

Vibrationally resolved excitation functions for direct ion-pair ($I^+ + I^-$) formation from photodissociation of I_2

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Excitation functions for ion-pair (I^- and I^+) formation from jet cooled I_2 in the region 120–140 nm (i.e. from threshold to just above the first ionisation limit of I_2), are reported. The mechanism for ion-pair formation is discussed in terms of coupling between Rydberg states and ion-pair states correlating with $I^- (^1S_0)$ and $I^+ (^3P_2)$.

1. Introduction

The excitation functions for ion-pair production from Br_2 , in the region of the photoionisation threshold, are remarkably simple in structure despite the high density of electronic states in this region [1]. This simplicity can be understood in terms of selective homogeneous coupling between a single Rydberg state and the continuum of an ion-pair state which dissociates to $Br^- (^1S_0)$ and $Br^+ (^3P_2)$. A similar model has been proposed to account for ion-pair formation from O_2 [2] and HF [3].

Ion-pair formation from I_2 was first observed by Morrison et al. [4], although only a low-resolution excitation function for I^+ was obtained. Further low-resolution data on the ion-pair threshold region were

reported by Myer and Samson [5]. Akopyan et al. [6] observed both I^+ and I^- formation in the region 100–140 nm, but again this was at low resolution and the excitation functions showed no evidence of vibrational structure.

In the present communication we report vibrationally resolved excitation functions for both I^- and I^+ formation in the region from threshold to above the first ionisation limit of I_2 (133.2 nm). These excitation functions are again found, as for Br_2 , to be remarkably simple in structure considering the very high density of Rydberg states present in the region just below the first ionisation limit.

2. Experimental

The molecular beam apparatus used for the present work has been described previously in some de-

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tail [1,7,8]. All of the results were obtained using beam line 11 of the NSLS facility of the Brookhaven National Laboratory.

The molecular beam was formed by passing argon through a heated trap (58°C) containing I₂ followed by a heated (95°C) glass nozzle of 200 μm diameter. The beam was collimated via a 1mm diameter skimmer located 5–10 mm down stream from the nozzle. The nozzle pressure was adjusted to obtain the maximum ion intensity. Typically, this was achieved at ≈270 Torr, as measured on a capacitance manometer. At nozzle pressures greater than this the ion signal decreased, presumably due to cluster formation.

3. Results and discussion

The excitation functions for I⁻ and I⁺, together with the I₂ photoionisation function, are shown in fig. 1. The I⁻ and I⁺ excitation functions are identical within experimental error, as was the case for Br₂ [1]^{a1}, and we conclude that both ions are formed via the same process. The energetic threshold for ion-pair formation lies at 138.6 nm which coincides with the onset of the steeply rising portion of both excitation functions. The weak structure to longer wavelengths must be due to excitation of vibrationally and rotationally hot molecules [9]. We estimate a vibrational temperature within the molecular beam of ≈250 K: the rotational temperature is expected to be much lower than this but the available resolution was insufficient to allow us to determine it.

The drop in intensity below 132.5 nm is close to the termination of the Rydberg series based on the ²Π_{3/2} core state and the opening of the channel leading to I₂⁺ [10,11].

The peak positions and energy separations for the I⁻ and I⁺ excitation functions are given in table 1. The separation between the main peaks (about 210–240 cm⁻¹) is similar to that for Rydberg states observed in this region [11]. We have previously ob-

^{a1} In ref. [1], fig. 1, the Br⁺ excitation function was slightly shifted to longer wavelengths by ≈0.075 nm during preparation of the diagram for publication. The excitation functions for Br⁺ and Br⁻ formation are in fact identical in shape and position, within experimental error.

