Potential energy curves for the ground and low-lying excited states of IBr calculated with relativistic effective core potentials and spin-orbit interactions.

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Abstract

Low-lying potential energy curves of the IBr molecule are calculated by a combination of the equation of motion coupled cluster method and the spin-orbit multireference configuration interaction with single excitations, employing in both cases accurate relativistic effective core potentials and an extended valence basis set. Dissociation curves and spectroscopic constants are presented for the ground and eight lowest excited states and the relation of the results to experiment is discussed.

1 Introduction

Heavier halogens have been favorite targets of spectroscopic studies for several decades [1]. This is mainly due to the fact that they represent rare cases of diatomic molecules, which absorb in a spectroscopically easily accessible visible and near-UV region. Such an absorption is mediated by strong spin-orbit interactions, which cause the formally (non-relativistically) forbidden low energy singlet-triplet transitions to be allowed. At the same time, a whole plethora of low-lying excited states is present in heavier halogen molecules due to spin-orbit splittings, which makes spectroscopic studies interesting, but also hardly possible without a theoretical and computational background.

The most intensely studied system among heavier halogens is certainly molecular iodine, which can be justly called the "hydrogen atom" of laser spectroscopists. Ground and excited states of the I_2 molecule have been investigated both by frequency domain [2-4] and pump-probe [5-7] experiments. These electronic states have been classified in a pioneering study by Mulliken [8] and later calculated at different levels of electronic structure theory including spin-orbit interactions and other relativistic effects [9-11]. Several experimental studies have also been devoted to heavier interhalogens, especially to the IBr molecule [12-20]. The ground and few low-lying potential energy curves have been obtained by fitting to the RKR points [20] and non-adiabatic dynamics in the $B(^3\Pi_{0+})/Y(0^+)$ states has been probed by a femtosecond experiment [18-19]. On the other hand, high quality calculations of the IBr molecule are available only for the ground state [9] and an accurate computational description of the excited potential curves in the whole interval from the Franck-Condon region to dissociation is still lacking. Such a calculation represents a non-trivial challenge, since both relativistic effects (primarily spin-orbit interactions and contractions of core orbitals) and correlations have to be accounted for properly.

The main goal of the present paper is to provide reliable *ab initio* low-lying potential energy curves of the IBr molecule. Our work has been motivated by a planned pump-probe measurement and wavepacket calculation, which will explore mainly the dynamics on the $A^3\Pi_1$ potential [21], as well as by the recent femtosecond experimental and simulation study mentioned above [18-19]. The aim has been to use accurate relativistic pseudopotentials, include the spin-orbit interactions, and account for a dominant portion of the correlation energy in order to obtain potentials, which would allow for a quantitative interpretation of the time-resolved measurement.

The paper is organized as follows. In Section II we describe in detail the computational methods employed. The potential curves and corresponding spectroscopic constants are presented and discussed in Section III. Finally, Section IV contains concluding remarks.

2 Computational Method

In molecules containing heavy atoms, such as iodine or bromine, relativistic effects, and spin-orbit (LS) interactions in particlar, cannot be neglected and in some cases even first order perturbative treatment is not accurate enough. Moreover, in order to obtain potential energy (PE) curves of a reasonable accuracy for the ground, as well as excited states, inclusion of dynamical correlation in a sophisticated way is absolutely essential. Unfortunately, methods which would simultaneously be able to describe both these effects (also for excited states) are computationally rather prohibitive and have not been implemented in generally available quantum chemical programs yet. Therefore, we have followed the usual route assuming that energy shift and splitting due to the spin-orbit interactions and the non-relativistic energy, computed by a method which includes dynamical correlation effects, are additive [9]. The validity of this assumption is then *a posteriori* checked by comparison of computed spectroscopic constants of the molecule in several states of interest with available experimental data.

The inner shell electrons have been treated using recent averaged relativistic effective core potentials (AREP) [22] and the spin-orbit potential has been employed for the description of the LS interactions [23-24]. In order to correctly describe excited states, we have augmented the valence basis set supplied together with the AREP [22] by three s and three p diffuse functions and three d functions, the final basis set size being $(8s8p3d/5s5p3d)$. The corresponding exponents have acquired the following values: $\zeta_s = \zeta_p = (0.0357, 0.01335, 0.005)$, $\zeta_d = (0.389, 0.0972, 0.0243)$ for bromine and $\zeta_s = \zeta_p = (0.030, 0.0116, 0.0045)$, $\zeta_d = (0.266, 0.0665, 0.0166)$ for iodine.

