

# Rotational perturbations in the (2 + 1) REMPI spectrum of the Rydberg state $[^2\Pi_{3/2}]_c 5d;1g$ of $I_2$

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## Abstract

Partly rotationally resolved (2 + 1) resonance-enhanced multiphoton ionization contour spectra of the vibrational bands corresponding to the  $[^2\Pi_{3/2}]_c 5d;1g \leftarrow X$  transition in iodine, recorded at room temperature, have been analyzed. Irregular band spectral structures could be simulated by assuming rotational line strengths to be dependent on rotational quantum number in the resonantly excited state at the two-photon level. The analysis allowed improved rotational constants ( $\bar{B}_{v'}$  and  $\bar{D}_{v'}$ ) and corresponding internuclear distances ( $r_{v'}$ ) for the Rydberg state to be evaluated, as well as the characteristic rotational parameters,  $\bar{B}'_c = 0.04047 \pm 0.00010 \text{ cm}^{-1}$ ,  $\alpha'_c = (1.3 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$  and  $r'_c = 2.562 \pm 0.003 \text{ \AA}$ . The anomalies in the rotational structure are ascribed to perturbation effects due to heterogeneous interaction between an ion-pair state and the Rydberg state. A candidate for the perturbing state is the  $D'(2g)$  state.

## 1. Introduction

A large number of gerade Rydberg states for iodine, in which the molecules have  $[^2\Pi_{3/2g}]$  or  $[^2\Pi_{1/2g}]$  cores but the Rydberg electrons are either in s or d orbitals, have been characterized via (2 + 1) REMPI analysis [1–10]. Transitions to gerade Rydberg states are found to be dominating in the REMPI spectra of iodine,  $Br_2$  [11–13] and  $Cl_2$  [14,15], while transitions to ion-pair states dominate the REMPI spectra of the interhalogens  $IBr$  [16,17] and  $ICl$  [18]. However, REMPI spectra for the homogeneous halogens also show a number of indications for interactions between excited Rydberg states and ion-pair states.

Thus for iodine weak features appearing on the sides of vibrational bands corresponding to transitions to the Rydberg state  $[^2\Pi_{3/2g}]_c 7s,1g$  (63200–64200  $\text{cm}^{-1}$  two-photon energy) are believed to represent ion-pair vibrational structure arising from an interaction between the Rydberg state and the  $\beta(1g)$  ion-pair state [19,20]. Several anomalies observed in the vibrational and band-head structures of spectra due to transitions to the  $[^2\Pi_{3/2g}]_c 5d;1g$  Rydberg state (59300–60500  $\text{cm}^{-1}$  two-photon energy) have been interpreted as being due to homogeneous interaction between the Rydberg state and the  $\beta(1g)$  ion-pair state [10]. A number of Rydberg state rotational contours (62500–65450  $\text{cm}^{-1}$  two-photon energy) have been found to show weak perturbations, which are believed to be due to interactions between the Rydberg states and the inner walls of one or more ion-pair states [7,10]. A similar picture seems

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to be observed in one-photon absorption spectroscopy of iodine [21]. All bands below  $60000\text{ cm}^{-1}$  are found to be blue degraded, all those between  $61000$  and  $63000\text{ cm}^{-1}$  are red degraded and the remainders are a mixture of the two.

For chlorine, bands shaded towards the red with very small vibrational frequency are found on the short wavelength side of a progression corresponding to transition to the  $^3\Pi_g$  Rydberg state [14]. These are attributed to two-photon excitations to levels above a double well barrier formed by mixing of the Rydberg state and an ion-pair state [22].

In this paper we present analysis of high resolution rotational ( $2 + 1$ ) REMPI spectra of  $I_2$  corresponding to transitions to the  $[^2\Pi_{3/2g}]_c5d;1g$  Rydberg state. In addition to showing several anomalies in the vibrational and band-head structures, rotational perturbations of different magnitude depending on vibrational quantum numbers in the excited state are observed. The irregularities are interpreted as being due to weak heterogeneous interaction between the Rydberg state and either of the two ion-pair states  $E(0_g^+)$  or  $D'(2g)$ . The analysis allows evaluations of more precise spectroscopic parameters for the  $[^2\Pi_{3/2g}]_c5d;1g$  Rydberg state than are available [10]. This paper is a part of a series of publications planned on analyses of rotational REMPI spectra of halogen containing compounds. The emphasis is on obtaining information on spectroscopic parameters of the states involved as well as to understand curve crossing and predissociation mechanisms [8–10,23].

