

Observation of a substantially-bound excited-core Rydberg state in I_2 by optical triple resonance

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Received 29 July 2005; in final form 8 September 2005

Available online 6 October 2005

Abstract

A substantially-bound ($D_e \sim 7000 \text{ cm}^{-1}$, $R_e \sim 3.1 \text{ \AA}$, $T_e \sim 60\,546 \text{ cm}^{-1}$) $6s$ Rydberg state of I_2 with 0_u^+ symmetry based on the lowest excited state of the ion core, previously labelled $a(^4\Sigma_{u,1/2}^-)$, has been identified using optical triple resonance via the $B(0_u^+)$ and $E0_g^+(^3P_2)$ states together with resonance ionization. The interactions with ground-core Rydberg states that the new state undergoes and the reasons why it is observed in the resonance ionization spectrum via the $E0_g^+(^3P_2)$ state, whilst the $A[^2\Pi_{u,1/2}]_c; 6s0_u^+$ state is not, are explained in terms of its electronic configuration.

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1. Introduction

In three recent papers [1–3] we have scanned the high-energy region of the I_2 electronic spectrum using optical triple resonance together with resonance ionization detection (OTR/RI). A short regular progression, assigned to a 0_u^+ $6s$ Rydberg state built on an excited ionic core, was observed between $67\,500$ and $68\,500 \text{ cm}^{-1}$ and molecular constants for this were reported [3]. In addition, in the energy range $60\,300$ – $65\,800 \text{ cm}^{-1}$, a long, heavily perturbed progression was observed [2]. In the current Letter, we present further data and an analysis of this perturbed region of the OTR/RI spectrum in which we have identified a new excited-core Rydberg state. Several ground-core Rydberg states and ion-pair states are known to lie in the same spectral region. The interaction of these states with the new 0_u^+ excited-core Rydberg state is analyzed to produce evidence for the electronic structure of the new state.

2. Experimental

The experimental arrangement has been described in detail previously [2] and comprised a laser system with three tuneable, excimer-pumped dye lasers, a pulsed molecular beam, a time-of-flight mass spectrometer and signal collection electronics. The counter-propagating dye laser beams intersected the molecular beam at 90° in the ionization region of the mass spectrometer. Mass-selected ions were collected at 90° to the laser and molecular beams. The pulsed jet was of conventional design and employed a commercial pulsed valve (General Valve, Iota One). Helium at a pressure of 300 – 900 Torr was passed over solid I_2 at room temperature and the resulting mixture of I_2 and carrier gas expanded through the nozzle that was warmed to $\sim 320 \text{ K}$.

In the excitation pathway for all spectra, the first intermediate state used was ($v = 22$) of the $B(0_u^+)$ valence state. For most of the spectra, the second intermediate state used was ($v = 41$) of the $E0_g^+(^3P_2)$ ion-pair state and, unless stated otherwise, ($v = 41$, $J = 25$) of the $E0_g^+(^3P_2)$ state, uniquely, was excited. Finally, the probe photon was scanned between 438 and 750 nm , exciting transitions from the $E0_g^+(^3P_2)$ state to higher-lying states, which were then ionized by absorption of at least one more photon. The spectra were recorded by monitoring I_2^+ . In the present

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OTR/RI studies we have measured the energies, relative to ($v = 0, J = 0$) of the ground state, of specific rotational levels of the final states and these are referred to as total energies. The total energies were obtained by adding the calibrated energy of the probe photon to the total energy of the rovibrational level of the $E0_g^+(^3P_2)$ state calculated from the published molecular constants [4]. Probe laser wavelengths between 500 and 600 nm were calibrated from the I_2 fluorescence excitation spectrum and all others from neon optogalvanic lines, resulting in errors of ± 0.2 and $\pm 0.5 \text{ cm}^{-1}$, respectively, and these dictate the experimental uncertainty of the measured total energies.

3. Results

3.1. Overview

The OTR/RI spectrum of I_2 between 60400 and 67500 cm^{-1} is shown in Figs. 1–3. The component of the spectrum that is indicated by an arrow in Fig. 2 was recorded via ($v = 31, J = 25$) of the $E0_g^+(^3P_2)$ state as this improved the signal intensity. Throughout the spectrum, only P, R doublets, indicative of parallel, one-photon transitions (from the $E0_g^+(^3P_2)$ state) are seen. The spectrum is dominated by a single Rydberg state progression with vibrational spacings that decrease from 140 to 70 cm^{-1} .