In the first computational step, we have employed the equation of motion coupled cluster method with single and double excitations (EOM-CCSD) [25], as implemented in the program ACES II [26], for calculations of the ground and excited state potential curves of the IBr molecule without the spin-orbit effect. Subsequently, we have used the spin-orbit multireference configuration interaction with single excitations (SO-MRCIS) [27-29] implemented in the Pitzer's version of the COLUMBUS program [30-31]. For each geometry and electronic state two energies have been evaluated, one with the LS potential and one without it. The difference between these two energy values, which represents the effect of the LS interaction, has been added to the EOM-CCSD energy, yielding thus the final energy.

3 Results and Discussion

Prior to the evaluation of the IBr potential curves calculations of the ground and six lowest excited states of the Br and I atoms have been performed using an accurate multireference spin-orbit configuration interaction (SO-MRCISD) approach [30-31] in order to verify the performance of present basis set. Results are presented and compared with the atomic spectroscopic data [32] in Tables 1 and 2. It can be seen, that the atomic excited states in the energy interval from zero to 8.5 eV are obtained with an accuracy better than 0.2 eV, the low-lying states even with an error smaller than 0.1 eV. We conclude that the basis set employed is suitable for calculations of ground and low-lying excited states of the IBr molecule.

The computed potential energy curves of the ground and six low-lying excited states of IBr are depicted in Fig. 1. In addition, Table 3 presents the corresponding spectroscopic constants extracted from the curves in Fig. 1, in comparison with available experimental data [33]. For the ground state, we have also evaluated the vertical ionization potential (IP) and the dissociation energy D_0, primarily to verify the accuracy of the calculations. IP of 9.85 eV (accidentally) perfectly coincides with the experimental value of 9.85 eV [33]. For the dissociation energy D_0 we predict 2.07 eV, while the experimental value is 1.8176 eV [33]. This small discrepancy, comparable, however, to the error in vertical excitation energies (see below), may be explained by a slightly suboptimal performance of the single-reference coupled cluster method at very large internuclear separations.

To further check the performance of the single reference EOM-CCSD approach, the approximate excitation levels (AEL) have been evaluated as a test of the validity for all the states of interest along the potential energy curves. For the range of internuclear distances up to 4 Å , this value does not exceed 1.2 for any of the states, which indicates an excellent performance of

EOM-CCSD approximation in this part of the potential energy curves. For larger internuclear separations, the effect of higher excitations becomes more pronounced and the AEL grows up to 1.4 around 8 Å . This may cause a certain loss of accuracy at larger interatomic distances, in agreement with the well-known fact, that one needs a multireference CC treatment to achieve a highly accurate description of bond breaking. However, since the AELs do not by far reach the value of 2.0, and since we have reproduced the the ground state dissociation energy satisfactorily, we expect the excitation energies to be meaningful also at large internuclear separations.

From Tab. 3 it can be seen, that the calculated vertical excitation energies T_e differ by 0.2–0.3 eV from the corresponding experimental data. The agreement of the vibrational and rotational constants with the spectroscopic data for the ground state, as well as for optically accessible low-lying A and B states, is even more satisfactory. This indicates, that the present calculations are most successful in describing the shapes of the potential curves. This is very important with respect to the intended study of wavepacket dynamics on the PE curves [21], where their shape is of a primary importance. Most of the potentials have a regular, single minimum behavior, however, two of the computed PE curves, corresponding to the $1^3\Pi_0^+$ and $2^3\Pi_2$ states, exhibit a maximum and two local minima, which is a consequence of avoided crossings.