## 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 a Lumonics Hyperdye 300 laser pumped by a Lumonics 510 excimer 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,  $330\text{--}337\text{ nm}$ . The frequency doubled beam was separated from the fundamental beam by means of a Pellin Broca prism and focused by a  $20\text{ cm}$  focal length lens into an ionization cell with two stainless steel electrodes and containing vapor pressure of iodine at room temperature. Current pulses were

amplified, integrated and fed into a multichannel analyzer for voltage peak height detection and recording. Average pulse heights for a fixed sampling time were recorded and displayed as a function of two-photon wavenumber ( $\bar{\nu}_{2h\nu}$ ) on an IBM/XT computer.

The laser was run at  $20\text{ Hz}$  repetition rate and a pulse sampling time of  $5\text{ s}$  used. The bandwidth of the dye laser beam was about  $0.05\text{ cm}^{-1}$ . The dye laser output was scanned in  $0.5\text{--}1.0\text{ cm}^{-1}$  steps for low resolution (overall) spectra but in  $0.02\text{--}0.1\text{ cm}^{-1}$  steps for high resolution spectra. Care was taken to prevent power broadening due to ac Stark effects by minimizing laser power for high resolution spectra scans. Calibration of the laser wavelength was achieved by recording neon and iodine atomic resonances at various wavelengths in the visible and UV region. The accuracy of the calibration in the spectral region studied here was found to be  $\pm 1\text{ cm}^{-1}$ .

## 3. Results and data analysis

### 3.1. REMPI spectra: main features

Fig. 1 shows the overall ( $2 + 1$ ) REMPI spectrum of iodine in the two-photon wavenumber region  $59400\text{--}60600\text{ cm}^{-1}$  (excitation wavelength region,  $\lambda_{\text{exc.}} \approx 330\text{--}337\text{ nm}$ ) (a) and rotational contours of the vibrational bands for  $[^2\Pi_{3/2g}]_c5d;1g$  (b). The overall spectrum has been normalized to the square of the laser power. The band-head structure of the vibrational bands for the  $[^2\Pi_{3/2g}]_c5d;1g$  system shows O and P heads characteristic of  $\Delta\Omega = 1$  ( $\Omega = 1 \leftarrow \Omega = 0$ ) transitions. Severe vibrational and rotational perturbations are observed in the spectral structure. (i) Intensities of the vibrational bands characteristically increase with frequency from ( $v' = 0, v'' = 1$ ) to ( $v' = 3, v'' = 0$ ) at which point they suddenly drop, (ii) spacing between the (0,0) and (1,0) bands closely resembles that observed for the spacing between the (1,0) and (2,0) bands, while the spacing between the (2,0) and (3,0) bands is significantly smaller, (iii) a noticeable increase in spacing between O and P heads ( $\Delta(OP)$ ) as  $v''$  decreases and  $v'$  increases is found, but the change in  $\Delta(OP)$  as  $v'$  increases from 2 to 3 is unusually large, (iv) band tails show irregular rotational structure with increas-

ing irregularity as  $v'$  increases. The first three of the above mentioned observations have been interpreted as being due to weak homogeneous interaction between the Rydberg state and the  $\beta(1g)$  ion-pair state [10], but the irregular rotational structure most probably is due to a different interaction. Although for the  $[^2\Pi_{3/2g}]_c 5d; \Omega_x g$  system bands no sharp edges are found, an overall degradation to the red is observed. This suggests that the Rydberg state is strongly mixed with an ion-pair state, more so than the  $[^2\Pi_{3/2g}]_c 5d; 1g$  state. In what follows analysis of the  $[^2\Pi_{3/2g}]_c 5d; 1g$  system vibrational contours will be emphasized.

Emphasis has been placed on analysis of the

vibrational and band-head structure. Rotational constants ( $\bar{B}_{v'}$ ) were derived directly from the spacing between the O and P heads ( $\Delta(OP)$ ), based on the knowledge of the rotational constants in the ground state ( $\bar{B}_{v''}$ ) [9]. Thereafter spectra were recalculated to show consistency in  $\Delta(OP)$  spacings between observed and calculated spectra. However, irregularities observed in the band-head structure could not be reproduced by the calculated spectra.

