



HAL
open science

Rydberg states of the Li₂ molecule studied by polarization labelling spectroscopy

A Grochola, P Kowalczyk, W Jastrzebski

► **To cite this version:**

A Grochola, P Kowalczyk, W Jastrzebski. Rydberg states of the Li₂ molecule studied by polarization labelling spectroscopy. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 2010, 43 (15), pp.155102. 10.1088/0953-4075/43/15/155102 . hal-00597863

HAL Id: hal-00597863

<https://hal.science/hal-00597863v1>

Submitted on 2 Jun 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Rydberg states of Li_2 molecule studied by polarization labelling spectroscopy

A Grochola, P Kowalczyk

Institute of Experimental Physics, University of Warsaw, ul. Hoża 69,
00-681 Warsaw, Poland

E-mail: Anna.Grochola@fuw.edu.pl

E-mail: Pawel.Kowalczyk@fuw.edu.pl

W Jastrzebski

Institute of Physics, Polish Academy of Sciences, Al.Lotników 32/46, 02-668 Warsaw,
Poland

E-mail: jastr@ifpan.edu.pl

Abstract. The polarization labelling spectroscopy technique is used to characterize three previously unknown $^1\Pi_u$ electronic states in $^7\text{Li}_2$ molecule. The states are identified, together with the $4^1\Pi_u$ and $6^1\Pi_u$ states reported before, as low lying members, $n = 3$ to 7 , of a molecular Rydberg series corresponding to excitation of the $n\rho\pi_u$ electron. The dependence of their properties on the principal quantum number n is discussed.

PACS numbers: 33.80.Rv, 33.20.Lg, 33.20.Vq, 42.62.Fi

Submitted to: *J. Phys. B: At. Mol. Opt. Phys.*

1. Introduction

Rydberg states of homonuclear alkali dimers have been studied by laser spectroscopy techniques since the 1980s (see e.g the pioneering experiments on Li₂ [1], Na₂ [2] and K₂ [3]). These states attract considerable interest for several reasons. The low-lying members of the Rydberg series represent the transition from molecular valence states to Rydberg states. Since for such states quantum chemistry calculations are still feasible, experimental studies provide ground for testing reliability of computational methods. Investigation of high-lying Rydberg states allows to deduce the ionization potential and spectroscopic constants of the ground state of the molecular ion to be deduced by extrapolation, without direct observation of the ion spectra. Highly excited Rydberg states are also interesting in themselves because of several phenomena specific to them, like gradual change of coupling between angular momenta (typically from Hund's coupling case a to d), breakdown of the Born-Oppenheimer approximation (caused by changing ratio between rotation energy and the difference of the electronic energies of consecutive electronic states) and coupling of discrete levels to the electronic continuum (which leads to autoionization).

The easiest way to reach molecular Rydberg states experimentally is by stepwise excitation via some intermediate, low lying level, because two visible photons can be used then. When we start from a ground molecular state of $^1\Sigma_g^+$ symmetry, the selection rules allow in this case excitation of $^1\Lambda_g$ states with $\Lambda = \Sigma, \Pi, \Delta$. Transitions to states of ungerade symmetry require an odd number of photons. This can be realized by one photon absorption, conceptually simple but experimentally less convenient since a UV or VUV radiation is needed. An alternative way is offered by the all-optical triple resonance spectroscopy (AOTR) [4], however this method, requiring three single mode tuneable lasers, is rather extravagant and beyond capabilities of most research groups.

As a result the disparity of experimental data on gerade and ungerade Rydberg states in alkali dimers is rather large. The highest observed $^1\Lambda_g$ states correspond to excitation of the Rydberg electron to a state with the principal quantum number $n = 40$ for Li₂ [5], $n = 70$ for Na₂ [6] and $n = 43$ for K₂ [3]. For $^1\Lambda_u$ states only in diatomic sodium, where the AOTR technique has been employed, the observations reach up to high n values [4], whereas for Li₂ and K₂ the experimental data are limited to low electronic states having rather a valence than Rydberg nature.