The Rydberg progression can be easily identified over the range 61700–66000 cm^{-1} , as shown in Fig. 2. The progression extends down to 60500 cm^{-1} but the vibrational spacings below 61700 cm^{-1} are very irregular as can be seen from Fig. 1 and, in addition, extra bands that do not fit into the progression are also observed. These extra bands belong to a ground-core Rydberg state (vibrational spacing $\sim 200 \text{ cm}^{-1}$) and an ion-pair state (vibrational spacing $\sim 20 \text{ cm}^{-1}$) and are seen only as a consequence of

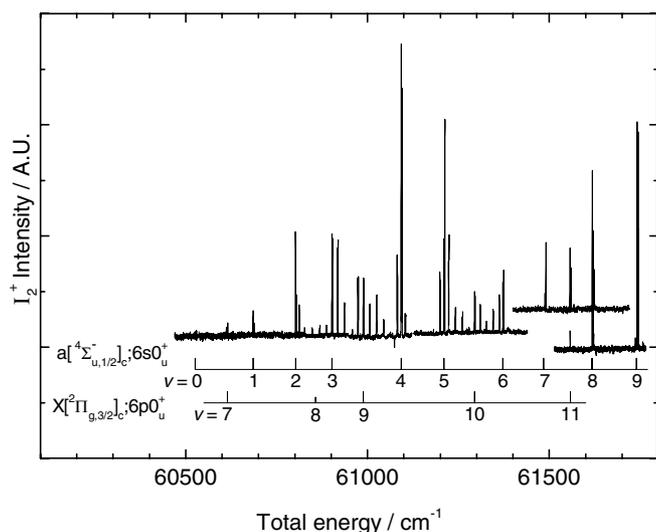


Fig. 1. The OTR/RI spectrum of I_2 over the range 60500–61750 cm^{-1} , recorded via ($v = 41, J = 25$) of the $E0_g^+(^3P_2)$ ion-pair state. The vibrational levels of the $a^4\Sigma_{u,1/2}^-; 6s0_u^+$ and the coupled $X^2\Pi_{g,3/2}^-; 6p0_u^+$ Rydberg states are shown.

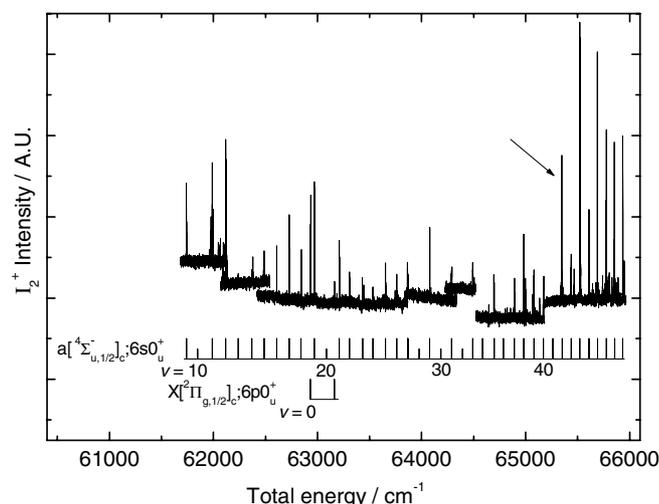


Fig. 2. The OTR/RI spectrum of I_2 over the range 61500–66000 cm^{-1} , recorded via ($v = 41, J = 25$) of the $E0_g^+(^3P_2)$ ion-pair state. The scan indicated by an arrow was recorded via ($v = 31, J = 25$) of the $E0_g^+(^3P_2)$ ion-pair state. The vibrational levels of the $a^4\Sigma_{u,1/2}^-; 6s0_u^+$ and the coupled mixed singlet/triplet $X^2\Pi_{g,1/2}^-; 6p0_u^+$ Rydberg states are shown.