### 3.2. Simulation calculations

We extended the recalculation mentioned above, based on the parameters derived in Ref. [10] to cover

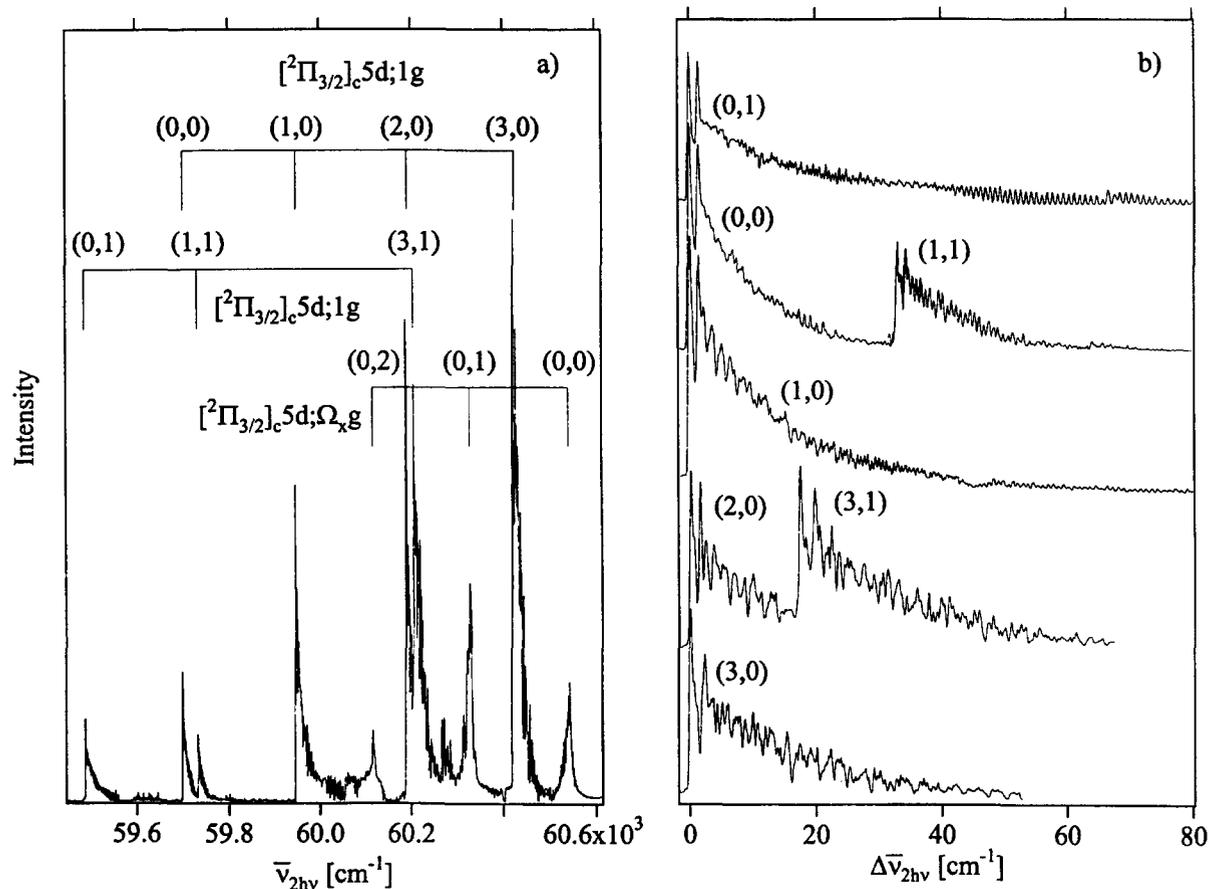


Fig. 1. (2 + 1) REMPI spectrum of iodine for resonance transitions to the Rydberg states  $[^2\Pi_{3/2g}]_c 5d; 1g$  and  $[^2\Pi_{3/2g}]_c 5d; \Omega_x g$ : Overall spectrum (a) and rotational contours for the  $[^2\Pi_{3/2g}]_c 5d; 1g$  state (b). Vibrational quantum numbers ( $v', v''$ ) are indicated. Rotational contours are plotted versus relative two-photon wavenumbers ( $\Delta \bar{\nu}_{2h\nu}$ ). Spectra for bands (1,1) and (1,0) were obtained by two overlapping scans to test for reproducibility of fine structure.

