Summary

- Eleven bands of Pd_2 have been studied by LIF spectroscopy;
- Confirmed the ground $X^3\Sigma_u^+$ state;
- Spectroscopic properties of the ground state have been obtained and second-order spin-orbit coupling has been observed;

Authors	Method of determination	Symmetry	Bond length (Å)	Vib. Freq. (cm^{-1})
Ozin et al.	matrix techniques	/	/	/
Lineberger et al.	Photo-detachment spectroscopy	$^3\Sigma_u^+$	/	210
This work	LIF spectroscopy	$^3\Sigma_u^+$ (0_u^-)	2.47	211.4



Comparison of the bond length of the nickel group and coinage group metal dimers

Thank you!