Adiabatic Potential-Energy Curves of the Lithium Dimer

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Introduction

The molecule Li_2 which besides H_2 is the smallest stable homonuclear molecule, has attracted the interest of many experimentalists and theoreticians during the last decade. A broad variety of spectroscopic phenomena is observed for Li_2, and the accurate specification of its electronic structures is of principal importance. For the applied sciences, Li_2 is of interest because it is an active laser medium.

While a large number of electronic states has been observed experimentally, the knowledge of the excited states of Li_2 is far from being complete. Apparently, only three singlet states of ungerade symmetry and just one triplet state are known from experiment. Of the low-lying states, the second $^1\Sigma_g^+$ and the first $^1\Pi_g$ state are missing which. Only the X state is known up to the dissociation limit. Lifetimes have only been measured for the states A and B. Perturbations in the lower region of the Rydberg series are not well analyzed.

This situation calls for theory to provide predictions of the potential curves and spectroscopic constants especially of the unobserved electronic states, to assist spectroscopists in the interpretation of observations and to provide calculated data of properties not easily amenable to measurement.

Computational Methods

Homonuclear diatomic molecules have a symmetry which arises from the invariance of the Hamiltonian when the two nuclei are interchanged. Each rotational level is assigned as symmetric (s), if its wavefunction remains the same and as antisymmetric (a), if its wavefunction changes sign upon interchanging the nuclei. Such molecules (Li_2) have $D_{\infty h}$ symmetry. For homopolar isotopically unsymmetric diatomic molecules, such as HD or $^6Li^7Li$ the situation is fundamentally different. In this case symmetry of the molecule is only $C_{\infty v}$ and mixing of (a) and (s) levels occurs.

The choice of pseudopotential and the basis set
ECP (Effective Core Potential): ECP2SDF with additional functions
CPP (Core Polarization Potential): $\alpha = 0.1915$, $\delta = 0.831$
cc-pv5z: basis set for d orbitals with additional functions

ECP2SDF		cc-pv5z
S	**P**	**D**
392,169555	96,625417	
77,676373	19,845562	3,751948
15,385230	4,076012	1,978300
3,047327	0,837158	1,043103
0,603579	0,171941	0,550000
0,069138	0,052079	0,290000
0,026502	0,019172	0,140000
0,010159	0,007058	0,061000
0,003894	0,002598	0,026579

Usage of the MOLPRO package
CASSCF (Complete Active Space Self-Consistent-Field)
MCSCF (Multiconfiguration SCF)
CI (Configuration Interaction)

Results

The numerical values of the potential energies of thirteen singlet and thirteen triplet states relative to the 2s + 2s asymptote have been calculated for nuclear separations of $3.2 \leq R \leq 80.0 a_0$. Our present calculations cover all electronic states arising from the six lowest asymptotes (2s + 2s, 2s + 2p, 2s + 3s, 2p + 2p, 2s + 3p, 2s + 3d) and asymptotic energies are shown and compared with alternative results in the table below.

	Present	Ref. [1]	Ref. [2]
2s + 2p	14916	14938	14904
2s + 3s	27201	27209	27206
2p + 2p	29822	29876	29808
2s + 3p	30931	31078	30925
2s + 3d	32113		31283

The adiabatic potential - energy curves for all states are shown in figures. We obtain very good agreement with Schmidt - Mink *et al.* theoretical results, so we consider that our potential - energy curves for states corresponding to the asymptotes 2p + 2p and 2s + 3p are reliable.

The adiabatic potential-energy curves of the Li_2 and Li_2^+ systems are very important for the spectroscopy of cold atoms and molecules, identification of the observed satellite bonds and photoassociation processes.