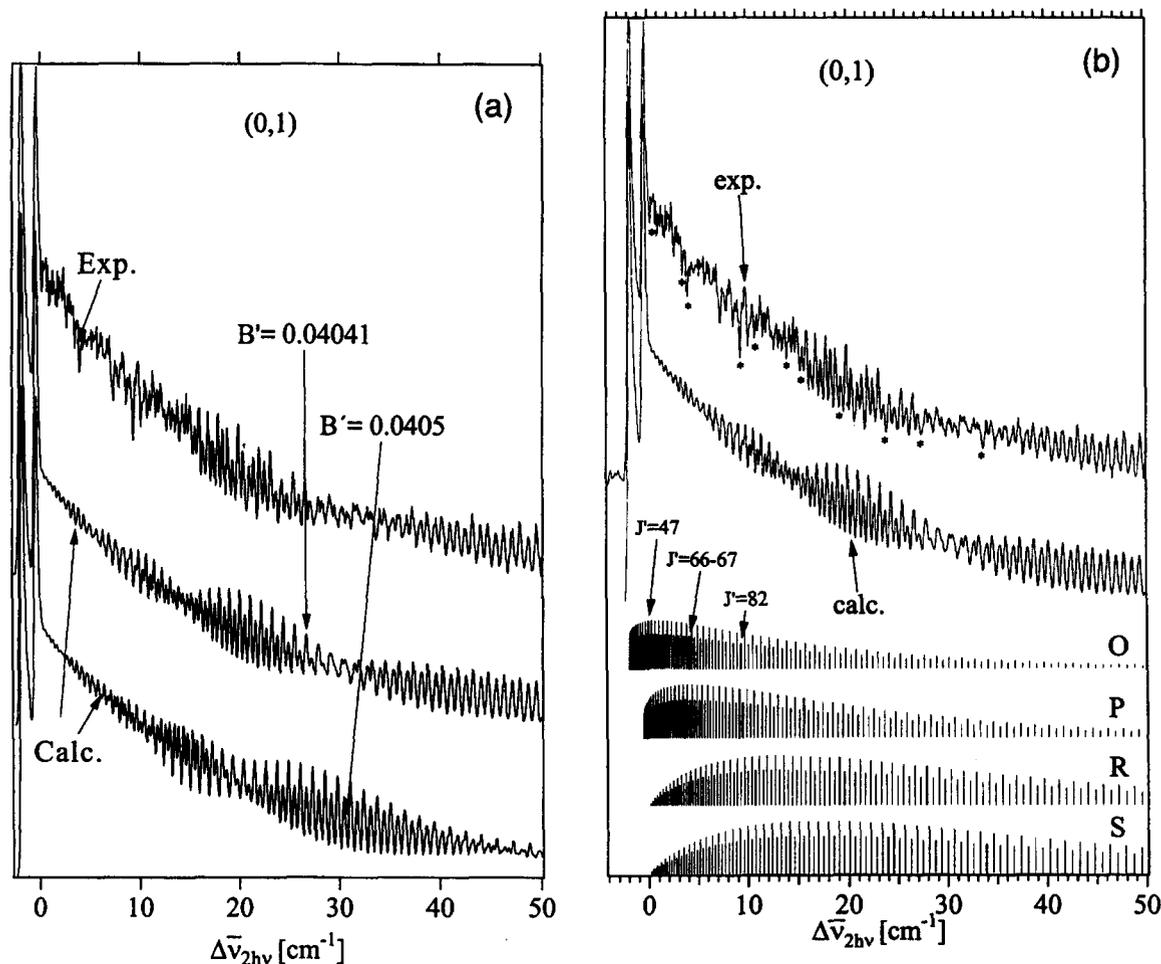
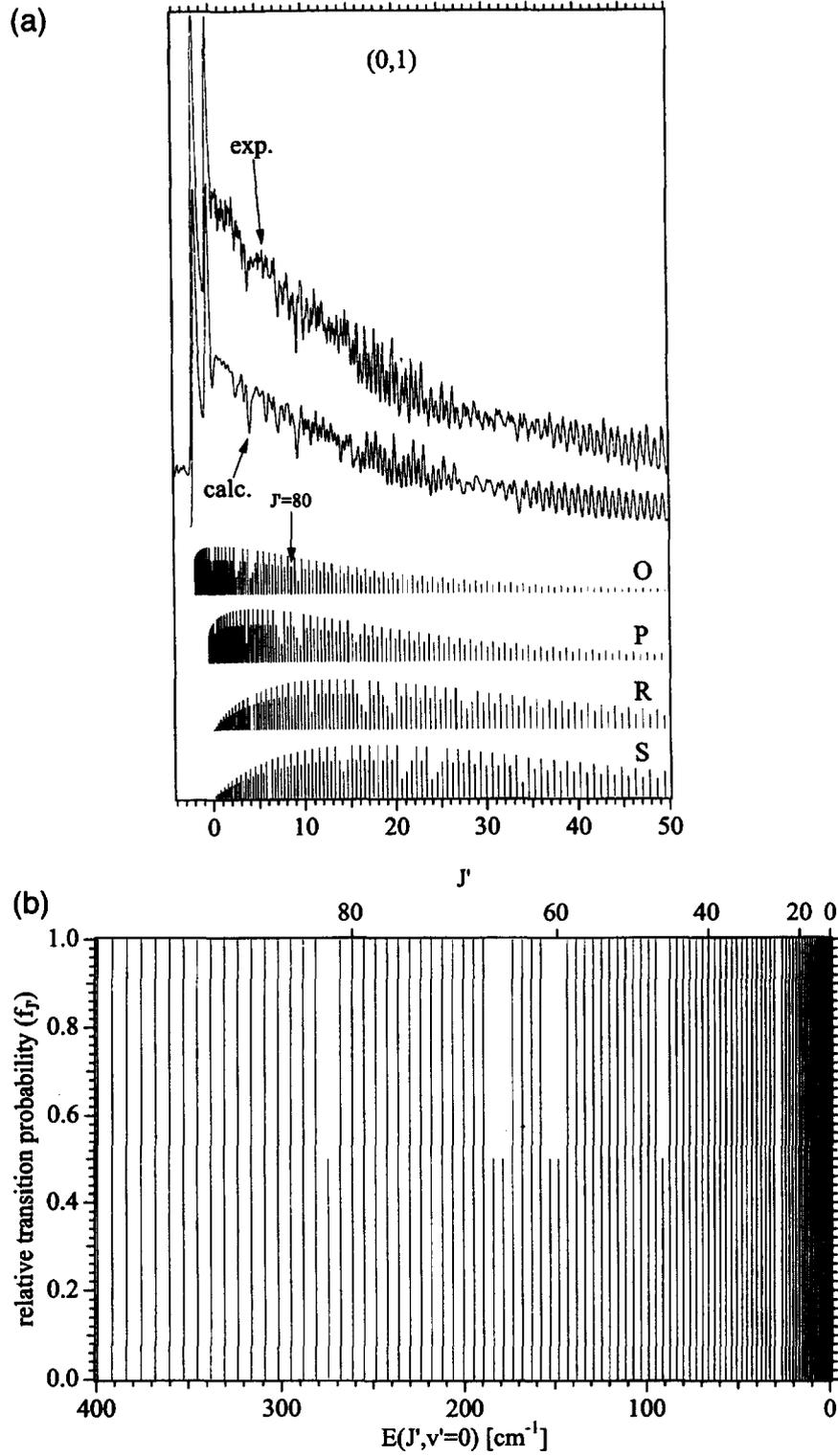