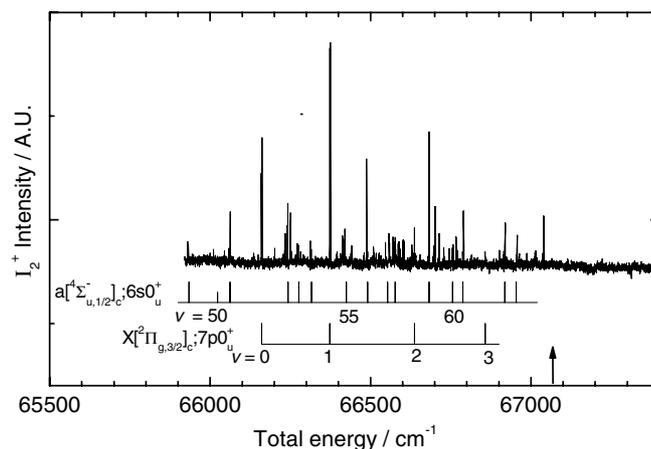


Fig. 3. The OTR/RI spectrum of I_2 over the range 65900–67400 cm^{-1} , recorded via ($v = 41, J = 25$) of the $E0_g^+(^3P_2)$ ion-pair state. The vibrational levels of the $a^4\Sigma_{u,1/2}^-; 6s0_u^+$ and the coupled $X^2\Pi_{g,3/2}^-; 7p0_u^+$ Rydberg states are shown. The arrow indicates the dissociation limit to $I(^2P_{3/2}) + I_{\text{Ryd}}([^3P_{2,k}]; 6s; ^4P_{5/2})$ at 67073 cm^{-1} .

interactions with the excited-core Rydberg state. The largest displacements ($\sim 30 \text{ cm}^{-1}$) are due to the interaction between the excited-core Rydberg state and the $X^2\Pi_{g,3/2}^-; 6p0_u^+$ ground-core Rydberg state caused by the crossing of the inner wall of the former ($v \sim 3$) with the outer wall of the latter ($v \sim 9$). The first four vibrational levels of the $X^2\Pi_{g,3/2}^-; 6p0_u^+$ state were observed in the high resolution VUV absorption spectrum, recorded by Venkateswarlu [5] and re-assigned by Ridley et al. [6]. The inner wall of the excited-core Rydberg state potential also crosses the potentials of the three other 0_u^+ ground-core Rydberg states below 69000 cm^{-1} , namely two $X^2\Pi_{g,1/2}^-; 6p0_u^+$ states and the $X^2\Pi_{g,3/2}^-; 7p0_u^+$ state. The OTR/RI spectrum shows that the excited-core Rydberg state is perturbed by one of the $X^2\Pi_{g,1/2}^-; 6p0_u^+$ states (see Fig. 2) and the

$X[{}^2\Pi_{g,3/2}]_c; 7p0_u^+$ state (see Fig. 3). There is no evidence in the OTR/RI spectrum of coupling between the excited-core Rydberg state and the second $X[{}^2\Pi_{g,1/2}]_c; 6p0_u^+$ state.

Over the range 60 700–61 700 cm^{-1} , each Rydberg state vibrational band has several ion-pair state vibrational levels associated with it. The local spacings between the vibrational levels label the ion-pair state as a first tier state, dissociating to $I^+({}^3P_2)$ and $I^-({}^1S)$, and therefore it must be the $D0_u^+({}^3P_2)$ state ($v \sim 350$) [7]. The interactions between the Rydberg states and the ion-pair state result in displacements of $\sim 5 \text{ cm}^{-1}$.

The observed total energies of ($J = 24$) of the excited-core Rydberg state vibrational levels, presented in Table 1, show that displacements of $\sim 5 \text{ cm}^{-1}$ are also observed between 61 700 and 66 000 cm^{-1} . The observed rotational splitting between ($J = 24$) and ($J = 26$) of the Rydberg bands is also irregular, varying between 3.0 and 1.2 cm^{-1} , as shown in Table 1. Both observations indicate that interactions between the excited-core Rydberg state and the $D0_u^+({}^3P_2)$ ion-pair state and/or ground-core Rydberg states continue throughout this region.