For a few years we have been involved in investigation of excited electronic states of lithium dimer accessible in one photon transitions from the ground state, using the polarization labelling spectroscopy method [7]. The electronic states observed in our recent experiments, $5^1\Pi_u$ [8] and $6^1\Pi_u$ [9], are the highest states of singlet ungerade symmetry characterized experimentally up to now (save fragments of another $^1\Pi_u$ state [10], see the Discussion section). In the current paper we present observation of three higher excited electronic states of $^1\Pi_u$ symmetry in Li₂, which apparently form, together with the previously studied $4^1\Pi_u$ [11, 12] and $6^1\Pi_u$ [9] states, a Rydberg series $^1\Pi_u(np\pi_u)$ with $n = 3 - 7$ (i.e. $4^1\Pi_u(3p\pi_u)$, $6^1\Pi_u(4p\pi_u)$, ...).

2. Experiment

Since the employed method and the experimental set up were identical to those used in our previous experiments on Li₂ [8, 9, 13], only a brief summary will be given here. Lithium dimers were formed in a heat pipe oven filled with metallic lithium (natural isotopic composition) and heated to 750 – 800 °C with a background pressure of 4 Torr of helium as a buffer gas. Known levels of the ground state of Li₂ were 'labelled' with fixed frequency light of a probe laser through the $A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ or $B^1\Pi_u \leftarrow X^1\Sigma_g^+$ transitions, specified in Reference [13]. Transitions from the labelled (v'' , J'') levels to the investigated electronic states were excited in a V-type optical-optical double resonance polarization spectroscopy scheme by a tuneable pump laser. The two laser beams co-propagated at a small angle, crossing in the centre of the heat pipe oven. The intensity of the probe beam was monitored through crossed polarizers placed on either side of the oven, so that double resonance signals appeared on a black background.

As the pump laser we used an optical parametric oscillator/amplifier system provided with a frequency doubler (Continuum, Sunlite EX, pumped with an injection seeded Nd:YAG laser, Powerlite 8000). The system delivered UV pulses of 3 mJ energy, 10 ns duration and a spectral width below 0.16 cm⁻¹, tuneable for purposes of the present experiment between 37300 and 40900 cm⁻¹. Calibration of wave number scans was achieved by recording the photogalvanic spectrum of argon and transmission fringes of a Fabry-Pérot etalon 0.5 cm long (both auxiliary signals observed at the fundamental frequency of tuneable OPO/OPA radiation). The resulting accuracy in absolute determination of wave numbers was better than 0.1 cm⁻¹. For the probe laser we employed either a cw Ar⁺-Kr⁺ laser operated on selected visible lines or a home built pulsed dye laser pumped synchronously by the same Nd:YAG laser as the OPO system and set on fixed wavelengths from the range 630 - 650 nm using HighFinesse WS-5 wavemeter.

3. Results

With growing excitation energy, molecular spectra of lithium can be expected to become increasingly congested and intricate, according to a growing number of states accessible for excitation. In addition, perturbations between electronic states should become more frequent, adding to the complexity of the spectra. These anticipations were only partially confirmed in the course of our experiment, since the investigated spectral range was dominated by three easily recognizable band systems having the ground $X^1\Sigma_g^+$ state of Li₂ as the lower state. The symmetry of all three upper states is clearly $^1\Pi_u$ as indicated by the presence of strong Q lines in the spectra. For the sake of clarity, in this section we shall refer to these states as $\alpha^1\Pi_u$, $\beta^1\Pi_u$ and $\gamma^1\Pi_u$. Fragments of other bands in the investigated range were too weak and too short to attempt their identification.

A visual inspection of the spectra related to the observed $^1\Pi_u \leftarrow X^1\Sigma_g^+$ systems revealed the presence of strong perturbations in the upper states. In particular, irregular

patterns of P , Q and R lines originating from the same rovibrational level in the ground state were apparent and in some cases the P and R lines could not be assigned unambiguously at all. It has been easily verified that the Q lines formed regular progressions while P and R lines behaved erratically, displaying shifts from the expected positions which occasionally exceeded 1 cm^{-1} . We conclude that the e parity levels of the investigated $^1\Pi_u$ states are strongly perturbed over a wide range of vibrational and rotational quantum numbers. This is consistent with perturbation by neighbouring $^1\Sigma_u^+$ states containing only levels of e parity and therefore able to influence only e levels of the $^1\Pi_u$ states. However, the perturbing states could not be directly seen in the spectra, presumably because of low Franck-Condon factors for excitation from the ground electronic state of Li₂. This made any attempt to deperturb the spectra futile and we had to confine our analysis to the observed Q lines, that is to f parity levels of the investigated $^1\Pi_u$ states. This problem has been encountered in our previous studies on highly excited states in Li₂, Na₂ and K₂ and solved in a similar way [9, 13, 14, 15, 16].