For higher lying states of a charge-transfer character, we have not been able to obtain converged SO-MRCI results, and also the EOM-CCSD method suffered from serious convergence problems. On the other hand, a semi-quantitative description of the charge-transfer states is sufficient for the modeling of the pump-probe signal. Therefore, we have computed the PE curve for the lowest $2^1\Sigma_0^+$ charge-transfer state, without inclusion of the SO effects. It is depicted together with the PE curve for the ground state (for comparison also without SO interactions) in Fig. 2 and its spectroscopic data are included in Tab. 3. At larger distances the curve is strongly attractive, which is typical for Coulombic charge-charge interactions. Finally, around 2.3 Å there is a clear trace of an avoided crossing with a higher lying charge-transfer state.

4 Conclusions

The ground and low-lying potential energy curves of the IBr molecule have been evaluated for a broad range of interatomic separations by a combination of the equation of motion coupled cluster method and the spin-orbit multireference configuration interaction with single excitations. We have shown that this approach, which employs relativistic effective core potentials and an extended valence basis set, provides accurate potential curves and spectroscopic constants in a good agreement with experimental data (whenever available). These potentials will be subsequently used in a dynamical wavepacket simulation, in direct relation to a planned femtosecond pump-probe experiment.

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References

[1] J. C. D. Brand and H. R. Hoy, Appl. Spectr. Rev. 23 (1987) 285.

[2] X. N. Zheng, S. L. Fei, M. C. Heaven, and J. Tellinghuisen, J. Chem. Phys. 96 (1992) 4877.

[3] T. Ishiwata, H. Takekawa, and K. Obi, J. Mol. Spectrosc. 159 (1993) 443.

[4] D. Inard, D. Cerny, M. Nota, and R. Bacis, Chem. Phys. 243 (1999) 305.

[5] M. Dantus, M. H. M. Janssen, and A. H. Zewail, Chem. Phys. Lett. 181 (1991) 281.

[6] M. Gruebele, G. Roberts, M. Dantus, R. M. Bowman, and A. H. Zewail, Chem. Phys. Lett. 166 (1990) 459.

[7] P. Farnara, H.-H. Ritze, V. Stert, and W. Radloff, Chem. Phys. Lett. 307 (1999) 1.

[8] R. S. Mulliken, J. Chem. Phys. 55 (1971) 288.

[9] S. Y. Lee and Y. S. Lee, Chem. Phys. Lett. 187 (1991) 302.

[10] C. Teichtel and M. Pelissier, Chem. Phys. 180 (1994) 1.

[11] W. A. deJong, L. Visscher, and W. C. Nieuwpoort, J. Chem. Phys. 107 (1997) 9046.

[12] X. N. Zheng, M. C. Heaven, and J. Tellinghuisen, J. Mol. Spectrosc. 164 (1994) 135.

[13] N. Nishimiya, T. Yukiya, and M. Suzuki, J. Mol. Spectrosc. 173 (1995) 8.

[14] P. Vogt, M. Schmitt, and W. Kiefer, Chem. Phys. Lett. 243 (1995) 64.

[15] D. R. T. Appadoo, P. F. Bernath, and R. J. Leroy, Can. J. Phys. 72 (1994) 1265.

[16] A. Kvaran, H. S. Wang, and G. H. Johannesson, J. Chem. Phys. 99 (1995) 4451.

[17] Y. S. Kim, Y.-J. Jung, and K.-H. Jung, J. Chem. Phys. 107 (1997) 3805.

[18] M. Shapiro, M. J. J. Vrakking, and A. Stolow, J. Chem. Phys. 110 (1999) 2465.

[19] M. J. J. Vrakking, D. M. Villeneuve, and A. Stolow, J. Chem. Phys. 105 (1996) 5647.

[20] K. P. Lawley, D. Austin, J. Tellinghuisen, and R. J. Donovan, Mol. Phys. 62 (1987) 1195.

[21] P. Kuzel, J. Pittner, and P. Jungwirth, in preparation.

[22] W. J. Stevens, M. Krauss, H. Basch, P. G. Jasien, Can. J. Chem. 70 (1992) 612.

[23] M. M. Hurley, L. F. Pacios, P. A. Christiansen, R. B. Ross, W. C. Ermler, J. Chem. Phys. 84 (1986) 6840.

[24] L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, W. C. Ermler, J. Chem. Phys. 87 (1987) 2812.

[25] J. F. Stanton, R. J. Bartlett, J. Chem. Phys. 98 (1993) 7029.

