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REMPI spectra of I₂. The [²Π_{3/2}]_c5d; 1g Rydberg state and interactions with ion pair states

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Abstract

Rotational contours of the (2+1) REMPI spectra of iodine due to resonance excitation to the [²Π_{3/2}]_c5d; 1g Rydberg state have been recorded at room temperature. Rotational parameters, \bar{B}_v , were estimated from the band-head structure and used to derive the band origin by spectral simulations. $T_e = 59683.9 \pm 1.5 \text{ cm}^{-1}$ and $\omega_e = 248.5 \pm 0.6 \text{ cm}^{-1}$ were obtained from vibrational analyses. Several anomalies observed in the vibrational and band-head structures are discussed and interpreted as being due to the homogeneous interaction between the Rydberg state and the β(1g) ion pair state.

1. Introduction

Recently, Donovan et al. published an extensive work on the overall (2+1) REMPI spectrum for I₂ [1]. They reassigned some gerade Rydberg states which had previously been observed by the same technique [2–7] and reported a total of 12 new band systems in the two-photon energy region 48000–75300 cm⁻¹. Most of the REMPI work on iodine in the literature deals with assignments of the Rydberg states observed. This has mainly been based on analyses of the vibrational structure of the spectra [2–7] and/or intensity alterations of the spectral systems as the polarisation of the excitation light is changed between linear and circular [1,3]. Assignments by virtue of rotational analyses of the vibrational bands have only been made to a limited extent [1,3,8,9]. Irregularities in intensity alterations as the polarisation of the excitation light is changed have been reported and explained as being due to predissociation processes [1]. Severe perturbations have been observed in rotational contours both in one-photon ab-

sorption spectroscopy [10] and REMPI [1,11,12]. According to Venkateswarlu [10] all bands below 60000 cm⁻¹ are blue degraded, all those between 61000 and 63000 cm⁻¹ are red degraded and the remainder are a mixture of the two. A similar picture seems to be observed in (2+1) REMPI. This is believed to be due to the interaction between Rydberg states and the inner walls of one or more ion pair states [1].

Recently, we published papers [8,9] on analyses of the rotational contours for the Dalby system [2,3] corresponding to resonance excitation to the Rydberg state [²Π_{1/2}]_c6s; 1g with a demonstration of the simulation analyses procedure used. These were the first papers in a series of publications on analyses of the rotational contours of halogen containing compounds with emphasis on obtaining information on the rotational parameters of the states involved, and to understand the possible curve crossing and predissociation mechanisms. In this Letter, we present measurements and analyses of the (2+1) REMPI spectra corresponding to resonance excitation to the

gerade Rydberg state $[^2\Pi_{3/2}]_c5d; 1g$ of iodine. From the analyses, based on the structure of the band heads, spectroscopic parameters relevant to the vibrational and rotational properties of the Rydberg state are derived. Perturbations observed in the spectra are discussed in terms of Rydberg–ion pair interactions.

2. Experimental

The apparatus used has been described in detail elsewhere [8,9] so only a brief report will be given here. Tunable radiation was generated by an excimer laser-pumped Hyperdye 300 laser. The output from the dye laser, using the dye CV 670, was frequency doubled by means of a KDP-D crystal to cover the wavelength range studied, 327–338 nm. The frequency doubled beam was separated from the fundamental beam by means of a Pellin Broca prism and focused by a 20 cm focal length lens into an ionization cell with two stainless steel electrodes and containing vapor pressure iodine at room temperature. Current pulses were amplified, integrated and fed into a multichannel analyser for voltage peak height detection and recording. Finally, REMPI spectra were obtained by recording and displaying the average pulse heights for a chosen sampling time as a function of two photon wavenumber ($\bar{\nu}_{2h\nu}$) using a personal computer.

The laser was run at 20 Hz repetition rate and a pulse sampling time of 5 s was used. The bandwidth of the dye laser beam was about 0.05 cm^{-1} . The laser power was kept as low as possible in order to prevent power broadening. Calibration of the laser wavelength was achieved by recording neon and iodine atomic resonances at various wavelengths in the visible and UV region.