Fig. 2. (a) Observed ((0,1) band for Rydberg state [ $^2\Pi_{3/2g}$ ] $_c5d;1g$ ; top) and calculated (middle and bottom) rotational contours. Calculated spectra were obtained for  $\bar{B}_{v'}$  = 0.0405  $\text{cm}^{-1}$  [10] (bottom) and for  $\bar{B}_{v'}$  = 0.04041  $\text{cm}^{-1}$  (derived from simulation of rotational line positions and best fit of intensities; middle). Bandwidth of rotational lines in calculated spectra is 0.32  $\text{cm}^{-1}$  (on the two-photon wavenumber scale ( $\bar{\nu}_{2hv}$ )). (b) Observed ((0,1) band for Rydberg state [ $^2\Pi_{3/2g}$ ] $_c5d;1g$ ; top) and calculated (below;  $\bar{B}_{v'}$  = 0.04041  $\text{cm}^{-1}$ ) rotational contours as well as rotational lines (O,P,R and S series; bottom). Observed dips in rotational structure are indicated by stars (\*) and rotational lines which match the dip positions are shown as broad lines marked by rotational quantum numbers in the Rydberg state ( $J' = 47, 66-67$  and 82).

the tail regions of the vibrational contours and tried to simulate peak positions and intensities in a way which has been described before [8,9]. Fig. 2a shows the observed (0,1) band along with two calculated spectra. The bottom calculated spectrum is derived

for the parameters given in Ref. [10], while the top one is obtained after changing the  $\bar{B}_{v'}$  and  $\bar{D}_{v'}$  parameters until a satisfactory fit of peak positions and the best fit of relative peak heights in the tail were obtained. Fig. 2b shows this latter calculated