[26] ACES II is a program product of Quantum Theory Project, University of Florida, J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K.-K. Baeck, P. Rozyczko, H. Sekino, C. Huber, and R. J. Bartlett. Integral packages included are VMOL (J. Almloef and P. R. Taylor); VPROPS (P. R. Taylor); and ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Joergensen, J. Olsen, and P. R. Taylor).

[27] R. M. Pitzer, N. W. Winter, J. Phys. Chem. 92 (1988) 3061.

[28] R. M. Pitzer, N. W. Winter, Int. J. Quant. Chem. 40 (1991) 773.

[29] H. L. Hsu, E. R. Davidson, R. M. Pitzer, J. Chem. Phys. 65 (1976) 609.

[30] R. Shepard, I. Shavitt, R. M. Pitzer, D. C. Comeau, M. Pepper, H. Lischka, P. G. Szalay, R. Ahlrichs, F. B. Brown, J. G. Zhao, Int. J. Quant. Chem., Quant. Chem. Symp. 22 (1988) 149.

[31] R. M. Pitzer, SO version of the program COLUMBUS, Ohio state University (1990).

[32] C. E. Moore, "Atomic energy levels", Circular of the National Bureau of Standards 467, Washington (1949).

[33] K. P. Huber, G. Herzberg, Molecular spectra and molecular structure, Vol.4. "Constants of diatomic Molecules", Van Nostrand Reinhold, New York (1979).

Figure Captions

Figure 1:

Potential energy curves of the ground and seven lowest excited potentials of the IBr molecule including the spin-orbit interactions. Energy is relative to the ground state minimum. Symbols represent the calculated points.

Figure 2:

Potential energy curve of the lowest charge-transfer state of the IBr molecule compared to the ground state. Spin-orbit interactions have not been included and energy is relative to the ground state minimum. Symbols represent the calculated points.

Table 1: Comparison of the calculated and experimental atomic energy levels for the Br atom

State	E(calc.) eV	E(exp.)[a] eV	ΔE eV
$^2P_{3/2}$	0.00	0.00	0.00
$^2P_{1/2}$	0.47	0.46	-0.02
$^4P_{5/2}$	7.78	7.86	0.09
$^4P_{3/2}$	7.93	8.05	0.12
$^4P_{1/2}$	8.18	8.29	0.11
$^2P_{3/2}$	8.19	8.33	0.14
$^2P_{1/2}$	8.38	8.55	0.17

[a] From Ref. [32]

Table 2: Comparison of the calculated and experimental atomic energy levels for the I atom.

State	E(calc.) eV	E(exp.)[a] eV	ΔE eV
$^2P_{3/2}$	0.00	0.00	0.00
$^2P_{1/2}$	0.94	0.94	0.00
$^4P_{5/2}$	6.63	6.77	0.14
$^2P_{3/2}$	6.79	6.95	0.16
$^4P_{1/2}$	7.36	7.55	0.19
$^4P_{3/2}$	7.42	7.66	0.24
$^2P_{1/2}$	7.58	7.83	0.25

[a] From Ref. [32]

Table 3: Spectroscopic constants of several low lying states of IBr.

State	T_e	r_e	ω_e	$\omega_e x_e$	B_e	α_e	D_e
	eV	Å	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	$10^{-8}\mathrm{cm}^{-1}$
$1^1\Sigma_0^+$	0	2.52	253.0	0.87	0.054	0.00020	1.0
$X^1\Sigma_0^+$ [a]	(0)	(2.46898)	(268.64)	(0.814)	(0.0568325)	(0.0001969)	(1.02)
$1^3\Pi_2$	1.62	2.88	150.9	0.79	0.042	0.00023	1.3
$1^3\Pi_1$	1.85	2.91	138.8	0.78	0.041	0.00025	1.4
$A^3\Pi_1$ [a]	(1.531)		(138.0)	(1.7)	(0.03803)		(3.0)
$1^3\Pi_0^+$	2.18	2.89	122.5	3.58	0.042	0.00057	1.9
$B^3\Pi_0^+$ [a]	(2.005)	(2.83)	(142.5)	(2.57)	(0.0432)	(0.00053)	(2.2)
$1^3\Pi_0^-$	2.18	3.03	97.7	0.62	0.038	0.00036	2.3
$1^1\Pi_1$	2.65	3.26	68.5	-0.24	0.033	0.00015	2.9
$2^3\Pi_2$	3.82	3.65	91.4	1.07	0.026	-0.00009	0.8
$2^3\Pi_0^+$	4.24	3.50	137.7	0.61	0.028	-0.00006	0.5
$2^1\Sigma_0^+$	7.36	3.15	181.8	1.05	0.035	0.00005	0.5