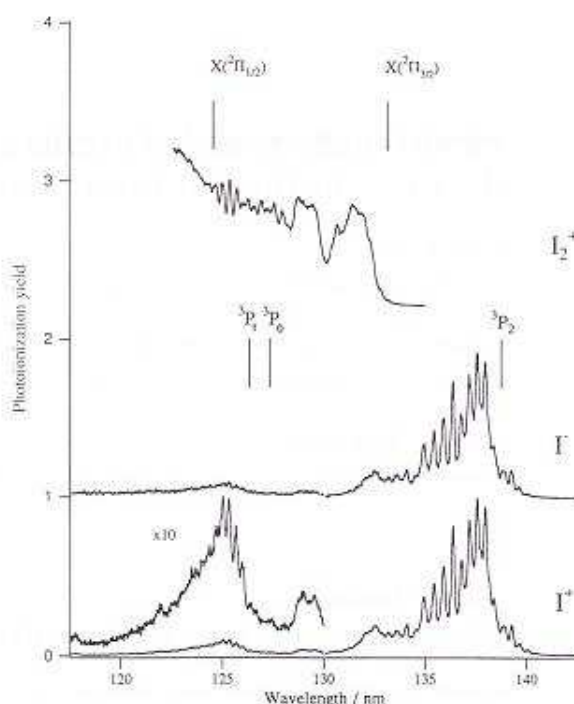


Fig. 1. Excitation functions for I⁻ and I⁺ formation together with the ionization function for the parent molecule, I₂. The thresholds for formations of I⁻ (¹S₀) + I⁺ (³P_{0,1,2}) and I₂⁺ (X ²Π_{1/2,3/2}) are indicated.

served the absorption and fluorescence excitation spectra of I₂ in this region, at medium resolution, and have found them to be very similar [10]. Some of the peaks in the ion-pair excitation function coincide with those in the absorption and fluorescence excitation spectra, but others are slightly displaced so that the ion-pair peaks lie in the wings of the other peaks. A similar displacement was observed for Br₂ where it was suggested [1] that the broad absorption bands might involve more than one overlapping Rydberg series. We suggest that this is also the case for I₂: work at higher resolution will be required to clarify this point.

The overall shape of the excitation functions for I⁻ and I⁺, in comparison with the simpler excitation functions observed for ion-pair formation from Br₂, suggests that more than one Rydberg state is involved. We note that the energetic window for ion-pair formation, below the ionisation limit for I₂, is wider than for Br₂. We may therefore expect more

Table 1
Peak positions and energy separations in the excitation functions for I^+ and I^-

Wavelength (nm)	Energy (cm^{-1})	Separation (cm^{-1})
140.0	71405	
139.7	71600	195
139.3	71795	195
138.9	72000	205
138.4	72255	255
138.0	72460	205
137.6	72660	220
137.2	72884	204
136.8	73090	206
136.4	73320	230
135.9	73564	244
135.5	73817	253
135.0	74094	277
134.6	74310	216
134.1	74560	250
133.6	74835	275
133.2	75075	240
132.6	75440	
129.6	77190	
129.0	77537	
128.1	78094	
127.4	78481	
126.4	79114	
126.0	79368	254
125.7	79568	200
125.3	79780	212
125.0	79971	191

Rydberg states to be involved in the ion-pair formation process in I_2 . Nevertheless, the observed excitation functions are remarkably simple when one considers the very high density of Rydberg states present in this region.

Our analysis suggests that at least four Rydberg states are involved in the iodine ion-pair excitation functions. In making our assignments we recall that the oscillator strength for transitions to Rydberg states declines very rapidly with increasing principal quantum number ($I \propto n^{-3}$). Thus Rydberg states with low principal quantum number will be strongly favoured. In assigning the Rydberg states we have used Venkateswarlu's analysis as a guide [11], but we note that his assignments were based on an ionisation energy which was too high by $\approx 716 \text{ cm}^{-1}$ (see ref. 12]; also this work, fig. 1). The longest wave-

length bands between 138.6 and 137.0 nm can be assigned as $[3/2]_c 9p\pi$. We chose the $np\pi$ configuration as opposed to the $np\sigma$ configuration for the reasons given earlier for Br_2 [1]. The profile for this first Rydberg system may be influenced by the onset function (i.e. the *threshold* function for ion-pair formation). We therefore tentatively assign the band at 138.0 nm as the (0,0) band (based on an $\text{IP} = 75098 \text{ cm}^{-1}$) and have based our simulations on this (see below). An alternative assignment is to the $[1/2]_c 7p\pi$ Rydberg state which lies close in energy and is favoured by having a lower principal quantum number. This assignment is attractive as it parallels our assignment for the Br_2 ion-pair excitation spectrum. However, as we shall see below the first assignment is more compatible with the assignment of adjacent bands at shorter wavelengths. It is of course possible that two Rydberg systems are superimposed.