3. Results and data analyses

3.1. REMPI spectra: main features

Fig. 1 shows an overall (2+1) REMPI spectrum of iodine in the two-photon wavenumber region $59200\text{--}61100\text{ cm}^{-1}$ (excitation wavelength region, $\lambda_{\text{exc}} \approx 327\text{--}338\text{ nm}$). The spectrum has been normalised to the square of the laser power. The spectral fea-

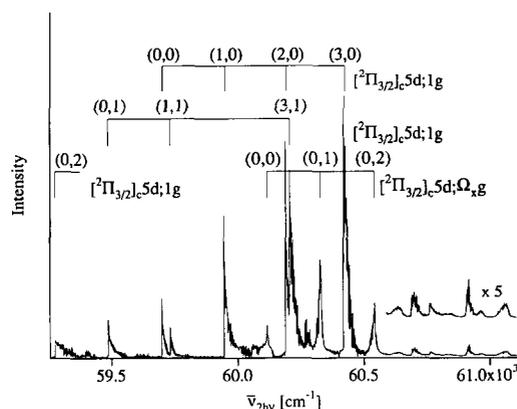


Fig. 1. (2+1) REMPI spectrum of iodine for two-photon resonance transitions from the ground state to the Rydberg states $[^2\Pi_{3/2}]_c5d; 1g$ and $[^2\Pi_{3/2}]_c5d; \Omega_x g$. Vibrational quantum numbers (v', v'') are indicated.

tures in this region have been assigned to resonance transitions to two Rydberg states in which the molecules have a $[^2\Pi_{3/2}]$ core of g symmetry and the Rydberg electrons are in 5d orbitals [1]. The peaks represent the vibrational bands as indicated. Furthermore, one of the states has been found to be an $\Omega=1$ state, judging from the shape of the rotational contours. The rotational contours and band heads of the vibrational bands for the $[^2\Pi_{3/2}]_c5d; 1g$ state are shown in Fig. 2 plotted on a relative two-photon wavenumber scale ($\Delta\bar{\nu}_{2h\nu}\text{ (cm}^{-1}\text{)}$).

The intensities of the vibrational bands of the $[^2\Pi_{3/2}]_c5d; 1g$ system characteristically increase with frequency from ($v'=0, v''=2$) to ($v'=3, v''=0$) at which point they suddenly drop and after which only small peaks and bumps, still unassigned, appear. The vibrational bands for $[^2\Pi_{3/2}]_c5d; 1g$ show clearly resolved O and P heads analogous in relative intensities to those observed for bands in the Dalby system [2,3], confirming that the state involved is $\Omega=1$ [1,3,8,9]. The positions of the O heads are presented in Table 1 along with the spacing between the O heads of neighbouring bands and the O and P peaks of the same bands. Notice that the spacing between the (0,0) and (1,0) bands closely resembles that observed for the spacing between the (1,0) and (2,0) bands (difference only about 4 cm^{-1}) while the spacing between the (2,0) and (3,0) bands is significantly lower. A noticeable increase in spacing between the O and P heads ($\Delta(OP)$) as v'' decreases

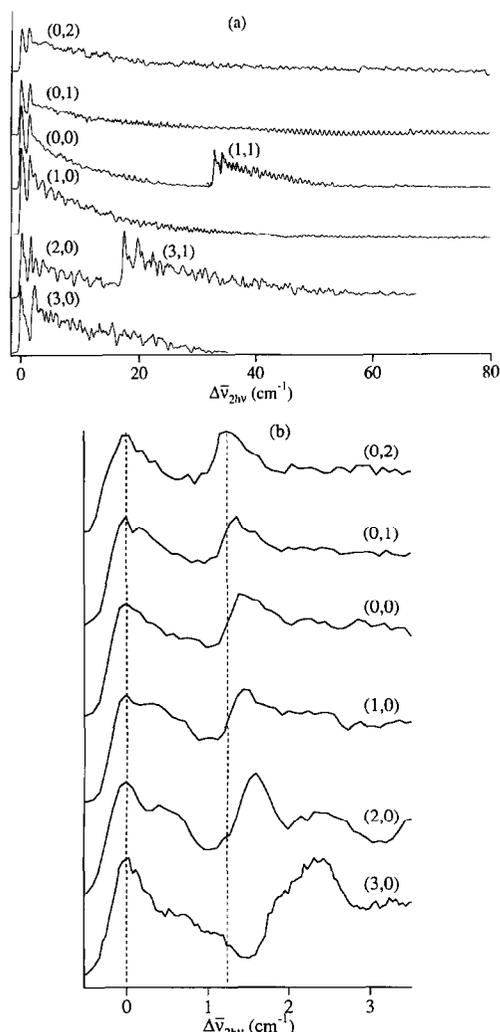


Fig. 2. (2+1) REMPI (a) rotational contours and (b) band heads for the $[^2\Pi_{3/2}]_c5d; 1g\leftarrow X$ resonance transition: relative intensities versus relative two-photon energies/wavenumbers. (v' , v'') assignments are indicated.