Fig. 3. (a) Simulations of the ( $v' = 0, v'' = 1$ ) vibrational bands for the Rydberg state [ $^2\Pi_{3/2g}$ ] $_c5d;1g$ . Observed (top) and calculated (below) rotational contours as well as rotational lines (O,P,R and S series; bottom) after reduction in relative transition probabilities, ( $f_{J'}$ ) (b) due to perturbation effects have been taken account of (see text). Rotational lines due to transitions to  $J' = 80$  (a) are shown as broad lines to guide the eye.



spectrum along with the rotational lines for O, P, R and S series and the experimental spectrum. Intensities of Q lines are negligible [8–10] and therefore are not shown on the figure. It is clear that irregularities, observed in the tail, are not reproduced by this means. Closer inspection of the nature of the irregularities reveals that these are dips in the otherwise regular structure predicted by the calculations. Furthermore, the dips seem to follow a regular pattern. Thus, for example, the dips marked with stars in Fig. 2b appear where rotational lines corresponding to transitions to  $J' = 47, 66\text{--}67$  and  $82$  in all series (O–S) appear. By lowering transition probabilities to these rotational levels as well as to levels  $J' = 26$  and  $60\text{--}61$  as shown on Fig. 3a a satisfactory fit was obtained.

Relative intensities,  $I_{\text{rel}}$ , for unperturbed  $J', v' \leftarrow J'', v''$  transitions can be expressed as [9]

$$I_{\text{rel}} = C_{v', v''} g_{J''} S_{J', J''} \exp(-\bar{E}_{J''} hc/kT), \quad (1)$$

where  $\bar{E}_{J''}$  is the rotational energy (in  $\text{cm}^{-1}$ ) for rotational levels in the ground state,  $J''$ ,  $S_{J', J''}$  is the two-photon transition strength [24], and  $g_{J''}$  is the degeneracy factor for  $J''$  which has been shown to consist of a product of the general degeneracy factor for a diatomic rotor,  $2J'' + 1$  and a nuclear statistics factor [9].  $C_{v', v''}$  is assumed to be a constant for a particular  $(v', v'')$  band. The simulation in Fig. 3a corresponds to assuming an additional  $J'$  dependence of rotational line intensities

$$I'_{\text{rel}} = f_{J'} I_{\text{rel}}, \quad (2)$$

where  $f_{J'}$  depends on  $J'$  and  $0 \leq f_{J'} \leq 1$ . Fig. 3b shows  $f_{J'}$  as a function of rotational energy levels for  $v' = 0$  in a histogram (bar) representation. Satisfactory fit was also obtained for the (0,0) band by using the same  $f_{J'}$  factors. Bands  $(v', 0)$  for  $v' = 1, 2, 3$  were also simulated to evaluate  $\bar{B}_{v'}$  and  $\bar{D}_{v'}$  constants as well as  $f_{J'}$  factors. Rotational constants ( $\bar{B}_{v'}$  and  $\bar{D}_{v'}$ ) are listed in Table 1 along with average internuclear distances,  $r_{v'}$  based on the rigid rotor approximation.

### 3.3. Interpretation of simulation results

Generally, observed irregularities in rotational line strengths in a  $(2 + 1)$  REMPI spectrum can be due to perturbations (i) in an intermediate state, that is

Table 1  
Rotational constants ( $\bar{B}_{v'}$  and  $\bar{D}_{v'}$ ) and internuclear distances ( $r_{v'}$ ) for the vibrational states ( $v'$ ) of the Rydberg state [ ${}^2\Pi_{3/2}$ ] $_c$ 5d;1g, obtained from simulation calculations

$(v', v'')$	$\bar{B}_{v'} (\text{cm}^{-1})$	$\bar{D}_{v'} (\text{cm}^{-1})$	$r_{v'} (\text{Å})$
(0,0)/(0,1)	$0.04041 \pm 0.0003$	$5.5 \times 10^{-9}$	$2.564 \pm 0.001$
(1,0)	$0.04028 \pm 0.0003$	$5.5 \times 10^{-9}$	$2.568 \pm 0.001$
(2,0)	$0.04016 \pm 0.0006$	$5.0 \times 10^{-9}$	$2.572 \pm 0.002$
(3,0)	$0.03947 \pm 0.0006$	$5.0 \times 10^{-9}$	$2.594 \pm 0.002$

reached with one photon, (ii) in the resonantly excited state at the two-photon level or (iii) in the ionization state, which is reached with three photons. Since irregularities in the rotational structure of the (0,1) and (0,0) bands (same  $v'$  state in the resonantly excited state) could be simulated by using the same  $f_{J'}$  factors the perturbation must be associated with the rotational energy level structure in the resonantly excited state at the two-photon level (i.e. case (ii) above). The perturbation effect is found to change as  $v' = 0 < v' = 1 < v' = 2 \sim v' = 3$ . Thus the sum of  $f_{J'}$  values for the same number of rotational levels,  $J'$  (hence similar rotational energy range)