Altogether 208, 153 and 86 Q lines were identified in the α , β and $\gamma^1\Pi_u$ states, respectively, for the main $^7\text{Li}_2$ isotopologue. The vibrational numbering in each state was established by assuming that the lowest of all the observed vibrational levels in a given state corresponds to $v = 0$. These numberings were supported by inspection of the isotope effect for a few Q lines assigned to $^6\text{Li}^7\text{Li}$ molecules. Although the Born-Oppenheimer approximation is not fully justified for lithium dimer [17], the measured isotope shifts allow confirmation of the correct vibrational numberings.

The measured positions of Q lines (limited to $^7\text{Li}_2$) were fitted to differences of term values of the upper and lower levels, expressed by a standard Dunham expansion. Ground state Dunham coefficients were fixed at the highly accurate values given by Wang *et al.* [17]. Trial fits with varying numbers of fitted constants allowed us to establish statistically defined sets of coefficients describing each of the three $^1\Pi_u$ states. Their values have been subjected to a rounding procedure suggested by Le Roy [18]. The Dunham coefficients listed in Table 1 reproduce the measured line positions with an accuracy consistent with the experimental uncertainty.

4. Discussion

In general, there are two methods of identification of excited molecular states. In one of them the state is assigned by atomic limits to which it dissociates. The method works well for the lowest electronic states where the atomic asymptotes are well separated. For higher excitation energies, a growing density of states leads to numerous avoided crossings between potential curves of Rydberg, valence and ion pair states and tracking of atomic limits becomes more involved. In such cases specification of dissociation limits of a given state usually does not provide reliable information about its properties in the region near equilibrium internuclear distance, unless a diabatic course of the potential curve is strictly followed. In another method the Rydberg states are classified according to the character of the outermost electron and labelled by its quantum numbers $n\ell\lambda$,

Table 1. The experimentally determined Dunham coefficients for the $\alpha^1\Pi_u$, $\beta^1\Pi_u$ and $\gamma^1\Pi_u$ states of ${}^7\text{Li}_2$ (the coefficients and rms errors all in units of cm^{-1}). The numbers in parentheses are 1σ uncertainties in units of the last digit.

	$\alpha^1\Pi_u$ state	$\beta^1\Pi_u$ state	$\gamma^1\Pi_u$ state
T_e	38320.65(3)	39192.58(3)	39753.42(6)
Y_{10}	257.535(15)	259.405(10)	260.402(39)
Y_{20}	-1.6953(23)	-1.6477(9)	-1.701(6)
$Y_{30} \times 10^2$	0.11(1)		
Y_{01}	0.474590(65)	0.463642(94)	0.44983(31)
$Y_{11} \times 10^2$	-0.4580(9)	-0.3835(29)	-0.196(14)
$Y_{21} \times 10^4$	0.257(8)		-2.3(3)
$Y_{31} \times 10^4$			0.417(27)
$Y_{02} \times 10^5$	-0.396(8)	0.190(11)	1.214(38)
$Y_{12} \times 10^6$		-0.467(36)	-1.45(15)
$Y_{03} \times 10^9$	-0.21(2)	-1.323(58)	-3.96(12)
$Y_{13} \times 10^{10}$		0.82(11)	1.8(5)
rms error of the fit	0.07	0.09	0.13
No. of levels in the fit	208	153	86
range of v	0 – 14	0 – 10	0 – 7

n being the principal quantum number and l , λ - quantum numbers of the electronic angular momentum and its projection on the internuclear axis, respectively.

