THE JOURNAL OF
PHYSICAL CHEMISTRY A

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pubs.acs.org/JPCA

An ab Initio Study of the E $^3\Pi_g$ State of the Iodine Molecule

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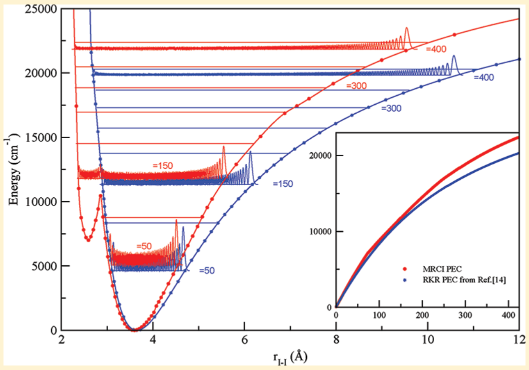
ABSTRACT: The E $^3\Pi_g$ state of the iodine molecule is studied by ab initio multireference methods coupled with effective core potentials and large basis sets. Two potential minima are found, a global featuring an ion-pair character, and a local presenting a purely Rydberg nature. Four avoided crossings along the dissociation coordinate attribute an interesting topology to its potential energy curve, and their effect on the vibrational levels of I_2 is discussed.



1. INTRODUCTION

The I_2 molecule has been studied by both experiment and theory; however, the nature of its higher electronic states has remained unexplored. In a landmark review paper on I_2, Mulliken[1] defined as valence states those whose electronic configurations are of the type $\sigma_g^2\sigma_u^2\sigma_g^m\pi_u^p\pi_g^q\sigma_u^{\,n}$ (*mpqn* in a shorthand notation) with $m + p + q + n = 10$, and the molecular orbitals $\sigma_{g,u}$ and $\pi_{u,g}$ correlating to the atomic valence 5s and 5p orbitals. The above-defined molecular states dissociate either to I($5s^25p^5$; ^2P) + I($5s^25p^5$; ^2P) or to I^+($5s^25p^4$; ^3P, ^1D, ^1S) + I^-($5s^25p^6$; ^1S).

At that time the E state was fairly well established experimentally (T_e = 41411 cm^{-1}, ω_e = 101.59 cm^{-1}, ω_ex_e = 0.238 cm^{-1}) and was considered to be a typical ion-pair state.[2] It was not certain, however, whether its symmetry was $^3\Pi_g$ (with an electronic configuration 1432) or $^1\Sigma_g^{\,+}$ (2242), although Waser and Wieland opted for the former assignment (see ref 1). Mulliken considered that the E state would tend to dissociate to I^+($5s^25p^4$; $^3P_0$) + I^-($5s^25p^6$; ^1S) but actually would end up to a ground state I(^2P) atom and another one of Rydberg character.

A year later, Wieland et al.,[3] reported the spectroscopic parameters of the E state (T_e = 41411.8 cm^{-1}, ω_e = 101.59 cm^{-1}, ω_ex_e = 0.2380 cm^{-1}, r_e ∼ 3.7 Å) on the basis of the analysis of the vibrational structures of the E($^3\Pi_{0_g^+}$) → B($^3\Pi_{0_u^+}$) 4000–4360 Å emission system. The same constants were reproduced virtually the same in the 1979 compilation by Huber and Herzberg,[4] whereas Tellinghuisen[5] fitted the existing vibrational data to a Morse potential and deduced a r_e value of r_e = 3.649 ± 0.002 Å.

Shortly after, Rousseau[6] conclusively assigned the E state to a $^3\Pi_{0_g^+}$ (1432) electronic configuration based on the small lifetime of the E → B emission system. On the basis of the E → B excitation system and through a sequential two-photon experiment, Williamson,[7] and simultaneously Cunha et al.,[8] reported revised molecular constants for the E state, in very good agreement with the values reported by Wieland et al.[3] On the basis of the same experimental technique, King et al.[9] obtained refined molecular constants for the E state and reported Rydberg–Klein–Rees (RKR) turning points. Brand and co-workers[10−12] studied the resonant two-photon E(0_g^+) ← B(0_u^+) ← X(0_g^+) transition by polarization spectroscopy and obtained accurate molecular constants and RKR turning points for the E potential energy curve (PEC) based on a global least-squares fit of 1050 assigned rotational transitions. Definitive evidence was also provided that the E 0_g^+ state correlates diabatically to the ground state of the separate ions with a D_e value of 30750 ± 50 cm^{-1} (=87.92 ± 0.14 kcal/mol), although the adiabatic dissociation limit should be I($5s^25p^5$; ^2P) + I($5s^25p^4$(^3P)$6s^1$; ^4P). During the experimental study of the 1_g I_2 state the occurrence of both B 1_g and B 0_g^+ transitions in the same spectra led Perrot et al.,[13] to the extraction of improved molecular constants for the E state.