Acknowledgments

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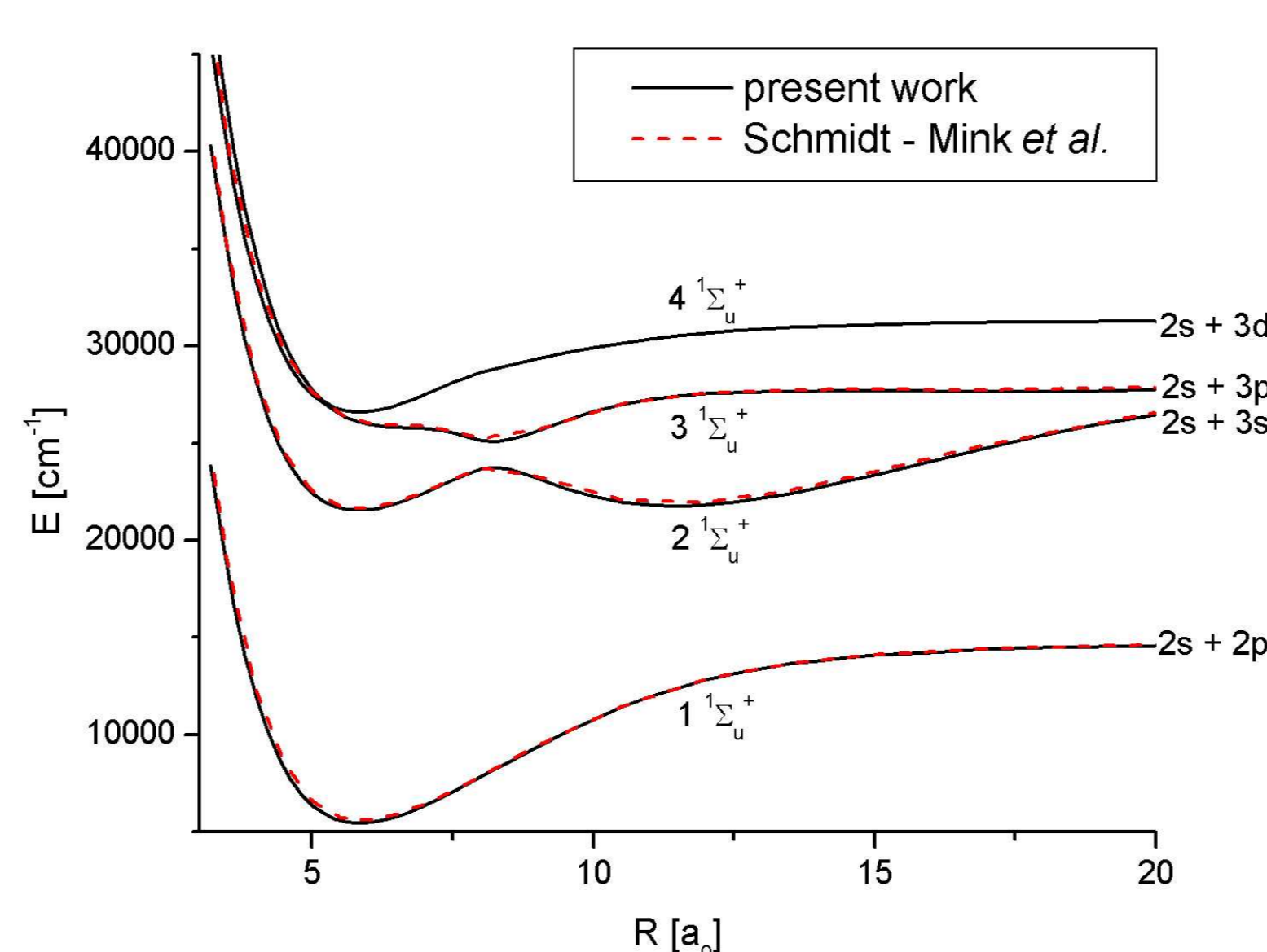