In the absence of reliable theoretical calculations concerning higher excited states of Li₂ we can try to assign (adiabatic) atomic asymptotes to the observed states only tentatively. First, we resort to a general rule that in case of transitions to highly excited molecular states the strongest ones are expected to the states corresponding to the allowed transitions between the asymptotic limits of the molecular states [1, 2, 19]. Since the observed transitions originate from the ground $X^1\Sigma_g^+$ state, which dissociates to 2s+2s lithium atoms, the three excited ${}^1\Pi_u$ states investigated in this work correlate most likely to 2s+np asymptotes. In other words, the Rydberg electrons in the observed excited states are most likely $np\pi_u$ electrons, because such orbitals display the best overlap with valence orbitals of the molecular ground state.

In a naïve approach one would assign the principal quantum number n by comparing separation of the potential wells of the observed states with energy differences between successive np atomic levels of lithium [20], the comparison based on an assumption that the molecular dissociation energies of the Rydberg states are not significantly influenced by a distant (Rydberg) electron. For reasons explained below we shall include in further discussion two lower lying molecular states, $4^1\Pi_u$ [11, 12] and $6^1\Pi_u$ [9]. The data

Table 2. Comparison of atomic and molecular energy spacings in lithium. All values are in cm⁻¹ units

atomic pair	ΔE (atomic)	ΔT_e (molecular)	molecular pair
4p – 5p	2546	2258	$4^1\Pi_u - 6^1\Pi_u$
5p – 6p	1375	1458	$6^1\Pi_u - \alpha^1\Pi_u$
6p – 7p	827	872	$\alpha^1\Pi_u - \beta^1\Pi_u$
7p – 8p	534	560	$\beta^1\Pi_u - \gamma^1\Pi_u$

presented in Table 2 apparently suggest that the five $^1\Pi_u$ states under consideration should correspond to $n = 4 - 8$. However, the near agreement of values of ΔE and ΔT_e is fortuitous. In Li₂ the order of asymptotes which are able to provide $^1\Pi_u$ states is 2s+2p, 2p+2p, 2s+3p, 2s+3d, ... (see Figure 1) and, in addition, it is known that the $3^1\Pi_u$ and $4^1\Pi_u$ states display an avoided crossing [11]. Therefore the fourth state of this symmetry must correspond diabatically to the third atomic limit, 2s+3p, and *not* to 2s+4p, as confirmed also by theoretical calculations [21]. This leads to an assignment of the discussed $^1\Pi_u$ states displayed in Table 3. Determination of n is connected directly with determination of the quantum defect $\delta_{n\lambda}$ for the states under consideration, related by the formula

$$T_{en} = T_\infty - Ry/[n - \delta_{n\lambda}]^2, \quad (1)$$

where T_e is the electronic energy of the given state at the potential minimum, T_∞ the energy difference between the potential minima of the Li₂ X¹Σ_g⁺ and Li₂⁺ X²Σ_g⁺ states (41538.5 cm⁻¹ [22, 17]) and Ry the Rydberg constant for ⁷Li₂ (109733.05 cm⁻¹ [10]). The assignment suggested in this work leads to a nearly constant value of the quantum defect for the whole series of $^1\Pi_u$ states, $\delta_{n\lambda} \approx -0.84$ (Table 3). We note that a negative value of δ is confirmed by the only existing theoretical calculation on sufficiently highly excited electronic states of Li₂, done by Spies [23]. Although his results apparently become less reliable with increasing excitation energy, the predicted value of $\delta \approx -0.5$ supports our assignment. The negative value of quantum defect shows that the Rydberg $^1\Pi_u$ states are shifted upwards comparing to the hydrogenlike positions. This may be somewhat surprising in view of a bonding character of the $n p \pi_u$ electron. However, we must note a very low position of the doubly excited 2p+2p asymptote in Li₂. The 2(C)¹Π_u state correlated with this asymptote pushes up all higher $^1\Pi_u$ states by a "domino effect", which results in an increase in their term energies and may cause that the quantum defects assume a negative value. Interaction with the doubly excited molecular state makes the potential curves of the investigated states shallower but this effect diminishes with growing n (see the evolution of D_e values in Table 3). This observation is compatible with the measured values of vibrational constants which increase systematically, as may be expected for potentials with gradually increasing depths, apparently to converge