Later on, Wilson et al.,[14] through the double resonance ionization nozzle cooled spectroscopy technique, have succeeded in extending the existing Dunham parameters for three ion-pair states of 0_g^+ symmetry. In particular, for the E state they covered vibrational levels in the range of v = 0–422, which led to an extended RKR PEC. The new potential correctly reproduced the observed intensity minima below 54000 cm^{-1}. Above this, they observed an irregular behavior attributed to homogeneous interactions with Rydberg states of 6s and 5d character at about 55000 and 60000 cm^{-1}, respectively.

Received: January 2, 2012
Revised: February 1, 2012
Published: February 1, 2012

It is clear by now that the E 0_g^+ state is very well studied experimentally. Unfortunately, this is not the case at the theoretical level. The first ab initio treatment of the E state, that we are aware of, is a pseudopotential MCSCF+CI study by Das and Wahl.[15] A relativistic treatment of the E state reveals that it is almost exclusively of $^1\Sigma_g^+$ symmetry with reported spectroscopic parameters, $r_e = 7.2\ \alpha_0$ (=3.81 Å), $\omega_e = 122\ \text{cm}^{-1}$, $\omega_e x_e = 0.45\ \text{cm}^{-1}$, and $T_e = 36500\ \text{cm}^{-1}$.[15] In a second theoretical report, Li and Balasubramanian,[16] used a CASSCF zeroth-order wave function followed by first-order, second-order, and relativistic configuration interaction (CI) calculations coupled with relativistic effective core potentials (ECP) to construct PECs of 44 electronic states of I_2 and 13 electronic states of I_2^+. The only numerical result reported in their account for the E state is a r_e value of 3.75 Å whereas its PEC is shown to correlate adiabatically to I(^{2}P) + I(^{4}P). More recently, two additional theoretical studies have focused on molecular states dissociating to I(^2P_J) + I($^2P_{J'}$), (J, J' = 1/2, 3/2), and thus excluding the E state.[17,18]

It is rather evident from this introduction that there is an almost complete lack of theoretical support concerning the E $^3\Pi_g$ state, despite the abundance of the available experimental data. Numerous collision studies between rare gas (Rg) elements and the E state of I_2,[19] along with extensive theoretical and experimental work on Rg–I_2 (X, B, E) van der Waals complexes[20−25] allude to a vivid interest on that particular ion–pair state of I_2. Accurate high level ab initio potentials are necessary for the interpretation and/or modeling of the experimental data. It is this gap that the present work aims to fill, and we think that it will also exert an impetus for more extensive work on the excited states of I_2. We also wanted to assess our presently available *state-of-the-art* computational panoply for a theoretically unknown molecular state of a rather heavy atomic element. To this end, multireference configuration interaction (MRCI) methods and relativistic ECPs together with large basis sets were employed for the construction of complete PECs of excited states of I_2 of $^3\Pi_g$ symmetry.

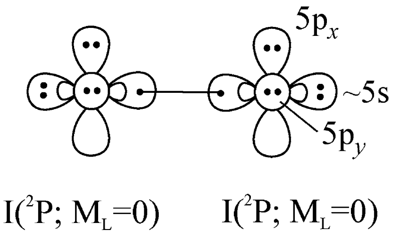
II. RESULTS AND DISCUSSION

The electronic configuration of the ground ^{2}P state of the I atom is [Ar]$3d^{10}4s^24p^64d^{10}5s^25p^5$. The [Ar+$3d^{10}$] electrons are described by the relativistic ECP28MDF effective core potential, whereas for the $4s^24p^64d^{10}5s^25p^5$ electrons the aug-cc-pV5Z-PP basis set[26] is employed generally contracted to [8s8p6d4f3g2h], giving rise to 139 × 2 spherical Gaussian functions.