3.2. Vibrational data

The total energy of the lowest vibrational level of the new Rydberg state that is seen in the OTR/RI spectrum recorded via ($v = 41$, $J = 25$) of the $E0_g^+({}^3P_2)$ state lies around 60 526 cm^{-1} . However, it is possible that the absence of further levels to lower energy is purely due to a declining FC overlap between ($v = 41$) of the $E0_g^+({}^3P_2)$ state and the final state. In order to rule out this possibility, the same total energy region was excited via ($v = 54$) of the $E0_g^+({}^3P_2)$ state, thus decreasing the inner turning point of the $E0_g^+({}^3P_2)$ state by 0.15 to 3.1 Å [4]. In addition, an unknown low J level(s) in the band head was used in an attempt to improve the signal-to-noise. The proposed ($v = 0$) band is indeed observed at the expected energy and all of the bands observed to lower energy are assigned as perpendicular transitions to the $1_u({}^1D_2)$ ion-pair state. The possibility still remains that the new state is only seen in the OTR/RI spectrum because it is coupled to the $X[{}^2\Pi_{3/2}]_c; 6p0_u^+$ state (i.e. without this it cannot be directly ionized to the ground state of the parent ion). If the coupling only switches on at 60 500 cm^{-1} , lower levels of the new state, including the real origin, will not be seen and we have not found a way to eliminate this possibility.

A three-term Dunham expansion was applied to the observed total energies of ($J = 24$) of the vibrational levels up to ($v = 49$) of the new Rydberg state and the results are shown in Table 1. Any level that was offset from the calculated value by more than 15 cm^{-1} was removed from the fit. The coefficients obtained were $Y_{00} = 60454.8$, relative to ($v = 0$, $J = 0$) of the ground state, $Y_{10} = 140.72$ and $Y_{20} = -0.603 \text{ cm}^{-1}$ and the use of an additional term did not significantly improve the fit. These vibrational constants are similar to those reported for both the $A({}^2\Pi_{u,3/2})$ and $a({}^4\Sigma_u^-)$ states of I_2^+ of 138 and -0.46 and

Table 1

Observed total energies, relative to ($v = 0$, $J = 0$) of the ground state, of ($J = 24$) of various vibrational levels of the $a({}^4\Sigma_{u,1/2}]_c; 6s0_u^+$ Rydberg state of I_2

v	Observed total energy (cm^{-1})	Rotational splitting (cm^{-1})	Calculated total energy (cm^{-1})	Observed–calculated (cm^{-1})
0	60526.4		60525.0	1.3
1	60684.8 ^a	2.7	60664.5	20.2
2	60802.0	2.6	60802.8	–0.8
3	60902.0 ^a	1.4	60939.9	–37.9
4	61092.7 ^a	2.9	61075.8	16.8
5	61209.9	2.2	61210.5	–0.6
6	61371.6 ^a	2.2	61344.0	27.5
7	61484.2	2.7	61476.3	7.9
8	61617.7	2.4	61607.4	10.3
9	61739.7	1.2	61737.2	2.5
10	–		61865.9	–
11	61988.0	1.9	61993.3	–5.3
12	62119.2	2.4	62119.6	–0.4
13	62237.6	1.7	62244.6	–7.0
14	62368.6	2.4	62368.5	0.1
15	62488.4	2.8	62491.1	–2.7
16	62607.4		62612.5	–5.1
17	62729.1	2.9	62732.7	–3.6
18	62842.7		62851.7	–9.0
19	62971.0	3.0	62969.5	1.5
20	–		63086.1	–
21	63207.5	2.5	63201.5	6.0
22	63308.5	2.5	63315.7	–7.2
23	63432.1	2.5	63428.7	3.4
24	63534.2	2.0	63540.5	–6.3
25	63651.0	2.0	63651.1	–0.1
26	63762.8	1.7	63760.4	2.4
27	63866.4	3.8	63868.6	–2.2
28	–		63975.5	–
29	64076.4	2.8	64081.3	–4.9
30	–		64185.8	–
31	64288.7	2.5	64289.2	–0.5
32	–		64391.3	–
33	64492.5	2.1	64492.2	0.3
34	64585.9	2.5	64591.9	–6.0
35	64696.3	2.5	64690.4	5.9
36	64788.6	2.3	64787.7	0.9
37	64892.4	2.8	64883.8	8.6
38	64980.3	2.2	64978.7	1.6
39	65080.3	1.6	65072.4	7.9
40	65170.0	2.3	65164.9	5.1
41	65258.6	2.3	65256.2	2.4
42	65349.0	1.5	65346.2	2.8
43	65436.6		65435.1	1.5
44	65520.9		65522.7	–1.8
45	65607.5		65609.2	–1.7
46	65692.1		65694.4	–2.3
47	65775.2		65778.5	–3.3
48	65854.0		65861.3	–7.3
49	65933.7		65942.9	–9.2
50	–		66023.4	–
51	66062.4 ^a		66102.6	–40.2
52	66243.3 ^a		66180.6	62.7
53	66276.0 ^a		66257.4	18.6
54	66315.6 ^a		66333.0	–17.4
55	66423.6 ^a		66407.4	16.2
56	66491.2 ^a		66480.6	10.6
57	–		66552.5	–
58	66575.9 ^a		66623.3	–47.4
59	66683.0 ^a		66692.9	–9.9
60	66755.7 ^a		66761.2	–5.5
61	66788.3 ^a		66828.4	–40.1
62	66919.3 ^a		66894.3	25.0
63	66953.9 ^a		66959.1	–5.2