[a] Experimental data from Ref. [33]

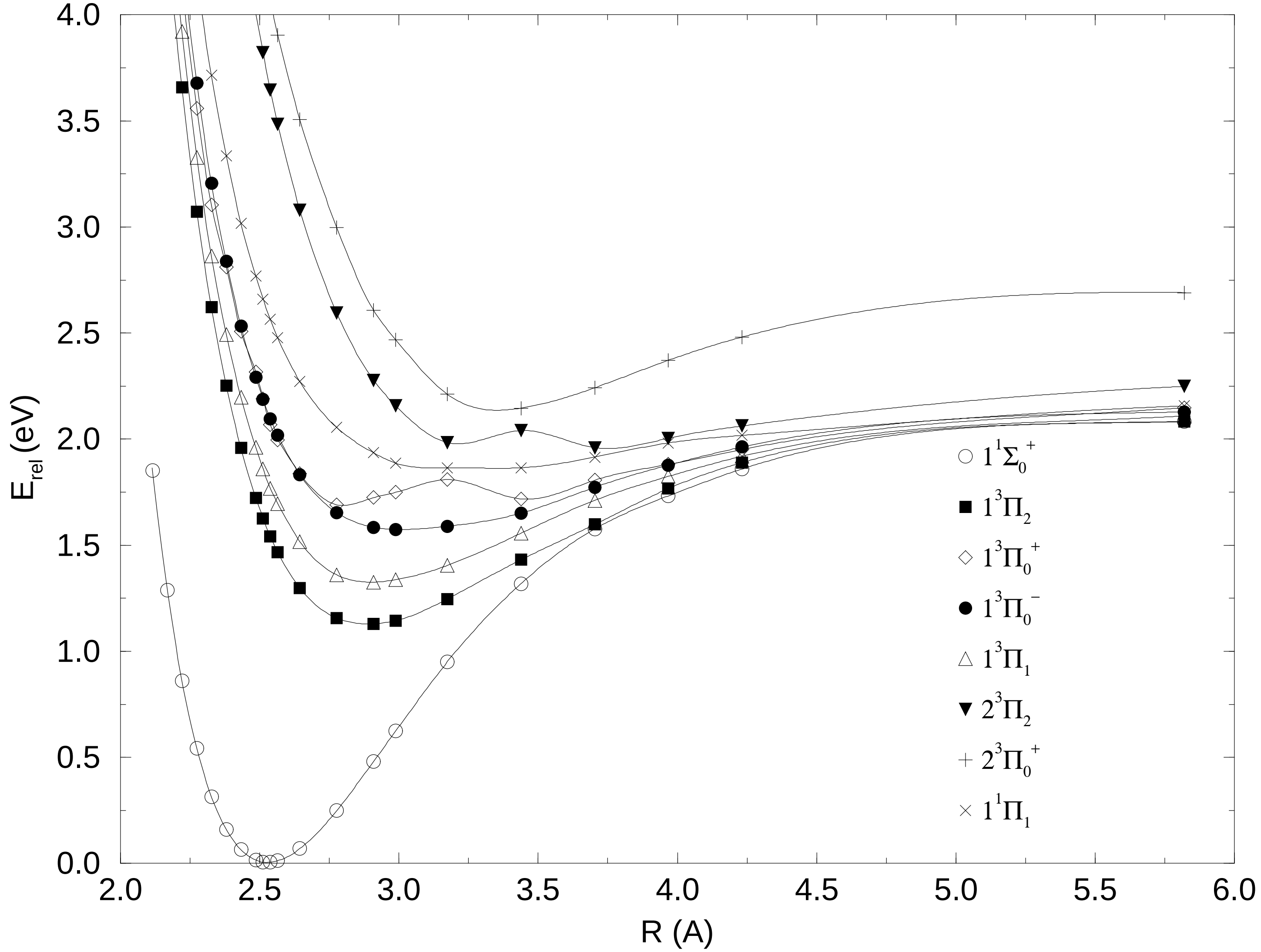