($v''=2\rightarrow 1\rightarrow 0$) and v' increases ($v'=0\rightarrow 1\rightarrow 2\rightarrow 3$) is found as also seen in the Dalby system. This effect has been shown to be consistent with decreasing rotational constants, $\bar{B}_{v''}$ and $\bar{B}_{v'}$, as the vibrational quantum numbers increase [9]. However, the change in the $\Delta(OP)$ as v' increases from 2 to 3 is unusually large. The shape of the band tails also differs significantly from that observed for the Dalby system. Regular alterations in the peak intensities and beat structure are characteristic of the shape of the tails of bands in the Dalby system. An analogous shape is also found

Table 1

O band-head positions (upper part), wavenumber difference between the O band heads (middle part) and spacing between O and P band heads ($\Delta(OP)$) (lower part) for (v' , v'') bands of the $(^2\Pi_{3/2})_c5d; 1g\leftarrow X$ transition (in cm^{-1})

v'	v''		
	0	1	2
0	59700	59487	59274
1	59947	59734	
2	60189		
3	60421	60207	
$(v'+1)-v'$		$\Delta(O)$	$\Delta(\Delta(O))$
1-0		247	4
2-1		243	11
3-2		232	
v'	v''		
	0	1	2
0	1.40 ± 0.10	1.40 ± 0.10	1.30 ± 0.08
1	1.46 ± 0.12	1.36 ± 0.06	
2	1.60 ± 0.06		
3	2.14 ± 0.16	2.28 ± 0.24	

for the ($v'=0$, v'') bands, most clearly seen for ($v'=0$, $v''=1$), while the structure for those corresponding to $v'>0$ gradually becomes more irregular as v' increases. We believe that the irregularities in both the vibrational and rotational structures are due to interactions between the Rydberg state and ion pair states.

3.2. Rotational constants for $[^2\Pi_{3/2}]_c5d; 1g$

A simple expression has been derived for estimating the rotational constants ($\bar{B}_{v''}$) of excited vibrational states as a function of $\Delta(OP)$, if the rotational constants for the ground state ($\bar{B}_{v''}$) are known [9],

$$\bar{B}_{v'} = \frac{\Delta(OP)\bar{B}_{v''}}{\Delta(OP) - 3\bar{B}_{v''}} \quad (1)$$

The difference between this expression and the analogous one in ref. [9] (Eq. (13)) is due to different definitions for $\Delta(OP)$. The values listed in Table 2 were derived for $[^2\Pi_{3/2}]_c5d; 1g$, by using $\bar{B}_{v''}$ values from ref. [9]. Furthermore, average internuclear distance values, $r_{v'}$, based on the rigid rotor approximation were evaluated. Notice that the sudden increase

Table 2

Rotational constants (\bar{B}_v) and internuclear distances (r_v) for the vibrational states (v') of the Rydberg state (${}^2\Pi_{3/2}$) $_c5d; 1g$, obtained from $\Delta(OP)$

(v', v'')	\bar{B}_v (cm ⁻¹)	r_v (Å)
(0, 0)/(0, 1)/(0, 2)	0.0405 ± 0.0002	2.561 ± 0.008
(1, 0)/(1, 1)	0.0404 ± 0.0002	2.562 ± 0.008
(2, 0)	0.0401 ± 0.0001	2.573 ± 0.004
(3, 0)/(3, 1)	0.0392 ± 0.0003	2.602 ± 0.011

in $\Delta(OP)$ from (2, 0) to (3, 0), as previously mentioned corresponds to a lowering in \bar{B}_v or an increase in r_v .