The rotational splitting between ($J = 24$) and ($J = 26$) is also shown. The calculated total energies are obtained from a Dunham expansion whose coefficients are 60454.8, 140.72 and -0.603 cm^{-1} .

^a Value omitted from fit.

128 and -0.38 cm^{-1} , respectively [8]. The Ω value of the $a(4\Sigma_u^-)$ state was not previously specified but we will assume here that ($\Omega = 1/2$).

3.3. Rotational data

The OTR/RI technique can be used to obtain accurate rotational constants of unperturbed vibrational levels of an electronic state by exciting a range of rotational levels in the intermediate state [3]. We tried to repeat this procedure for several vibrational levels of the new Rydberg state but all were too perturbed to obtain accurate B values. The best estimate obtained using this approach places R_e for the state between 3.0 and 3.3 Å.

In an attempt to indirectly determine R_e for the new Rydberg state, the OTR/RI spectrum was recorded via ($v = 0$) of the $E0_g^+(3P_2)$ state. The lowest vibrational level of the Rydberg state that could be observed was ($v = 17$) around $62\,700 \text{ cm}^{-1}$. This places the outer wall of the Rydberg state at this energy vertically above the inner wall of the $E0_g^+(3P_2)$ state potential at ($v = 0$), i.e. at 3.6 Å [4] as shown in Fig. 4. This further places R_e of the Rydberg state potential at 3.1 Å, assuming that it can be described by the Morse potential discussed below and that we have been able to observe ($v = 0$).

This value for R_e adds further weight to the vibrational numbering described above. In that experiment, the second intermediate state, ($v = 54$) of the $E0_g^+(3P_2)$ state, had an inner turning point of 3.1 Å and hence must have a good Franck–Condon (FC) overlap with ($v = 0$) of the new Rydberg state. Consequently, it is reasonable to conclude that the lowest-energy member of the progression observed,

with a total energy for ($J = 24$) at $60\,526 \text{ cm}^{-1}$, is ($v = 0$). An R_e of 3.1 Å gives a B value of 0.0276 cm^{-1} . Using a total energy of $60\,526 \text{ cm}^{-1}$ for ($J = 24$) gives a total energy of $\sim 60\,509 \text{ cm}^{-1}$ for ($v = 0, J = 0$) of the Rydberg state and hence $T_e \sim 60\,546 \text{ cm}^{-1}$.

4. Discussion

The potential energy curves of the two excited-core Rydberg states seen in the OTR/RI spectra are shown in Fig. 4. The potential for the new, deeply-bound Rydberg state up to $66\,000 \text{ cm}^{-1}$ is shown as a Morse potential ($T_e = 60\,546 \text{ cm}^{-1}$, $D_e = 8210 \text{ cm}^{-1}$, $\omega_e = 140.72 \text{ cm}^{-1}$, $\omega_e x_e = 0.603 \text{ cm}^{-1}$ and $R_e = 3.1 \text{ Å}$). An extrapolation of this potential suggests that it correlates with the upper of the two asymptotes shown in Fig. 4. However, extrapolations of Morse curves are unreliable and hence it cannot be certain that this is the correct correlation. The potential for the shallow-bound Rydberg state is shown as an RKR potential using the molecular constants obtained from a previous OTR/RI study [3].