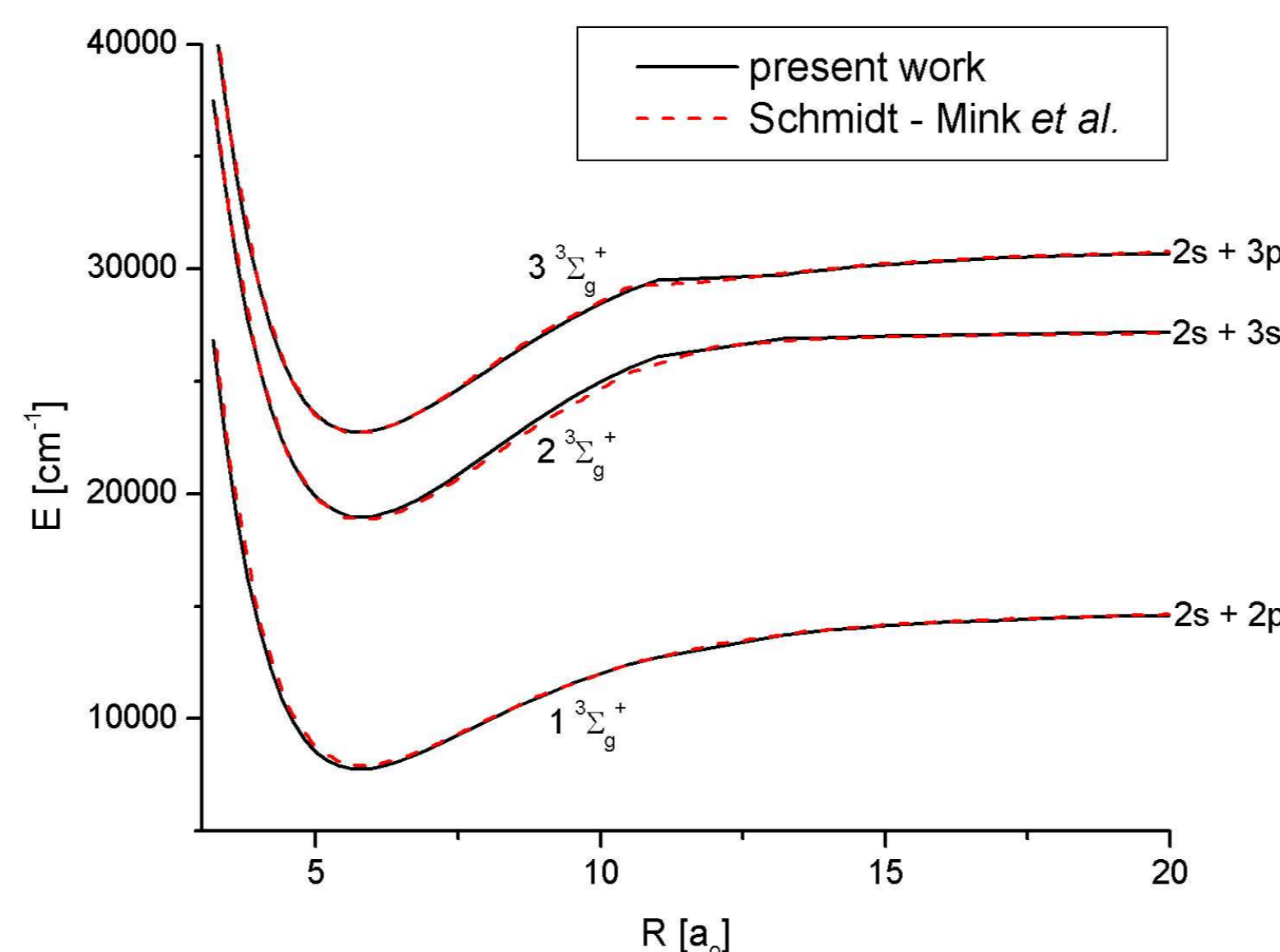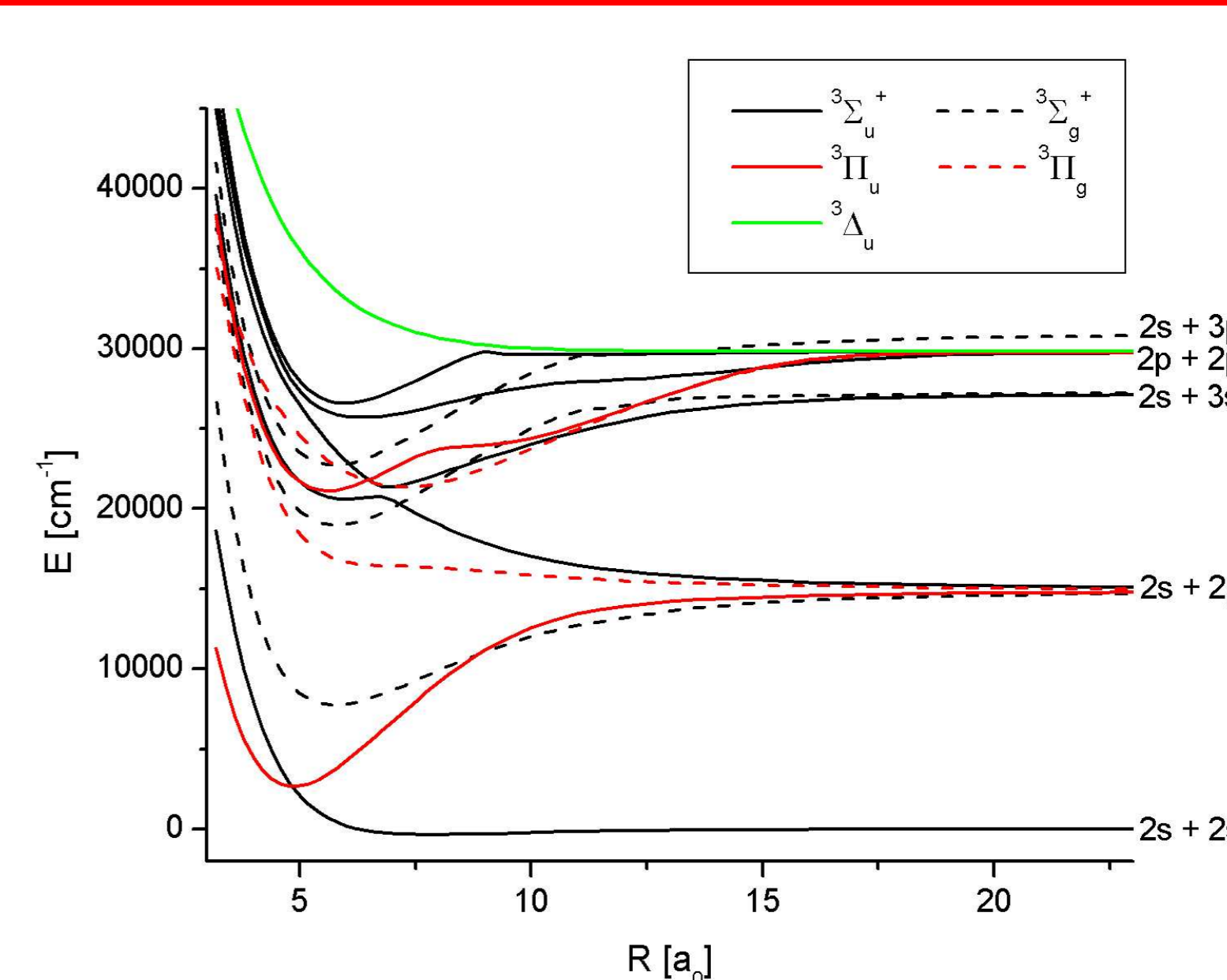11) C. Chin, R. Grimm, Phys. Rev. A 69, 033612 (2004)