The strong band observed at 136.4 nm and the change in peak separation in this region suggest that a second Rydberg system starts in this region, and this can be assigned as $[3/2]_c 10p\pi$, with the (0,0) band at 136.8 nm. There is no ambiguity here with states based on the $[1/2]_c$ core.

The next member of this series, the $[3/2]_c 11p\pi$ state, should lie at 135.8 nm and the band intensities in this region suggest that weak absorption to this state may be present. Indeed, we have not been able to produce a good fit between simulated and observed spectra without including the $[3/2]_c 11p\pi$ state. However, as we shall discuss below, the observed band intensities may well be modified by interactions between the Rydberg and ion-pair states and thus arguments based on band intensities and simulated spectra may not be reliable in detail. It is perhaps a little surprising that the peaks for all three Rydberg systems remain essentially in phase throughout the region 134.5–138.0 nm, and this may argue in favour of fewer Rydberg states being involved.

The overall decline in intensity from 137.5 nm, to shorter wavelengths, is compatible with the expected dependence on principal quantum number. However, below 134.5 nm the intensity reaches a broad plateau with some superimposed structure. This is possibly due to the rapidly rising density of states in this region which offsets the decline in the oscillator strength for the individual transitions. We therefore

propose that features in this region can be assigned to the $[3/2]_c 12p\pi$ and higher Rydberg states in this series. A further broad peak at ≈ 133 nm is observed just below the first ionisation limit and this may possibly be assigned as $[1/2]_c 8p\pi$.

Further weak structure is observed at shorter wavelengths. The onset at 126 nm coincides with the opening of the ion-pair channel leading to I^+ ($^3P_{1,0}$). The observation of clearly resolved structure so close to the $X^2\Pi_{1/2}$ ionisation limit of I_2 suggests that an excited Rydberg configuration, based on the $A^2\Pi_{3/2}$ core state may be involved. The position of this system is consistent with the assignment as $[A\ 3/2]_c 8s$. The decline in intensity of this system to shorter wavelengths is probably due to the opening of the second ionisation channel leading to the spin-orbit excited state of the ion (i.e. $I_2^+ X^2\Pi_{1/2}$ core). We note that the structure in the ionisation continuum for I_2^+ is very similar to that in the ion-pair excitation functions and this is compatible with an auto-ionising state based on the $A^2\Pi_{3/2}$ state of the ion.

Fig. 2 shows our attempt to simulate the ion-pair excitation functions based on the analysis presented above. With only three Rydberg states plus a quasi-

continuum tail (at ≈ 132.5 nm, to represent the convergence limit) we obtained a reasonable fit to the experimental data. The spectra are based on Franck-Condon factor calculations for transitions from the ground state to Morse potentials which were used to represent the Rydberg states. Potential curve parameters for the Rydberg states are given in table 2. The small differences between calculated and experimental spectra that remain can be attributed to intensity borrowing through mixing between Rydberg and ion-pair states.

A near perfect fit can be obtained by including six Rydberg states (plus a quasi-continuum tail) in simulated spectra, as illustrated in fig. 3. However, in-

Table 2
Spectroscopic parameters for the Rydberg states used to calculate ion yield curves marked 9p, 10p and 11p on figs. 2 and 3

Assignment	$\lambda^{a)}$ (nm)	ω_e (cm^{-1})	r_e (nm)
$[3/2]_c 9p\pi$	138.0	210.5	0.2599
$[3/2]_c 10p\pi$	136.8	229.0	0.2578
$[3/2]_c 11p\pi$	135.8	229.0	0.2578

^{a)} Wavelength of (0,0) band.