The construction of the zeroth-order wave function relies on the complete active space self-consistent field (CASSCF) method that ensures proper dissociation to the adiabatic fragments. Dynamical correlation was extracted by single and double replacements out of the reference wave function (CASSCF+1+2 = MRCI), whereas the internally contraction scheme as implemented in the MOLPRO 2006 package[27] was used to keep the ensuing CI spaces at tractable levels. Size nonextensivity errors were accounted for by the multireference analog of the Davidson correction, denoted as +Q in what follows.[28]

The I atom is described fairly well. The first excited ^{4}P($5s^25p^4$(^{3}P)$6s^1$) state lies 6.841(6.880) eV higher than the ground ^{2}P($5s^25p^5$) state at the MRCI(+Q) level of theory as compared to the experimental (M_J averaged) value of 6.886 eV.[29] Furthermore, the ionization energy IE = 10.390 (10.497) eV and electron affinity EA = 3.151 (3.255) eV of iodine, calculated at the same level of theory, are also in very good accord with the experimental values of 10.454[29] and 3.059 eV,[30] respectively.

Two ground I(^{2}P) atomic states give rise to 12 $|\Lambda\Sigma\rangle$ molecular states of $^1(\Sigma_g^+[2],\Sigma_u^-,\Pi_g,\Pi_u,\Delta_g)$ and $^3(\Sigma_u^+[2]\ \Sigma_g^-,\Pi_g,\Pi_u,\Delta_u)$ spatial and spin symmetry. The ground state of the molecular species being of $^1\Sigma_g^+$ symmetry results from the $|^2P;\ M_L = 0\rangle \otimes |^2P;\ M_L = 0\rangle$ asymptotic product and features a genuine 2 electron σ bond. The essence of the chemical interaction is captured by the following valence bond Lewis (vbL) diagram well established in the chemical literature.[31]



For its description a CASSCF wave function was constructed by distributing the 14 valence electrons ($5s^25p^5$ × 2) to 8 molecular orbitals correlating to the atomic 5s + 5p valence shell. The ensuing MRCI expansion resulted in ~2 × 10^6 configuration functions (CF) internally contracted to ~800000 CFs under D_{2h} symmetry restrictions. Size nonextensivity errors amount to ~18(4) mE_h at the MRCI(+Q) level of theory. Numerical results are reported in Table 1 together with available experimental data.

The next three higher dissociation channels I($5s^25p^5$; ^{2}P) + [I($5s^25p^4$(^{3}P)$6s^1$; ^{4}P), I($5s^25p^4$(^{3}P)$6s^1$; ^{2}P)] and I^+($5s^25p^4$; ^{3}P) + I^-($5s^25p^6$; ^{1}S) at 6.841 (6.880) [6.886], 7.130 (7.165) [6.934], and 7.239 (7.242) [7.395] eV higher than the ground channel at the MRCI(+Q)[expt][29] level, respectively, give rise to five molecular states of $^3\Pi_g$ symmetry. The E $^3\Pi_g$ state originates adiabatically from the first excited dissociation channel, which is of mixed character, valence + Rydberg. Its correct description at all internuclear distances demands Rydberg orbitals in the active space of the zeroth-order reference wave function. To this end, a CASSCF wave function was constructed by allotting 10 electrons to 14 orbitals that correlate to 5p, 6s, and 6p. The CASSCF wave function amounts to 219660 D_{2h} symmetry restricted CFs. Eleven states of $^3\Pi_g$ symmetry were state-averaged to capture correctly the valence–Rydberg–ion-pair mixing along the dissociation coordinate. In the subsequent MRCI treatment 14 electrons were correlated through all single and double replacements from an internal space generated by the distribution of 10 electrons to 11 orbitals. The CI space thus created contains ~3.7 × 10^9 CFs internally contracted to ~60 × 10^6 CFs. Size nonextensivity errors amount to 19(4) mE_h at the MRCI(+Q) level of theory.