Figure 1. Experimental RKR potential energy curves of the selected ${}^1\Pi_u$ states in Li₂ with their related asymptotes. The states belonging to the Rydberg series ${}^1\Pi_u(np\pi_u)$ are depicted by thick lines. The diabatic course of the $4{}^1\Pi_u$ potential is shown. The ${}^1\Pi_u$ state reported by Ross *et al.* [10] is marked with a dashed line and labelled with a question mark.

to the corresponding value of the ground state of molecular ion, Li₂⁺. On the other hand, the values of rotational constants behave against the expectations, since they clearly diverge from the ionic value. Decrease of B_e values, i.e. increase of equilibrium distances with growing n would mean in a simplistic picture that the molecular bond is weakened. At present we cannot explain our observation and theoretical calculation of potential curves for higher excited states in Li₂ would be highly desirable to get more insight into this problem. It must be stressed that an alternative assignment of the observed Rydberg series, as $6{}^1\Pi_u(5p\pi_u)$, $\alpha{}^1\Pi_u(6p\pi_u)$, ..., leading to a plausible value of quantum defect $\delta \approx 0.16$, would mean that a low number of the series corresponding to $n = 4$ has not been detected experimentally. In successive experiments done in our laboratory ([13, 12, 8, 9] and the present work) we have investigated excitation spectra of Li₂ in the full range of excitation energies between 29000 and 41000 cm⁻¹ and found no ${}^1\Pi_u$ state which might be the missing low member of the series. This experimental fact makes the alternative assignment unlikely.

We note at this juncture a ${}^1\Pi_u$ state with $T_e \approx 37260$ cm⁻¹ observed via fluorescence from some higher states and assigned as $5p{}^1\Pi_u$ by Ross *et al.* [10]. Since this state could not be seen in transitions from the ground X¹ Σ_g^+ state in our experiment and its term value does not fit the Rydberg formula (1) established here for ${}^1\Pi_u(np\pi_u)$ states, we must conclude that the assignment by Ross *et al.* is incorrect and the state in question belongs to another electronic configuration. With the results of the present experiment, we may speculate about its identity. The ${}^1\Pi_u$ state discussed in reference [10] lies between the $6{}^1\Pi_u$ and $\alpha{}^1\Pi_u$ states and therefore must correlate diabatically with atomic asymptotes placed between $2s+4p$ and $2s+5p$. This leaves only two asymptotes: $2s+4d$ and $2s+4f$. The ${}^1\Pi_u$ state was seen in a transition to the $1{}^1\Delta_g(2p+2p)$ state [10]. Assuming that the states mentioned above preserve to some extent their asymptotic character even close to R_e , both possible assignments would lead to a two electron process in the ${}^1\Pi_u \rightarrow 1{}^1\Delta_g$ transition, either $(2s+4d) \rightarrow (2p+2p)$ or $(2s+4f) \rightarrow (2p+2p)$, with the first of them clearly more probable. Therefore the assignment of the state of reference [10] as ${}^1\Pi_u(2s+4d)$ is to be preferred. We also note that to the best of our knowledge no

Table 3. Selected molecular constants for the Rydberg states of ⁷Li₂ along with the corresponding constants for the ground state of the molecular ion. The units are cm⁻¹, except for quantum defect δ . The 4¹ Π_u state is strongly perturbed by the neighbouring 3¹ Π_u state [11] and its potential curve is highly irregular, therefore the ω_e and B_e values are not given.

state	at. asymptote (diabatic)	T_e	δ	ω_e	B_e	D_e
4 ¹ $\Pi_u(3p\pi_u)$	2s+3p	34605.7 [12]	-0.98			4942
6 ¹ $\Pi_u(4p\pi_u)$	2s+4p	36863.2 [9]	-0.845	253.6	0.4801	8123.0
$\alpha^1\Pi_u(5p\pi_u)$	2s+5p	38320.6	-0.840	257.5	0.4746	9211.6
$\beta^1\Pi_u(6p\pi_u)$	2s+6p	39192.6	-0.839	259.4	0.4637	9714.8
$\gamma^1\Pi_u(7p\pi_u)$	2s+7p	39753.4	-0.840	260.4	0.4499	9980.6
			⁷ Li ₂ ⁺	263.1	0.500	10465.3 [22]

electronic state correlating to f configuration has been recognized experimentally for any of the alkali dimers. However, *ab initio* calculations would be necessary to resolve this question which cannot be answered definitely from spectroscopic observations alone.