$$F = \sum_{J'=0}^{J'_{\text{max}}} f_{J'} \quad (3)$$

is found to be about  $96.8 \pm 1.2$ ,  $90.6 \pm 2.0$ ,  $49.4 \pm 8.5$  and  $56.8 \pm 7.5$  for  $J'_{\text{max}} = 100$  for  $v' = 0, 1, 2$  and  $3$ , respectively. The rotational perturbation observed is due to an interaction between the Rydberg state and a close lying state. The  $J'$  level selectivity of the perturbation suggests that the perturbing state is a bound one, with discrete rotational energy levels. A continuum perturbing state would lead to continuous perturbation changes. According to perturbation theory introduction of an interaction term into the wave equation produces shifts of the zero-order energy levels as well as mixing of the zero-order wavefunctions for the two states involved [25,26]. The simulation analysis described above assumes no significant shift of lines. Within experimental uncertainties this corresponds to about  $\leq 0.4 \text{ cm}^{-1}$  shift of energy levels (on the two-photon wavenumber scale  $\bar{\nu}_{2h\nu}$ ). In the limit of two-level resonance interactions this would correspond to a value of  $\leq 0.4 \text{ cm}^{-1}$  for the matrix element of the perturbation function, which can be compared with that of  $H_{\text{Ry,ip}} \approx 25\text{--}42 \text{ cm}^{-1}$ ,

which has been suggested to be due to weak homogeneous interaction between the Rydberg state and the  $\beta(1g)$  ion-pair state [10]. The interaction of concern here, we believe is a still weaker, heterogeneous, one between the Rydberg state and the  $E(0_g^+)$  or the  $D'(2g)$  ion-pair state, which both belong to the lowest energy cluster of ion-pair states (see also discussion below).

The following qualitative analysis further supports the criterion that the perturbing state is ion-pair in nature and that the perturbation could be due to weak heterogeneous interaction. The three gerade ion-pair states which correlate with the ground state ion species have been analyzed to derive term values for high vibrational levels [27,28]. No rotational analy-

ses of these states are available in this region. The six ion-pair states which correlate with  $I^+(^3P_2) + I^-(^1S)$  are all spectroscopically similar, however [29]. Therefore rotational Dunham coefficients for the better characterized  $D(0_u^+)$  ion-pair state [30,31] along with information on the vibrational energy spacing for the gerade states were used to estimate the relative ion-pair rovibrational level energies close to that of the  $v' = 0-3$  rovibrational levels detected for the Rydberg state [ $^2\Pi_{3/2g}$ ] $_c 5d;1g$  ( $59800-60800\text{ cm}^{-1}$ ). Thus the following assumptions were made, (i) that the vibrational energy level spacing in the ion-pair state ( $d\bar{E}(v_{ip})/dv_{ip}$ ) drops from about  $22.5\text{ cm}^{-1}$  to about  $18.5\text{ cm}^{-1}$  with increasing vibrational quantum number ( $v_{ip}$ ) in this energy region,