The PEC of the E $^3\Pi_g$ state presents an interesting topological structure, the result of four avoided crossings with the first and higher $^3\Pi_g$ states. The first avoided crossing occurs at around 26 Å(=50 α_0) at which distance [1/50 E_h ~ ($E_{\text{supermolecule}}$[(I^+; ^{3}P) + (I^-; ^{1}S)] − $E_{\text{supermolecule}}$[(I; ^{2}P) + (I; ^{4}P)])] the transfer of the ion-pair nature to the E $^3\Pi_g$ state is

Table 1. Total Energies E (E_h), Bond Distances r_e (Å), Dissociation Energies D_e (kcal/mol), Harmonic Frequencies ω_e (cm^{-1}) and Anharmonic Corrections $\omega_e x_e$ (cm^{-1}), Zero Point Energies ZPE (cm^{-1}), and Energy Separation T_e (eV) of the X $^1\Sigma_g^+$ and E $^3\Pi_g$ States of I_2 at the MRCI(+Q) Level of Theory

state	method	$-E$	r_e	D_e[a]	ω_e	$\omega_e x_e$	ZPE	T_e
$X^1\Sigma_g^+$	MRCI	589.664 76	2.689	42.1	216.6	0.517	108.5	0.0
	MRCI+Q	589.705 4	2.687	44.9	219.5	0.512	109.7	0.0
	expt[b]		2.666_3	35.57	214.50_2	0.614_7		0.0
			Global Minimum					
$E^3\Pi_g$	MRCI	589.477 20	3.592	82.9	106.5	0.190	53.2	5.10
	MRCI+Q	589.516 4	3.593	85.2	104.1	0.226	52.0	5.14
	expt[c]		3.647	87.9	101.39	0.205		5.13
			Local Minimum					
	MRCI	589.443 62	2.588				154.8	
	MRCI+Q	589.479 6	2.589				147.0	

[a] With respect to the adiabatic fragments. [b] Reference 4. [c] Reference 12.

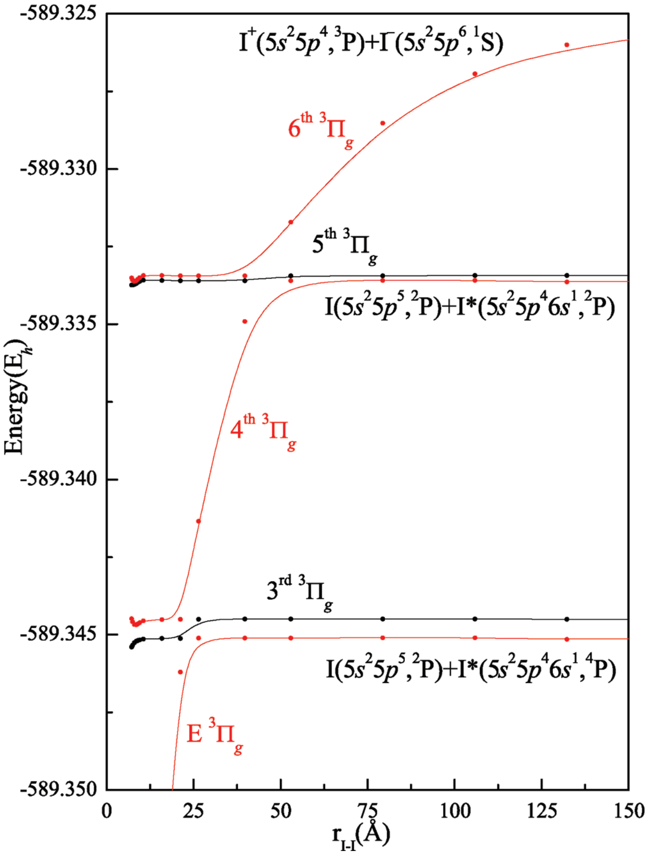


Figure 1. MRCI PECs of five states of $^3\Pi_g$ symmetry dissociating to I(^{2}P) + [I*(^{4}P), I*(^{2}P)] and I$^+$(^{3}P) + I$^-$(^{1}S).