Ground State
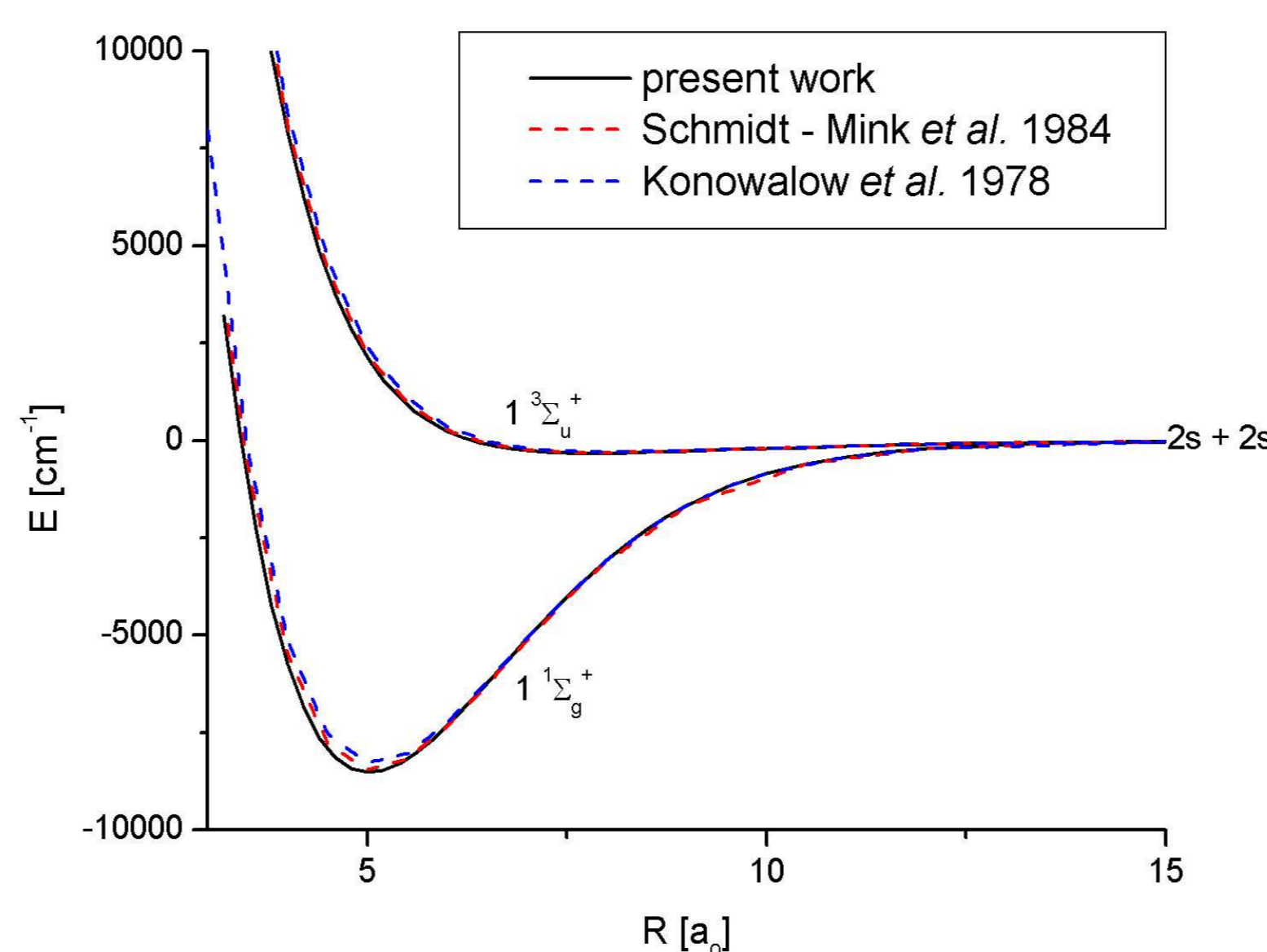