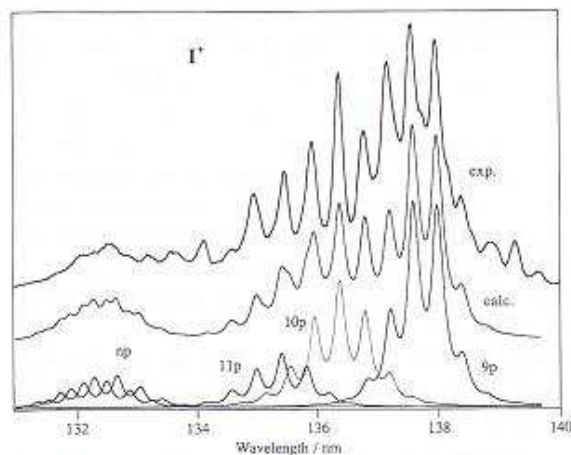


Fig. 2. Observed (top) and calculated excitation functions for I^+ (I^-) formation (see table 2 and text for further clarification). The calculated curve is a sum of curves due to transitions to three Rydberg states $[3/2]_c n p\pi$, where $n=9, 10, 11$ (marked 9p, 10p and 11p) and a quasi-continuum tail. Each calculated (v', v'') band is plotted as a Lorentzian-shaped peak. The population in ground state vibrational levels is taken as a Boltzmann distribution with a vibrational temperature of 250 K.

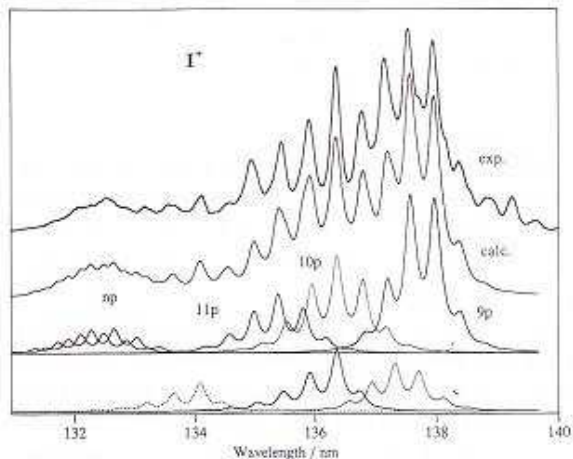


Fig. 3. Observed (exp) and calculated (calc) excitation functions for I^+ (I^-) formation. The calculated curve is a sum of curves due to transitions to six Rydberg states and a quasi-continuum tail. The states used in fig. 2 are shown separately (i.e. 9p, 10p, 11p, np) from the three additional states (shown in the lowest panel) needed to produce the calculated spectrum. These states have not been assigned (see text for discussion). Further details of the simulation are given in the caption to fig. 2.

interactions between the Rydberg and ion-pair states (i.e. those that produce the ion pairs) are almost certain to distort the intensity profile. Such interactions and distortions have been clearly identified and characterised in previous work at lower energies for Br_2 , IBr and ICl [13–15]. In the present case of ion-pair production the ion-yield profile can be considered as the product of two terms, the Franck–Condon factors for excitation to the Rydberg state and a vibrational overlap term which determines the efficiency of the coupling between the Rydberg and ion-pair states. Alternatively, one could consider the absorption process as a transition to a mixed Rydberg/ion-pair *resonance*. In view of this we feel that it is probably meaningless to assign the three additional Rydberg states and their inclusion in fig. 3 is purely illustrative.

Ion-pair formation has also been observed from Cl_2 and has been interpreted in terms of heterogeneous interaction between Rydberg and ion-pair states [9]. For the reasons given above and in our earlier discussion on Br_2 [1] we prefer to interpret our results on both I_2 and Br_2 in terms of homogeneous interaction.

In the case of Cl_2 the threshold for ion-pair formation lies above the molecular ionisation energy and thus ion-pair formation will be in competition with autoionisation processes. It should also be emphasised that in all cases ion-pair formation competes with excited atom formation as the ion-pair state, which causes the predissociation discussed above, will cross lower Rydberg states of the same symmetry and will interact with them also. Indeed, excited atom production following predissociation of high Rydberg states of I_2 has been reported [10].

In summary, we have observed clearly resolved vibrational structure in the excitation functions for ion-pair production (I^- and I^+) from I_2 . The main structure below the I_2 ionisation limit is assigned to homogeneous coupling between three (zero-order) Rydberg states (together with a weaker tail from Rydberg states close to the ionisation limit) and the ion-pair continuum. A further system, associated with

an excited core state, is observed at higher energy.

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