3.3. Recalculation of rotational contours and band origin evaluations

The method for the simulation calculation of the rotational contours has been described before [8,9]. Spectra for the [${}^2\Pi_{3/2}$] $_c5d; 1g$ state were calculated, based on the rotational constants mentioned above and the corresponding second-order rotational constants evaluated by

$$\bar{D}_v = 4\bar{B}_v^3 / \omega_c^2 \quad (2)$$

A Boltzmann distribution corresponding to room temperature was assumed and the bandwidth of rotational lines was varied until satisfactory fits were obtained. As expected, the irregularity observed in the tail of the bands mentioned above could not be reproduced. On the other hand, the spacing between the O and P heads in the calculated spectra were found to be close to that observed, as seen in Fig. 3. The band origins ($\bar{\nu}_{2\nu}^0(v', v'')$) could be evaluated by comparison of the calculated and experimental spectra from

$$\bar{\nu}_{2\nu}^0(v', v'') = \bar{\nu}_{2\nu}(O) + |\Delta\bar{E}_{J', J''}(O)|, \quad (3)$$

where $\Delta\bar{E}_{J', J''}(O)$ is the wavenumber value for the O head peak derived from the calculated spectrum and $\bar{\nu}_{2\nu}(O)$ is the position of the O head according to the experimental spectrum (Table 1). These values are listed in Table 3 along with the difference values. Notice that the spacing between the (2, 0) and (3, 0) band origins, hence the energy difference between $v'=2$ and $v'=3$, is significantly lower than that between $v'=0$ and 1, and between $v'=1$ and 2 as found

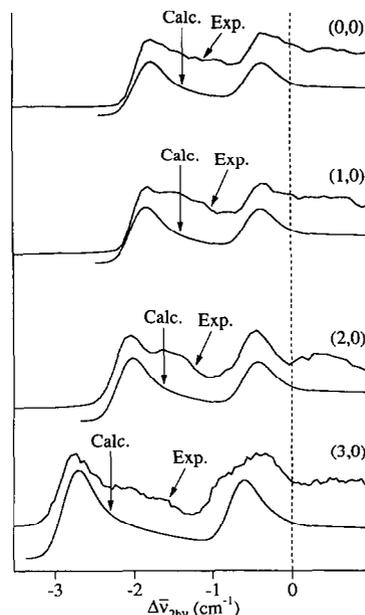


Fig. 3. Observed (top) and calculated (below) (2+1) REMPI band heads for the [${}^2\Pi_{3/2}$] $_c5d; 1g \leftarrow X$ resonance transition, ($v', v''=0; v'=0-3$). The x axis scale ($\Delta\bar{\nu}_{2\nu}$) equals $\Delta E_{J', J''}$ (see definition in text/Eq. (3)). Bandwidths of rotational lines in calculated spectra are 0.18 cm⁻¹ (see ref. [9]).

Table 3

Band origins, $\bar{\nu}_{2\nu}^0$ (cm⁻¹), of the vibrational bands for the (${}^2\Pi_{3/2}$) $_c5d; 1g \leftarrow X$ transition

(v', v'')	$\bar{\nu}_{2\nu}^0$	$\Delta(\bar{\nu}_{2\nu}^0)$	$\Delta(\Delta(\bar{\nu}_{2\nu}^0))$
(0, 2)	59276		
(0, 1)	59489		
(0, 0)	59702	246	3
(1, 0)	59948	243	
(2, 0)	60191	233	10
(3, 0)	60424		

for the spacing between corresponding heads, mentioned before.

4. Interpretation and discussion

The two anomalies noted in sections 3.2 and 3.3 concerning relatively low values of both the rotational constant and the vibrational energy of the $v'=3$ level for [${}^2\Pi_{3/2}$] $_c5d; 1g$ are consistent with the idea of a homogeneous interaction between the Rydberg state and an ion pair state. Ion pair states will cross

the outer wall of the Rydberg state. A gerade $\Omega=1$ ion pair state which will cross the Rydberg state at an energy larger than that of the $v'=3$ level (assuming a first-order approximation/unperturbed state), can interact with the Rydberg level to cause an effective downward shift in the zero-approximation energy level (see Fig. 4). The relative magnitude of the perturbation effects of the vibrational levels in the ion pair state on the $v'=3$ level will be determined by the vibrational contribution to the matrix element of the perturbation function [13,14],

$$H_{\text{Ry,ip}} = \langle v'_{\text{Ry}} | H' | v'_{\text{ip}} \rangle. \quad (4)$$