Since the potential energy curves of both states correlate with a 6s Rydberg atom and a ground state atom as shown in Fig. 4, they must be 6s Rydberg states and, from the symmetry, T_e and R_e , must be based on excited states of I_2^+ of ungerade parity. The four lowest-energy excited states of I_2^+ that can give rise to an ns Rydberg state with a 0_u^+ component under Ω, ω coupling are $a(4\Sigma_{u,1/2}^-)$, $A(2\Pi_{u,1/2})$, $2\Sigma_{u,1/2}^+$ and $2\Sigma_{u,1/2}^-$.

The $A(2\Pi_{u,3/2,1/2})$ and one of the two $a(4\Sigma_u^-)$ Ω -components have been observed with resolved vibrational structure, although the absolute numbering has not been determined [8–10]. The onset of the vibrational bands in the optical double resonance zero electron kinetic energy (ZEKE) spectrum sets upper limits of $86\,022$ and $86\,367 \text{ cm}^{-1}$ for the $a(4\Sigma_u^-)$ and $A(2\Pi_{u,3/2})$ states, respectively, and these were thought to be near the true IEs [8]. The spin–orbit coupling in the $A(2\Pi_u)$ state, obtained from the energy difference between the band maxima in the photoelectron spectrum (PES) [11], is $\sim 6400 \text{ cm}^{-1}$. Hence, the IE for the $A(2\Pi_{u,1/2})$ state is predicted to be $\sim 92\,767 \text{ cm}^{-1}$.

The effective quantum number, n^* (i.e. $n - \delta$), is commonly used to assign Rydberg states. This can be obtained using the conventional Rydberg equation,

$$E_n = IE - R/(n - \delta)^2,$$

where E_n is the energy of the electronic origin of the Rydberg state, IE is the ionization energy of the appropriate state of the ion and δ is the quantum defect. The n^* of the $X[2\Pi_{g,3/2,1/2}]_c;6s$ Rydberg states in I_2 , ICl and IBr have been reported [6,12] to vary only slightly over the range 1.97–2.03. The IEs of the $a(4\Sigma_{u,1/2}^-)$ and $A(2\Pi_{u,1/2})$ states yield lower limit n^* values of 2.07 and 1.84, respectively, for the origin of the present state. Thus, using this criterion, the $a[4\Sigma_{u,1/2}]_c;6s0_u^+$ assignment appears most reasonable. The somewhat high value of n^* if the state has an $a(4\Sigma_{u,1/2}^-)$ core is explained if T_e of the Rydberg state is

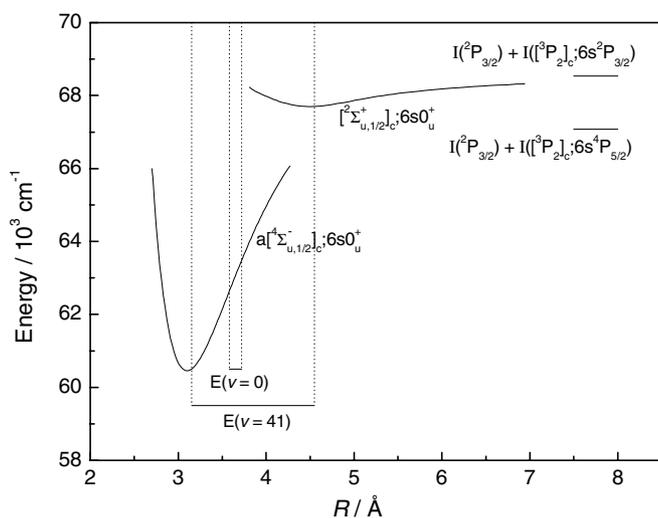


Fig. 4. The potential energy curves of the two excited-core Rydberg states observed in the OTR/RI spectra of I_2 . The deeply-bound state is represented by a Morse function generated by the molecular constants obtained from the current data and the shallow-bound state by RKR points reported previously [3]. The FC windows of two $E0_g^+(3P_2)$ ion-pair state vibronic levels are shown [4]. The two lowest $I + I_{Ryd}$ dissociation limits are indicated.

raised by $\sim 1000 \text{ cm}^{-1}$ through interaction with the $F0_u^+(^3P_0)$ and $F'0_u^+(^1D_2)$ ion-pair states whose potentials lie ~ 11000 and 4000 cm^{-1} , respectively, below the T_e of the new Rydberg state.