Sigma States
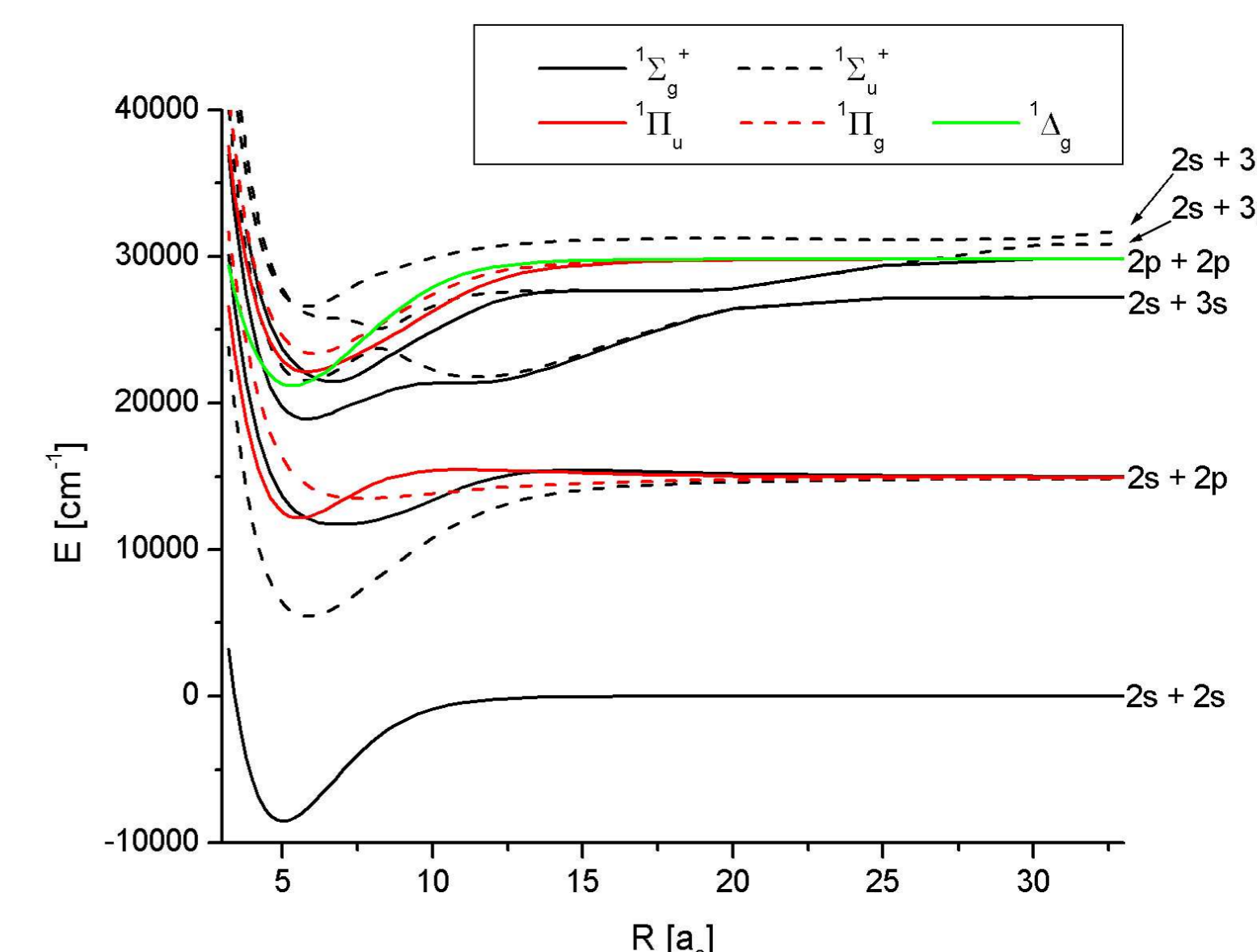