observed (Figure 1). The first (global) minimum of the E state appears at r_e = 3.592 (3.593) Å at the MRCI(+Q) level of theory and consequently reflects the well established character of I$^+$I$^-$ ion-pair (Figure 2). This is clearly corroborated by the main CASSCF equilibrium configurations (only valence electrons are counted),

$$\left|E^3\Pi_g\right\rangle_{\text{global}} \approx 0.80\left|1\sigma_g^2 2\sigma_g^1 1\pi_{x,u}^2 1\pi_{y,u}^2 1\sigma_u^2 2\sigma_u^2 1\pi_{x,g}^1 1\pi_{y,g}^2\right\rangle$$
$$-0.49\left|1\sigma_g^2 2\sigma_g^2 1\pi_{x,u}^1 1\pi_{y,u}^2 1\sigma_u^2 2\sigma_u^1 1\pi_{x,g}^2 1\pi_{y,g}^2\right\rangle$$

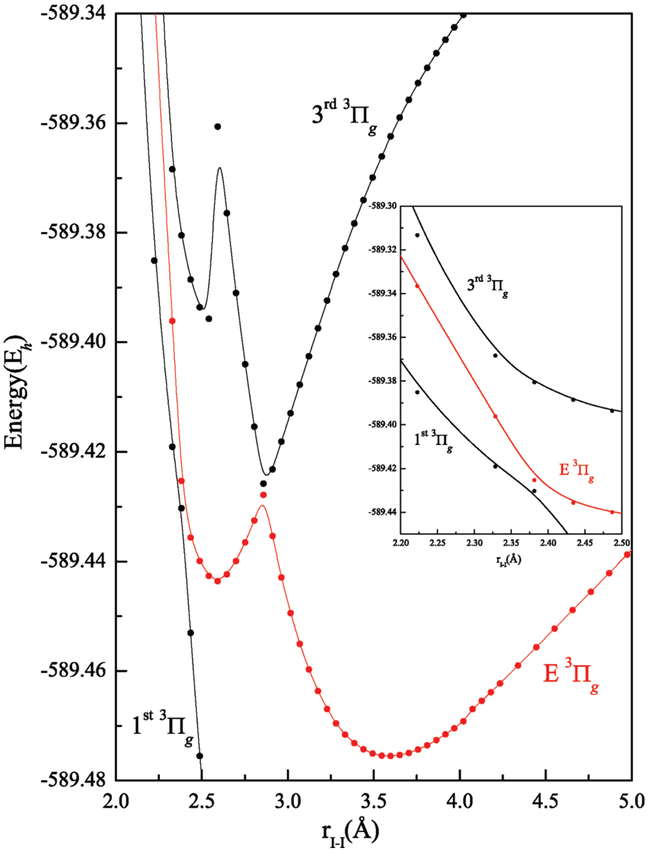
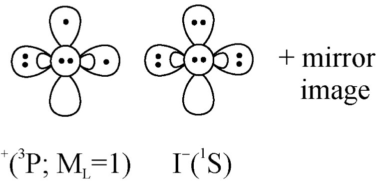


Figure 2. MRCI PECs of the first, E, and third $^3\Pi_g$ states. Details of the third and fourth avoided crossings are shown in the inset. See text for a thorough discussion.

and the corresponding Mulliken atomic distributions $5s^{2.0}5p_z^{1.43}5p_x^{1.46}5p_y^{1.95}$. All the above are nicely transcribed to the following vbL icon.

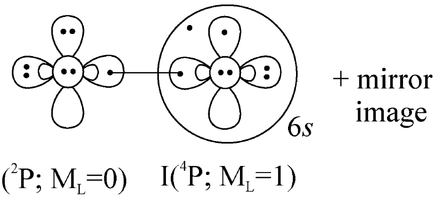


Our numerical data, shown in Table 1, pertaining to the usual spectroscopic parameters r_e = 3.592 (3.593) Å, ω_e = 106.5 (104.1) cm^{-1}, $\omega_e x_e$ = 0.190(0.226) cm^{-1}, and T_e = 5.10(5.14) eV at the MRCI(+Q) level of theory compare nicely with the existing experimental values of r_e = 3.647 Å, ω_e = 101.39 cm^{-1}, $\omega_e x_e$ = 0.205 cm^{-1}, and T_e = 5.13 eV[12] considering the size of the molecule and the approximations engaged. The MRCI(+Q) binding energy with respect to the adiabatic fragments, i.e., I(5s^{2}5p^5; ^{2}P) + I(5s^{2}5p^4(^{3}P)6s^1; ^{4}P) is found to be D_e = 82.9 (85.2) kcal/mol, whereas with respect to the diabatic ion-pair fragments, I$^+$(5s^{2}5p^4; ^{3}P) + I$^-$(5s^{2}5p^6; ^{1}S), is D_e = 97.3 (94.1) kcal/mol. We should notice at this point that a purely Coulombic attraction at the equilibrium r_e = 3.592 Å distance accounts for a stabilization energy of 92 kcal/mol, in excellent agreement with the above ab initio value, in further support of the ion-pair equilibrium character.