The PES [11] shows that the $A(^2\Pi_{u,1/2})$ state of I_2^+ is bound by $\sim 4000 \text{ cm}^{-1}$. As the shallow-bound excited-core Rydberg state is only bound by $\sim 800 \text{ cm}^{-1}$ [3], it is assigned as the $[^2\Sigma_{u,1/2}^-]_c; 6s0_u^+$ state rather than the $A[^2\Pi_{u,1/2}]_c; 6s0_u^+$ state.

Two questions arise from the assignments proposed. First, why are transitions to the $A[^2\Pi_{u,1/2}]_c; 6s0_u^+$ state not observed in the present OTR/RI spectra. Secondly, why does the $a[^4\Sigma_{u,1/2}^-]_c; 6s0_u^+$ state, seemingly a pure triplet state, undergo significant interactions with three mixed singlet/triplet ground-core Rydberg states [6] but not with the pure triplet $X[^2\Pi_{g,1/2}]_c; 6p\sigma 0_u^+$ state.

In order to answer these questions, we must consider the electronic configurations of the states involved. The $E0_g^+(^3P_2)$ state at $R \geq R_e$ is a mixture of the 0_g^+ components of two major configurations; $^3\Sigma_g^-$ (2242) and $^3\Pi_g$ (1432) in Mulliken's notation [13], and as $R \rightarrow \infty$ their weights are 2:1. Neither of these single MO configurations dissociates properly to give a pure ion-pair state and as $R \rightarrow \infty$ the proper description of the $E0_g^+(^3P_2)$ state is $\sqrt{2}(^3\Sigma_g^-(2242 + 2422)) - ^3\Pi_g(1432 + 2341)$. Around R_e , the 'valence' configurations (2422) and (2341) will still be present in significant amounts, given the similarity of the spacing of the T_e values of ion-pair states to those of the states of the positive ion with which they correlate, indicating that the asymptotic ionic structures are largely undisturbed at R_e ($\sim 3.6 \text{ \AA}$).

In order to access the (2421) configuration of the $a[^4\Sigma_{u,1/2}^-]_c; 6s0_u^+$ state, the proposed assignment for the new Rydberg state, the minor configuration (2422) of the $E0_g^+(^3P_2)$ state provides the only route, via a simple $\sigma_u \rightarrow 6s$ transition. If the present $6s$ Rydberg state was based on the $A(^2\Pi_{u,1/2})$ state of the core then it would seem equally facile to use the minor configuration (2341) to effect the same electron shift and the two possibilities for the final state cannot be discriminated between on this basis. However, de Jong et al. [14] have pointed out that the $A(^2\Pi_{u,1/2})$ (234) state is strongly mixed with the $^2\Sigma_{u,1/2}^+$ (2421 + 2241) state, whereas the $a(^4\Sigma_{u,1/2}^-)$ state is mixed with the $^2\Sigma_{u,1/2}^-$ state without change in the (2421) configuration. This introduction of the minor configuration (2421) into the description of the $A(^2\Pi_{u,1/2})$ state opens up two contributions to the transition dipole from the $E0_g^+(^3P_2)$ state, using the minor configurations (2341) and (2422) to reach their target configurations in the superposition present in the $A(^2\Pi_{u,1/2})$ state. If the phasing of these transition dipoles leads to near-cancellation, then the final state cannot be accessed from the $E0_g^+(^3P_2)$ state. Since the transition dipole for $a[^4\Sigma_{u,1/2}^-]_c; 6s0_u^+ \leftarrow E0_g^+(^3P_2)$ is dominated by a single component, no destructive interference arises. A consequence of a near-cancellation of the transition dipole to the $A[^2\Pi_{u,1/2}]_c; 6s0_u^+$ state is that there must be a correspond-

ing enhancement in the transition to the $6s$ Rydberg based on the nominally $^2\Sigma_{u,1/2}^+$ core state through its added $A(^2\Pi_{u,1/2})$ -state component. We assign this $^2\Sigma_{u,1/2}^+$ configuration to the higher-energy shallow-bound 0_u^+ Rydberg state that can be accessed from the $E0_g^+(^3P_2)$ state.