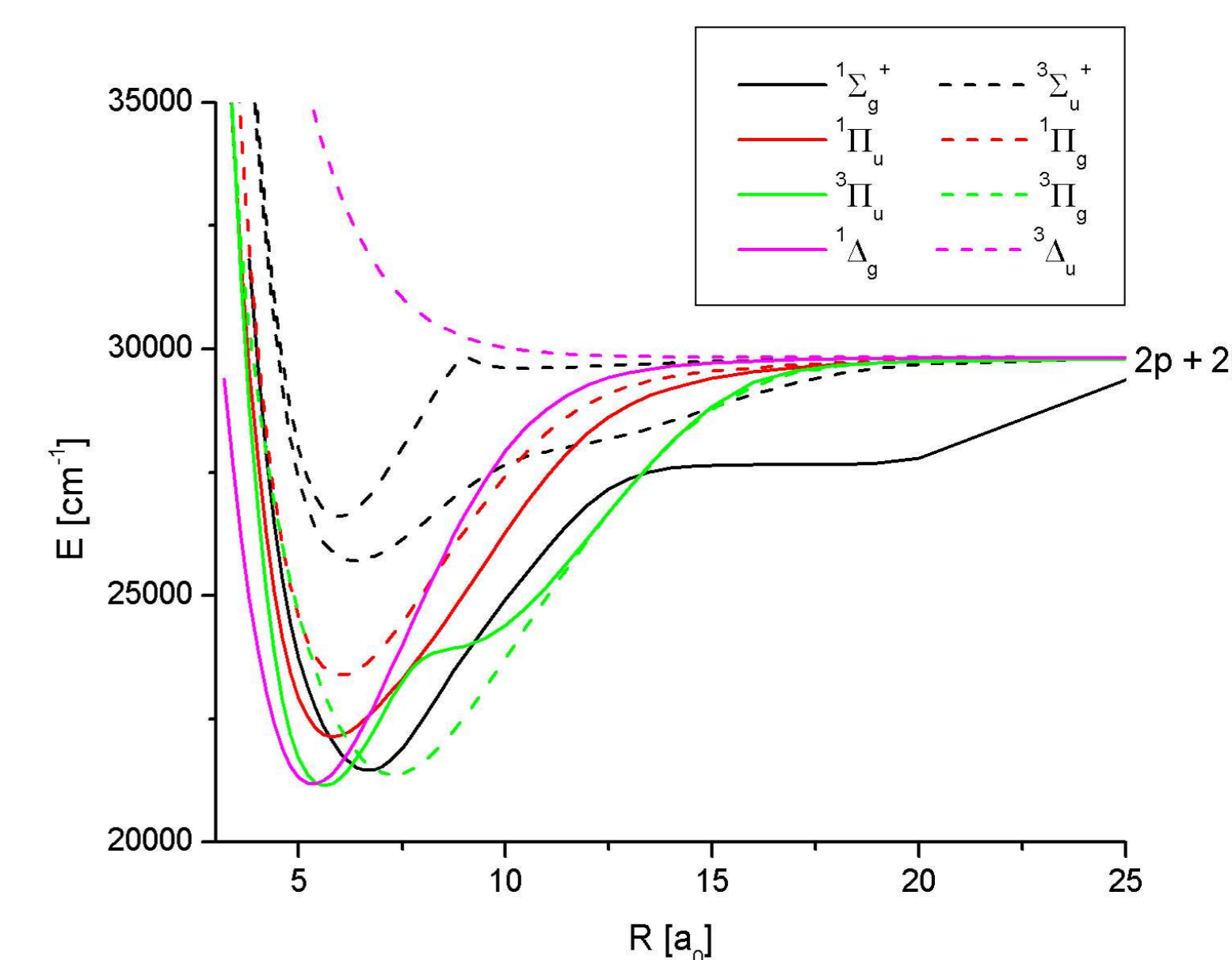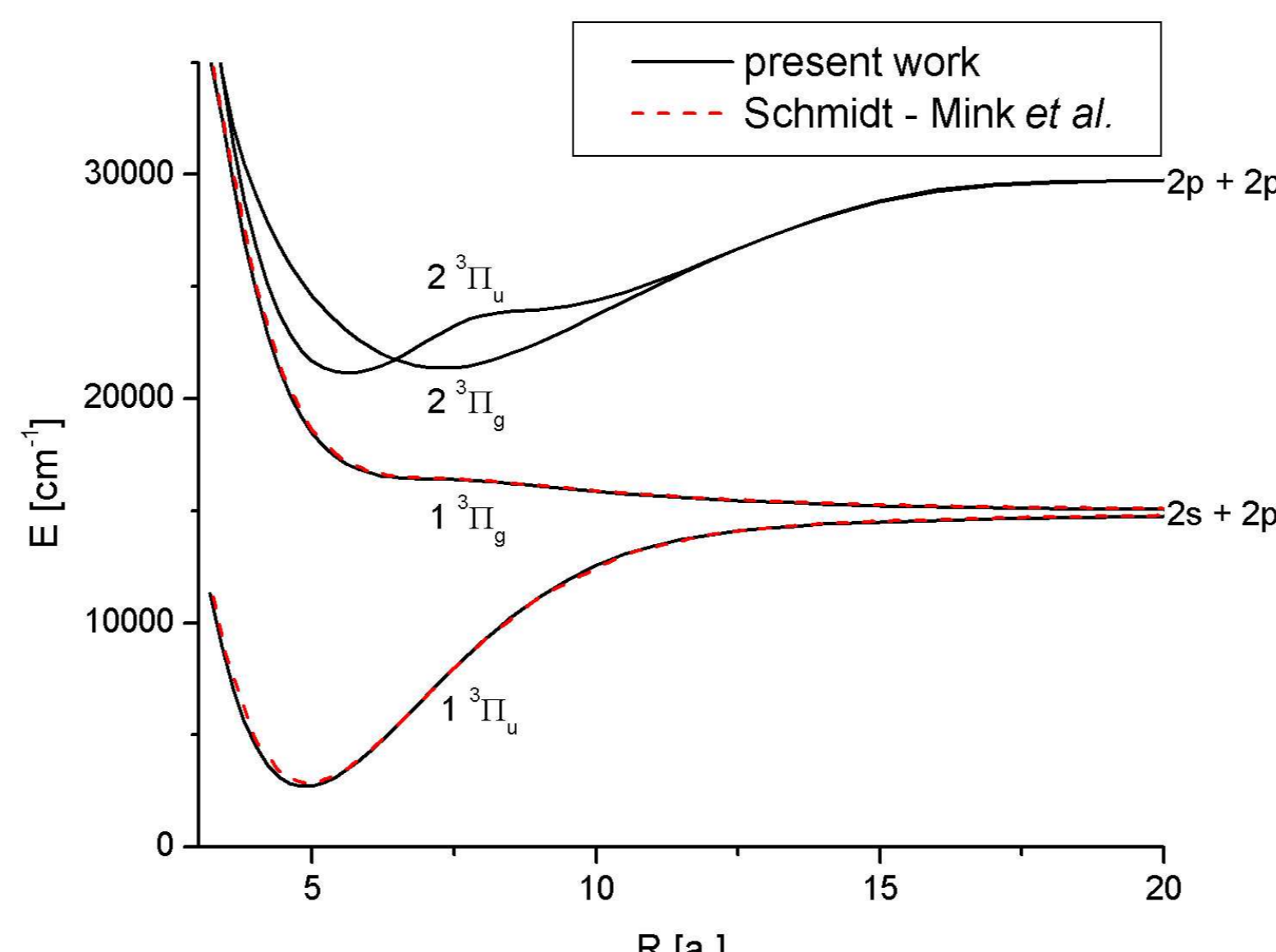