A second avoided crossing at 2.86 Å with the third $^3\Pi_g$ state (Figure 2) is responsible for the local minimum of pure Rydberg character at r_e = 2.588(2.589) Å at the MRCI(+Q) level of theory completely undetected at all previous studies. Its main equilibrium CASSCF configuration reads

$$\left|E^3\Pi_g\right\rangle_{\text{local}} \approx 0.96\left|1\sigma_g^2 2\sigma_g^2 3\sigma_g^1 1\pi_{x,u}^2 1\pi_{y,u}^2 1\sigma_u^2 1\pi_{x,g}^1 1\pi_{y,g}^2\right\rangle$$

where 3σ_g is a 6s6p$_z$ hybrid orbital. The bonding situation is captured clearly by the following vbL icon.



Comparing the above vbL diagram with the one of the X $^1\Sigma_g^+$ state, we observe that one π_g electron of the X-state is promoted to a Rydberg 3σ_g orbital, and the two electron σ_g bond stays intact. The bond strength of this local minimum is D_e = 61.8(62.1) kcal/mol with respect to the adiabatic dissociation channel I(^{2}P) + I*(^{4}P) at the MRCI(+Q) level of theory whereas an energy barrier of 10 kcal/mol separates it from the global minimum.

As we move on to the repulsive part of the E $^3\Pi_g$ PEC, two more avoided crossings occur: the third one at 2.38 Å (see inset of Figure 2) with the repulsive part of the first $^3\Pi_g$ state, which dissociates to two ground I(^{2}P) state atoms, and the last (fourth) one at 2.22 Å with the repulsive part of the third $^3\Pi_g$ state that emanates from the I(^{2}P) + I*(^{4}P) channel. As a result of the avoided crossing at 2.38 Å, the first and E $^3\Pi_g$ states interchange their valence and Rydberg character, whereas the fourth avoided crossing restores the Rydberg character of the E state, and passes the valence character to the third $^3\Pi_g$ state.

A $^3\Pi_g$ Hund case (a) state gives rise to Ω states of 0_g^+, 0_g^-, 1_g, and 2_g symmetry when spin−orbit (SO) effects are taken into account. We have performed SO calculations within an ”unperturbed” space consisting only of states of $^3\Pi_g$ symmetry. As can be seen in Figure 2, both local and global minima of our $^3\Pi_g$ state are quite far from other states of the same symmetry, so our ”unperturbed” space consists only of its six $|\Lambda\Sigma\rangle$ components. Because in our case $\Delta\Lambda = 0$, only the z-component of the SO operator makes a non-zero contribution resulting in a complete coincidence of the Ω = 0 states with the “unperturbed” $^3\Pi_g$ state, whereas the 1_g and 2_g states separate by ∓12 mE_h, respectively, at each single calculated point, making their PECs completely parallel to the one of the $^3\Pi_g$ state. Also on the basis of the accumulated experimental evidence (see ref 4) concerning the succession of the molecular states around 40000 cm^{-1}, we are entitled to compare the spectroscopic E 0_g^+ state with the one presently calculated.