The above description of the electronic structure of the $A(^2\Pi_{u,1/2})$ state of the ion core and the a state of mixed $^4\Sigma_{u,1/2}^-$ and $^2\Sigma_{u,1/2}^-$ character refers to $R \geq 3.1 \text{ \AA}$ (R_e). As R decrease to $2.6\text{--}2.9 \text{ \AA}$, where the crossings of the new Rydberg state with the $X[^2\Pi_{g,3/2,1/2}]_c; mp$ Rydberg states begin, the core configurations change somewhat as a result of the increasing energy separation of the π_g , π_u , σ_g and σ_u orbitals. The (2421) + (2241) components of the $A(^2\Pi_{u,1/2})$ state rapidly separate out, leaving the state the pure doublet, $^2\Pi_{u,1/2}$ (234). When combined with the $6s$ electron, this must make a pure triplet 0_u^+ state, $[1_u^+ 1_u^- \pi_g^-] 6s^-$ in the detailed spin-orbit notation of Condon and Shortly [15] specifying m_l and m_s of each π_u electron. Were this to be the new $6s$ state, then it would show a strong interaction with the purely triplet $X[^2\Pi_{g,1/2}]_c; 6p\sigma 0_u^+$ state, $[\pi_u^+ 1_g^+ 1_g^-] 6p\sigma^-$. No such interaction is observed.

In contrast, the lowest-energy $1/2_u$ state of the core, $a(^4\Sigma_{u,1/2}^-)$, (in reality a mixture of $^4\Sigma_{u,1/2}^-$, $^2\Sigma_{u,1/2}^+$ and $^2\Sigma_{u,1/2}^-$) retains its (2421) configuration at smaller R . The lowest 0_u^+ state based on the (2421) $_u\Sigma_{1/2}$ core is $\pi_u^+(c_1 1_g^+ 1_g^- + c_2 1_g^- 1_g^+)(\sigma_u^- 6s^+ - \sigma_u^+ 6s^-)$ where the coefficients c_1 and c_2 give the contributions of the two possible pairings of spin and orbital angular momentum in the π -orbitals. The $(1^- 1^+)$ arrangement has the lower spin-orbit energy and presumably predominates. This 0_u^+ state cannot couple with the pure triplet $X[^2\Pi_{g,1/2}]_c; 6p\sigma 0_u^+$ state, but can clearly mix with both the other $X[^2\Pi_{g,1/2}]_c; 6p0_u^+$ states, e.g. $X[^2\Pi_{g,3/2}]_c; 6p\pi = [\pi_u^+ 1_g^+ 1_g^-] 6p\pi^-$. The observed interactions with ground-core Rydberg states are thus explained if the new Rydberg state is based on the lowest ungerade state of the core, $^4\Sigma_{u,1/2}^-$, rather than the $^2\Pi_{u,1/2}$.

5. Conclusion

A substantially bound ($D_e \sim 7000 \text{ cm}^{-1}$) $6s$ Rydberg state of I_2 with 0_u^+ symmetry and based on an excited state of the ion core has been identified using OTR/RI. The core state is assigned as $a(^4\Sigma_{u,1/2}^-)$, while recognizing that this contains a significant admixture of $^2\Sigma_{u,1/2}^-$. The interactions with ground-core Rydberg states that the new state undergoes are explained in terms of its dominant electronic configuration at small R . The change in the state's configuration as R increases is used to explain why it is observed in the OTR/RI spectrum from the $E0_g^+(^3P_2)$ state while the corresponding state based on the A state of the core, $A[^2\Pi_{u,1/2}]_c; 6s0_u^+$ is not.

Acknowledgement

A.M.S. thank the Göran Gustafsson foundation for a scholarship.

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