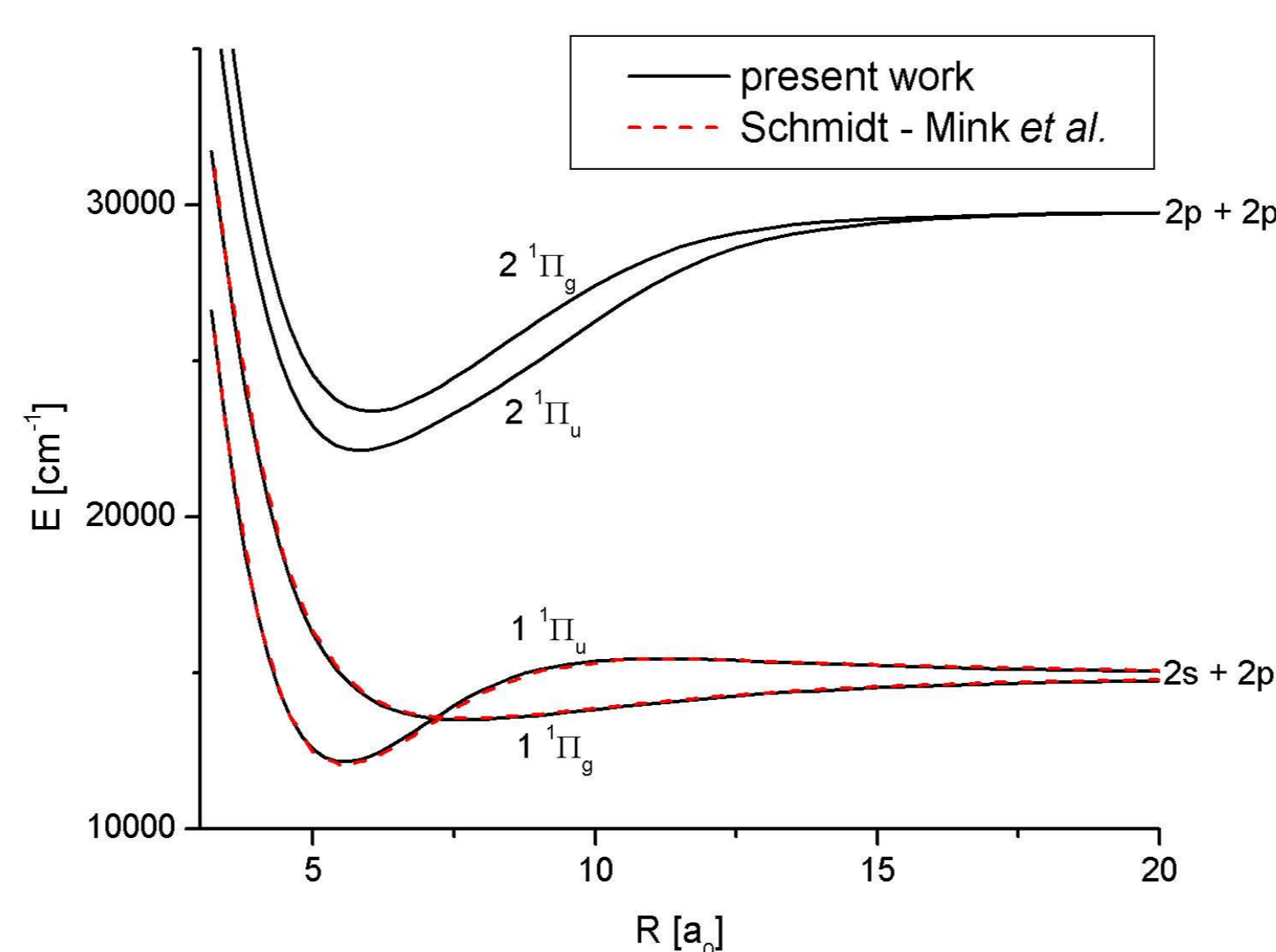