Figure 1, Pittner and Jungwirth

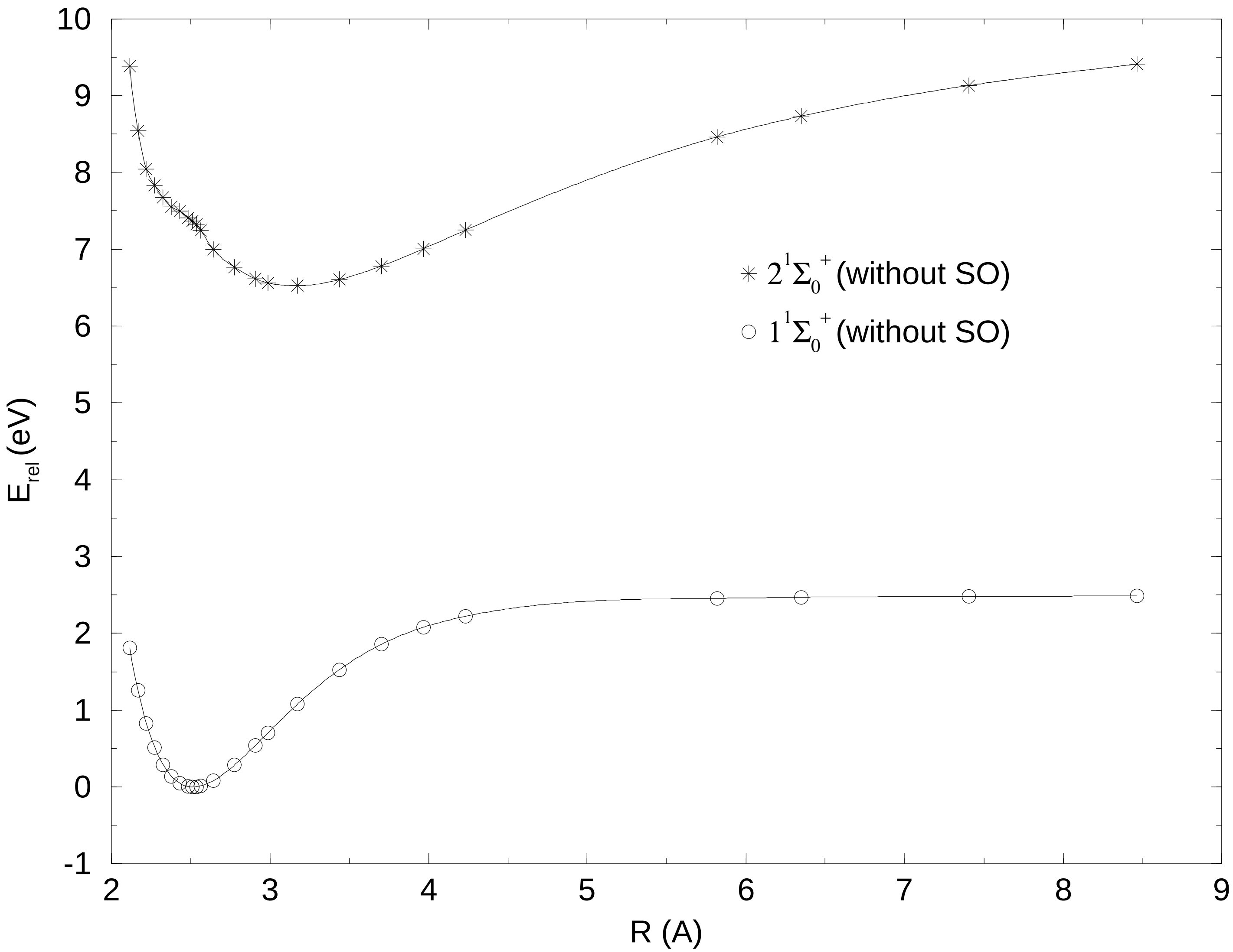

Figure 2, Pittner and Jungwirth