5. Conclusion

In the range of 38300–41700 cm⁻¹ above the minimum of the ground state of Li₂ we have observed and characterized three states of ¹ Π_u symmetry, which together with the 4¹ Π_u and 6¹ Π_u states known from other experiments form a Rydberg series corresponding to excitation of the $np\pi_u$ electron. The negative value of the quantum defect for the series suggests interaction with the low lying valence C¹ Π_u state correlated to doubly excited atomic configuration 2p+2p. The present work shows advantages of the polarisation labelling spectroscopy technique because simplified spectra and sensitive detection are crucial for investigation of Rydberg states.

Acknowledgments

This work has been funded in part by grant N N202 203938 from the Polish Ministry of Science and Higher Education.

References

- [1] Bernheim R A, Gold L P and Tipton T 1983 *J. Chem. Phys.* **78** 3635.
- [2] Carlson N W, Taylor A J, Jones K M and Schawlow A L 1981 *Phys. Rev. A* **24** 822.
- [3] Broyer M, Chevaleyre J, Delacretaz G, Martin S and Wöste L 1983 *Chem. Phys. Lett.* **99** 206.
- [4] Chang E S, Li J, Zhang J, Tsai C C, Bahns J and Stwalley W C 1999 *J. Chem. Phys.* **111**, 6247.

- [5] Schwarz M, Duchowicz R, Demtröder W and Jungen Ch 1988 *J. Chem. Phys.* **89** 5460.
- [6] Martin S, Chevaleyre J, Bordas M Chr, Valignat S, Broyer M, Cabaud B and Hoareau A, *J. Chem. Phys.* **79** 4132.
- [7] Jastrzębski W and Kowalczyk P 1995 *Phys. Rev. A* **51** 1046.
- [8] Jędrzejewski-Szmek Z, Grochola A, Jastrzebski W and Kowalczyk P 2007 *Chem. Phys. Lett.* **444** 229.
- [9] Grochola A, Jastrzebski W and Kowalczyk P 2008 *Mol. Phys.* **106** 1375.
- [10] Ross A J, Martin F, Adohi-Krou A and Jungen Ch 2004 *J. Mol. Spectrosc.* **227** 158.
- [11] Theiss W, Müschenborn H J and Demtröder W 1990 *Chem. Phys. Lett.* **174** 126.
- [12] Jędrzejewski-Szmek Z, Grochola A, Jastrzebski W and Kowalczyk P 2010 *Opt. Appl.*, in print.
- [13] Kubkowska M K, Grochola A, Jastrzebski W and Kowalczyk P 2007 *Chem. Phys.* **333** 214.
- [14] Grochola A, Kowalczyk P, Jastrzebski W, Głódź M 2006 *Chem. Phys. Lett.* **430** 247.
- [15] Jackowska I, Jastrzębski W and Kowalczyk P 1997 *J. Mol. Spectrosc.* **185** 173.
- [16] Grochola A, Jastrzebski W and Kowalczyk P, Magnier S and Aubert-Frécon M 2004 *J. Mol. Spectrosc.* **224** 151.
- [17] Wang X, Magnes J, Lyyra A M, Ross A J, Martin F, Dove P M and Le Roy R J 2002 *J. Chem. Phys.* **117** 9339.
- [18] Le Roy R J 1998 *J. Mol. Spectrosc.* **191** 223.
- [19] Kowalczyk P, Schühle U and Engelke F 1989 *Z. Phys. D* **13** 231.
- [20] Radzig A A and Smirnov P M 1985 *Reference Data on Atoms, Molecules and Ions* (Berlin: Springer).
- [21] Jasik P and Sienkiewicz J E 2009 *Proceedings of the 41st EGAS Conference*, Gdańsk, Poland.
- [22] Roche A L and Jungen Ch 1993 *J. Chem. Phys.* **98** 3637.
- [23] Spies N 1990 Ph.D. thesis, Universität Kaiserslautern.