$|v'_{\text{Ry}}\rangle$ and $|v'_{\text{ip}}\rangle$ in Eq. (4) refer to the vibrational wavefunctions for the vibrational levels in the Rydberg state ($v'=3$) and the ion pair state, respectively. H' represents the interaction between vibration and electronic motion [13]. The interaction produces repulsion-type shifts in the zero-approximation energy levels, inversely dependent on their separation. A larger overlap will be found for the ion pair vibrational states at energies higher than $v'_{\text{Ry}}=3$ compared to that for the lower energy levels. Therefore, the downward shift because of the interaction from the higher-lying levels will exceed the upward shift due to the lower-lying levels as demonstrated in Fig. 4. Furthermore, because of the difference in internu-

clear distances, the rotational constants for the ion pair state will be smaller than for the Rydberg state, hence the rotational energy levels will be more closely spaced for the ion pair levels than for the Rydberg level. Therefore, the energy spacing between interacting J levels with the same quantum numbers (i.e. homogeneous interaction) will be J/energy dependent. Assuming that the v'_{Ry} level effectively interacts with a single higher-lying v'_{ip} level an estimate of the vibronic matrix element, $H_{\text{Ry,ip}}$ and the effective energy spacing between the two zeroth-order levels ($\Delta E_{\text{Ry,ip}}$) can be made from

$$\Delta E(v'_{\text{Ry}}) = \frac{H_{\text{Ry,ip}}^2}{\Delta E_{\text{Ry,ip}}}, \quad (5)$$

$$B(v'_{\text{Ry}}) = B^0(v'_{\text{Ry}}) \left[1 - \left(\frac{H_{\text{Ry,ip}}}{\Delta E_{\text{Ry,ip}}} \right)^2 \right] + B^0(v'_{\text{ip}}) \left(\frac{H_{\text{Ry,ip}}}{\Delta E_{\text{Ry,ip}}} \right)^2, \quad (6)$$

derived from perturbation theory. $\Delta E(v'_{\text{Ry}})$ is the effective lowering of the $v'_{\text{Ry}}=3$ level ($\approx 4\text{--}7 \text{ cm}^{-1}$), $B^0(v'_{\text{Ry}})$ and $B^0(v'_{\text{ip}})$ are the zeroth-order/unperturbed rotational constants for $v'_{\text{Ry}}=0$ and v'_{ip} , respectively ($B^0(v'_{\text{Ry}}) \approx 0.040 \text{ cm}^{-1}$ (see Table 2); $B^0(v'_{\text{ip}}) \approx 0.01 \text{ cm}^{-1}$ (see below)). $B(v'_{\text{Ry}})$ is the perturbed rotational constant for $v'_{\text{Ry}}=3$ (0.0392 cm^{-1}). Thus, $H_{\text{Ry,ip}}$ is found to be about $25\text{--}42 \text{ cm}^{-1}$ and $\Delta E_{\text{Ry,ip}} \approx 150\text{--}250 \text{ cm}^{-1}$. The FCF, $\langle v'_{\text{Ry}} | v'_{\text{ip}} \rangle$, is about 0.01, hence the electronic part of the matrix element will be no greater than about 400 cm^{-1} . This value is characteristic of a weak homogeneous interaction rather than a major avoided crossing. A similar effect has been found for oxygen [15].

The ion pair state involved is most probably the $\beta(1g)$, correlating with $\text{I}^+(^3\text{P}_2) + \text{I}^-(^1\text{S})$, which is expected to cross the Rydberg state in this energy region. The $\beta(1g)$ state has been analysed to determine spectroscopic constants from low rovibrational levels only ($\beta(1g)$: $\omega_e = 105.0 \text{ cm}^{-1}$, $T_e = 40821 \text{ cm}^{-1}$ and $r_e = 3.61 \text{ \AA}$ for $0 \leq v' \leq 68$ [16,17]). The 12 ion pair states which correlate with $\text{I}^+(^3\text{P}_{2,1,0}) + \text{I}^-(^1\text{S})$ are all spectroscopically similar, with average internuclear distances $\approx 3.53\text{--}3.68 \text{ \AA}$, and vibrational frequencies $\omega_e \approx 95\text{--}106.6 \text{ cm}^{-1}$ [18]. Dunham coefficients for the better characterised $\text{D}(\text{O}_v^+)$ ion pair state [19,20] ($\omega_e \approx 95.0 \text{ cm}^{-1}$, $T_e = 41029 \text{ cm}^{-1}$ [19]