Because a RKR extended potential curve is available in the literature[14] for the E $^3\Pi_g$ state of I$_2$, we compare the emerged aspects of the present work with the experimental ones. In Figure 3, MRCI and RKR curves are plotted together, showing quite large differences as the energy increases. The RKR curve is more anharmonic than the MRCI one even at low energies, whereas the second (local) minimum is absent. On the basis of these two PECs, vibrational bound state calculations were carried out, aiming to investigate the effect of the potential form on the vibrational states. In Figure 3, some selected

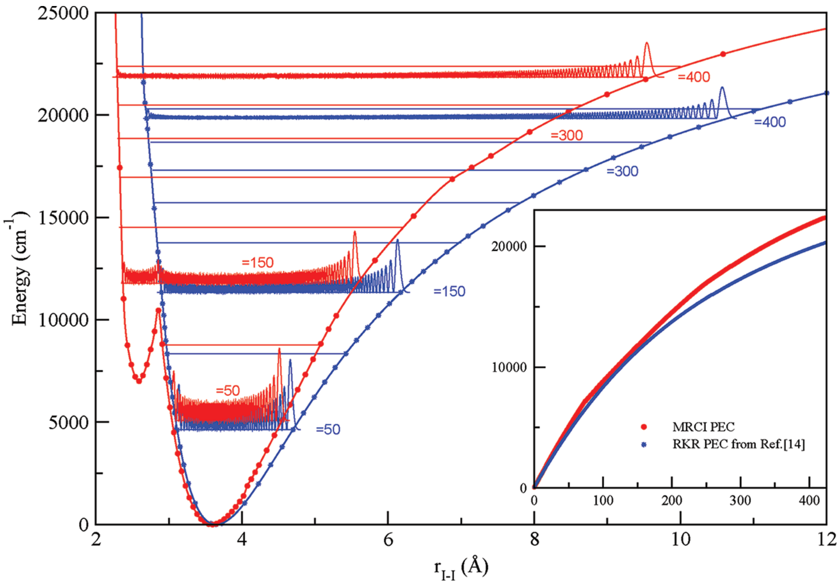


Figure 3. MRCI (red circles) and RKR (blue stars) (see ref 14) PECs of the E $^3\Pi_g$ state along with some of their vibrational levels. The calculated vibrational energies for both PECs (v up to 423) are shown in the inset. The zero of the PECs is shifted to their corresponding T_e values: 41411.76 (RKR) and 41134.26 (MRCI) cm^{-1}.

energy values and the corresponding eigenfunctions are shown, whereas the energies of all (up to $v = 423$) levels appear in the inset panel. One can see that at the low energy regime, e.g., $v < 100$, no large discrepancies are found between the two potentials. However, as expected, the presence of the second minimum clearly affects the higher vibrational states. The corresponding wave functions for these levels ($100 < v < 200$) are shifted to shorter I−I distances for the MRCI PEC, without significantly affecting the energy values, whereas at higher v levels, e.g., $v > 200$, larger differences in both probability distributions and energy values are obtained. We should note here that, at these high energies (between 52000−56000 cm^{-1}), the experimentalists have pointed out unexpected irregularities in the band intensities of the spectrum, suggesting a possible avoided crossing in the repulsive branch of the E state, as a result of the interaction the ion-pair state with Rydberg ones.[14] Their speculation is found to be in complete accordance with our present results, where such avoided crossing occurs at 51994 cm^{-1} (Figure 2).

III. FINAL REMARKS

We have studied the E $^3\Pi_g$ state of I_2 through multireference variational methods using relativistic ECPs and large basis sets. The main feature of this state is the existence of two potential minima at 3.592 Å (global minimum) and 2.588 Å (local minimum) with ion-pair and Rydberg character, respectively. The bond strength of the global minimum is calculated to be $D_e = 82.9$ (85.2) kcal/mol with respect to the adiabatic $I(^2P) + I^*(^4P)$ dissociation channel, and 97.3 (94.1) kcal/mol with respect to the diabatic $I^+(^3P) + I^-(^1S)$ ion-pair fragments at the MRCI(+Q) level of theory, respectively. For the first time a second local minimum is found for the E state, 21.1 (23.1) kcal/mol above the global minimum, the result of a severe avoiding crossing at 2.86 Å with an incoming third $^3\Pi_g$ state. Two more avoided crossings at 2.38 and 2.22 Å between the first-E, and E-third $^3\Pi_g$ states confer an interesting topology to the PEC of the E state. Comparison with available experimental data indicates that the MRCI PEC describes correctly its physics. However, for a more complete analysis further experimental data at higher energies will be needed.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Centro de Calculo (IFF), CTI (CSIC), and CESGA for CPU time allocation. This work has been supported by DGICYT, Spain, Grant No. FIS2010-18132.

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