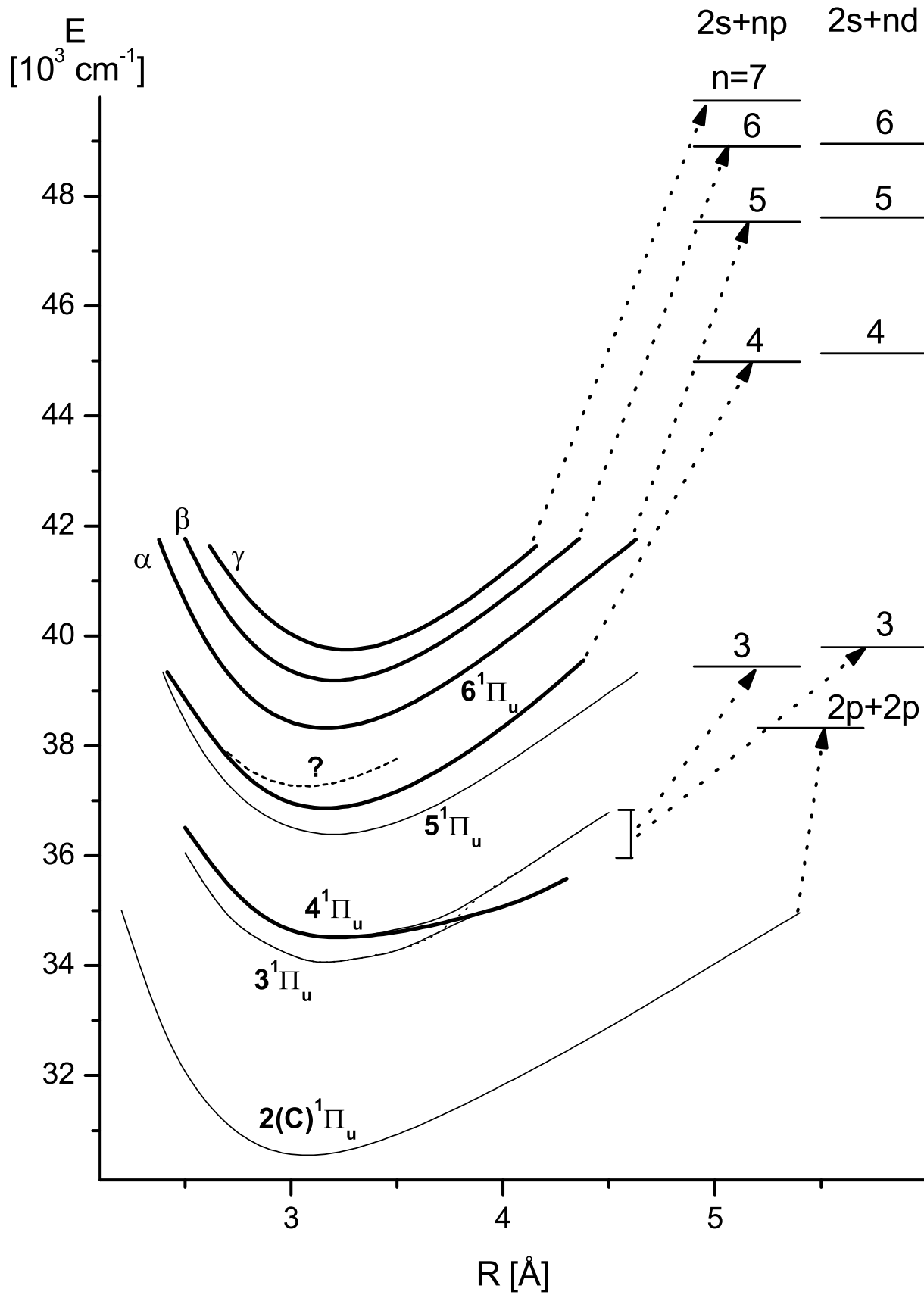


Figure 1 (figure1.eps)