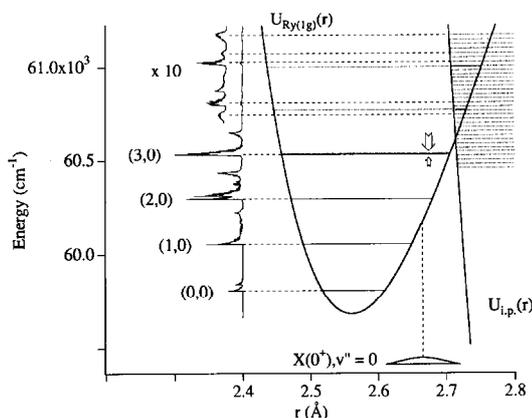


Fig. 4. Semi-schematic representation of excited states and energy levels populated in two-photon resonance excitation correlated with features in the $(2+1)$ REMPI spectrum. $U_{\text{Ry}(1g)}(r)$ is a diabatic/unperturbed Morse potential curve for the $[^2\Pi_{3/2}]_e5d; 1g$ Rydberg state and $U_{\text{ip}}(r)$ represents (the inner wall of) an ion pair state. Solid energy levels are based on observations, while dotted levels are according to expectation (see text for further clarification).

and $r_e = 3.56 \text{ \AA}$ [18]) and the T_e value for the $\beta(1_g)$ state, therefore, could be used to estimate the ion pair vibrational energy level spacing ($20\text{--}22 \text{ cm}^{-1}$) and $B^0(v'_{ip})$ ($\approx 0.01 \text{ cm}^{-1}$) at energies close to that of $v' = 0\text{--}5$ for the Rydberg state [$^2\Pi_{3/2}$] $_c5d$; 1g. The energy level spacing of about $20\text{--}22 \text{ cm}^{-1}$ is much smaller than that between $v'_{Ry} = 3$ and the effective v'_{ip} level described in the model above ($150\text{--}250 \text{ cm}^{-1}$), clearly indicating that several ion pair vibrational levels must be included in the perturbation.

A standard extrapolation of $\bar{B}_{v'}$ values versus $v' + \frac{1}{2}$ [9,13], ignoring $\bar{B}_{v'=3}$, gives estimated values of $\bar{B}_e = 0.0406 \pm 0.0003 \text{ cm}^{-1}$ and $r_e = 2.56 \pm 0.01 \text{ \AA}$. T_e , the frequency (ω'_e) and the anharmonicity constant ($\omega_e x'_e$) for the [$^2\Pi_{3/2}$] $_c5d$; 1g Rydberg state can be evaluated by a least-squares fit of the data in Table 3 according to the expression

$$\bar{\nu}_{2\nu}^0(v', v'') = T'_e + \omega'_e(v' + \frac{1}{2}) - \omega_e x'_e(v' + \frac{1}{2}) - \omega''_e(v'' + \frac{1}{2}) + \omega_e x''_e(v'' + \frac{1}{2}), \quad (7)$$

for known values for ω''_e and $\omega_e x''_e$ [21]. Least-squares fit analyses of $\bar{\nu}_{2\nu}^0(v', v'')$ versus $v' + \frac{1}{2}$ data points gave $T'_e = 59683.9 \pm 1.5 \text{ cm}^{-1}$, $\omega'_e = 248.5 \pm 0.6 \text{ cm}^{-1}$ and $\omega_e x'_e = 1.96 \pm 0.15 \text{ cm}^{-1}$ if the value for $v' = 3$ was left out. Both rotational parameters (B_e and r_e) and the vibrational frequency (ω_e) closely resemble that found for other Rydberg states [3,9,10,22,23]. Thus, for the slightly lower energy gerade Rydberg state [$^2\Pi_{1/2}$] $_c6s$; 1g, r_e was found to be 2.5656 \AA and $\omega_e = 241.8 \pm 0.5 \text{ cm}^{-1}$ according to our analyses of the Dalby system [9]. The anharmonicity constant, on the other hand, is found to be significantly larger than that for the unperturbed [$^2\Pi_{1/2}$] $_c6s$; 1g state ($0.64 \pm 0.07 \text{ cm}^{-1}$ according to ref. [9] and $0.58 \pm 0.36 \text{ cm}^{-1}$ according to ref. [3]), which might suggest that the downward repulsion perturbation due to the effect of the ion pair state as mentioned above also affects $v' = 2$ to some extent.