Pi States

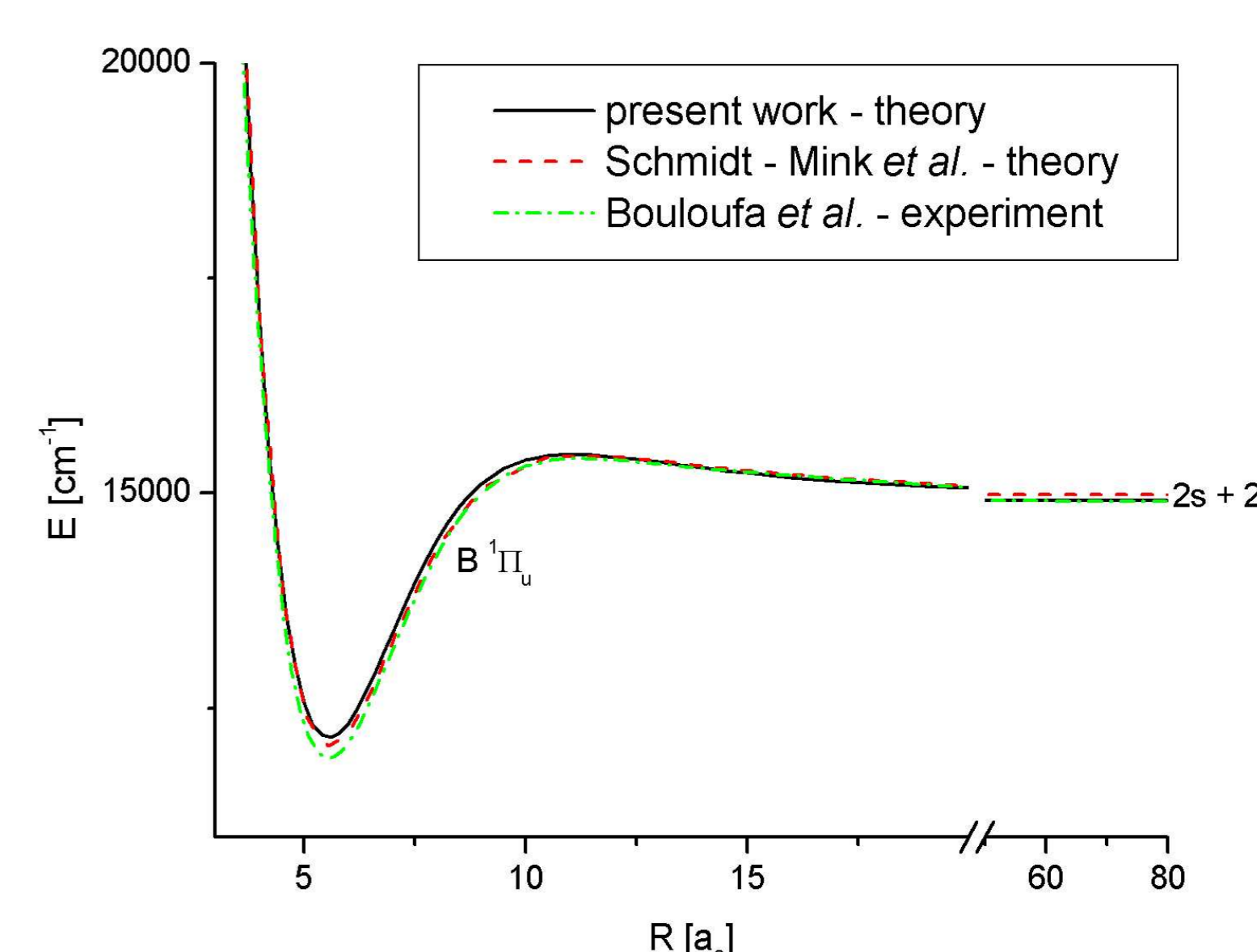## Singlet States

Triplet States

2p + 2p Asymptote States

Comparison with Experiment

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