The steadily growing intensity of vibrational bands as $(v' = 0, v'' = 0) < (v' = 1, v'' = 0) < (v' = 2, v'' = 0) < (v' = 3, v'' = 0)$ is unusual compared to that observed for most Rydberg spectra. Most commonly, for unperturbed systems ($v' = 1, v'' = 0$) or ($v' = 2, v'' = 0$) are believed to be the strongest in bell-shaped band spectra, whether in absorption [10,24], photoionization [23] or REMPI [1–3,8,9]. This has been predicted by a Franck–Condon factor calculation for

typical Rydberg state←ground state transitions [23]. This intensity anomaly can most probably be ascribed to an intensity borrowing due to either of the two Rydberg ion pair interactions mentioned above. Such an intensity borrowing is a phenomenon well-known to occur when an absorbing state interacts with a longer lived state [14].

The spectra region above the ($v' = 3, v'' = 0$) band ($\bar{\nu}_{2\nu} \approx 60550 \text{ cm}^{-1}$) will now be considered with reference to Fig. 4. The sudden drop in peak intensity beyond ($v' = 3, v'' = 0$) suggests that the avoided crossing of the $\Omega = 1$ Rydberg and ion pair states occurs between $v'_{Ry} = 3$ and 4. As discussed above, the spectral features corresponding to transitions to energies below the crossing bear a strong resemblance to Rydberg state transitions. The features observed at higher energies, on the other hand, bear more resemblance to ion pair state transitions. The intensities are smaller, due to less favourable Franck–Condon overlaps of ground state vibrational wavefunctions and wavefunctions with mostly ion pair state character due to large difference in internuclear distances. Furthermore, the spacing between the peaks and bumps in this region is smaller than that between the vibrational levels in typical Rydberg states. Further inspection of the structure above 60550 cm^{-1} reveals two types of peaks, those at $60700, 60765$ and 60920 cm^{-1} with sharp short wavenumber edges and blue degraded tails, and those at $60636, 60835, 60967$ and 61067 cm^{-1} with no sharp edges but a slight or insignificant degradation to the red (see Fig. 1). In Fig. 4 vibrational levels for $v'_{Ry} \geq 3$, calculated by use of ω'_e and $\omega_e x'_e$, are shown as dotted lines. Thus, unperturbed vibrational levels of the Rydberg state are predicted to be close to the relatively strong 60700 and 60920 cm^{-1} peaks in the former group. We, therefore, believe that the shape of these two peaks is due to a relatively large Rydberg state character in the mixing state. The peak at 60765 cm^{-1} , on the other hand, could either partly or solely belong to the other observed Rydberg state series ([$^2\Pi_{3/2}$] $_c5d$; Ω_xg in Fig. 1), mentioned before. Those belonging to the latter group mentioned above, are mostly of ion pair character.

The Rydberg series corresponding to transitions to the [$^2\Pi_{3/2}$] $_c5d$; Ω_xg state shows more diffuse structure than found in the [$^2\Pi_{3/2}$] $_c5d$; 1g series and is somewhat similar to that observed in the mixing re-

gion above 60550 cm^{-1} . This suggests that the Rydberg state involved is mixed with an ion pair state.

5. Conclusion

Analyses of the vibrational structure and band heads of the (2+1) REMPI spectrum for the $[^2\Pi_{3/2}]_c5d; 1g$ Rydberg state have been performed to derive spectroscopic parameters for the resonance excited state. Anomalies observed both in the vibrational and rotational structures and spectral intensities have been ascribed to a homogeneous interaction between the Rydberg state and an $\Omega=1$ ion pair state. The crossing of the two states occurs just above $v'=3$ of the Rydberg state. The diffuse spectral structure observed for transitions to higher-lying levels is interpreted as being due to the mixing of the two states above the curve crossing region. The ion pair state involved is most probably the $\beta(1g)$ state, which belongs to the first cluster of ion pair states which correlate with $I^+(^3P_0)+I(^1S)$. Finer perturbations observed in the rotational contours await further analyses [25].

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