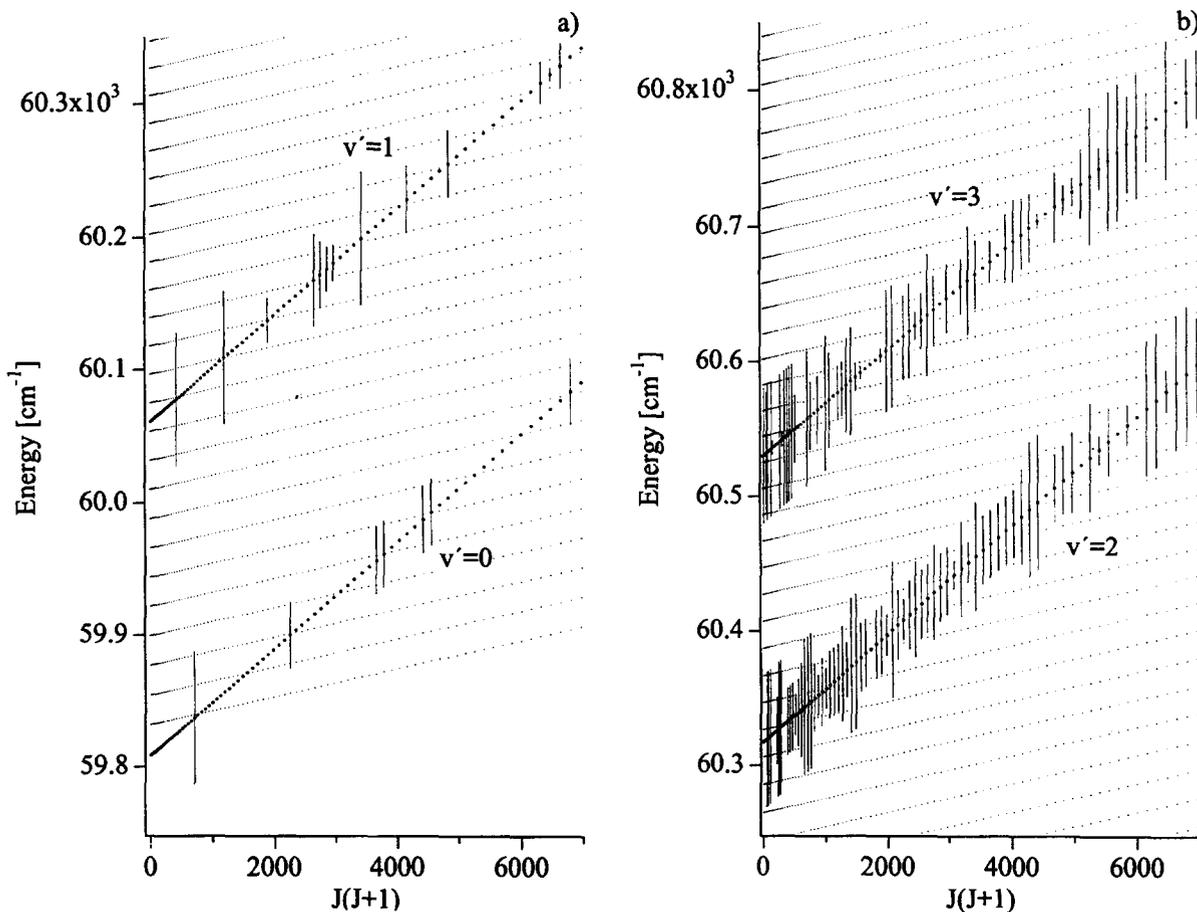


Fig. 4. Energies of rovibrational levels in the Rydberg state [ $^2\Pi_{3/2g}$ ] $_c 5d;1g$  (big dots) and in an ion-pair state (small dots) as a function of  $J(J+1)$  for vibrational quantum states  $v' = 0$  and  $1$  (a) and  $v' = 2$  and  $3$  (b) in the Rydberg state. Lengths of vertical lines are proportional to  $1 - f_J$ , and hence indicate relative strength of rotational perturbation (see text for further clarification).

(ii) that the second derivative ( $d^2\bar{E}(v_{ip})/dv_{ip}^2$ ) is near constant, about  $0.1 \text{ cm}^{-1}$  and (iii) that  $\bar{B}(v_{ip})$  is about  $0.01 \text{ cm}^{-1}$ . Slight variation in  $T_e$  (hence shift of rovibrational energy levels) for the ion-pair state was allowed for in accordance to the uncertainty in the term values for the ion-pair states [27,28]. Fig. 4 shows possible rovibrational energies of an ion-pair state plotted with energies for the Rydberg state levels as a function of  $J(J+1)$ . The  $J'$  dependent decrease in rotational line intensities (hence magnitude of coupling of  $J'$  levels with the ion-pair state) is shown by plotting vertical bars proportional to  $1-f_{J'}$ .  $T_e$  for the ion-pair state in Fig. 4a was adjusted in such a way as to minimize distance of

crossing points between the energy level curves for the two states where rotational perturbations were observed. It is noteworthy how many of the couplings (decreases in rotational lines) indeed seem to occur for  $J'$  levels close to crossings of the Rydberg and ion-pair energy curves for  $v'=0$  and 1 as plotted on Fig. 4a; i.e perturbations observed in the Rydberg states occur for  $(J',v')$  Rydberg levels with energies,  $\bar{E}(J',v')$  which satisfy

$$\bar{E}(J',v') = \bar{E}(J'_{ip},v'_{ip}); \text{ for } J' \approx J'_{ip}, \quad (4)$$

where  $E(J'_{ip},v'_{ip})$  is the energy of the rovibrational level  $(J'_{ip},v'_{ip})$  as plotted on Fig. 4a. This suggests

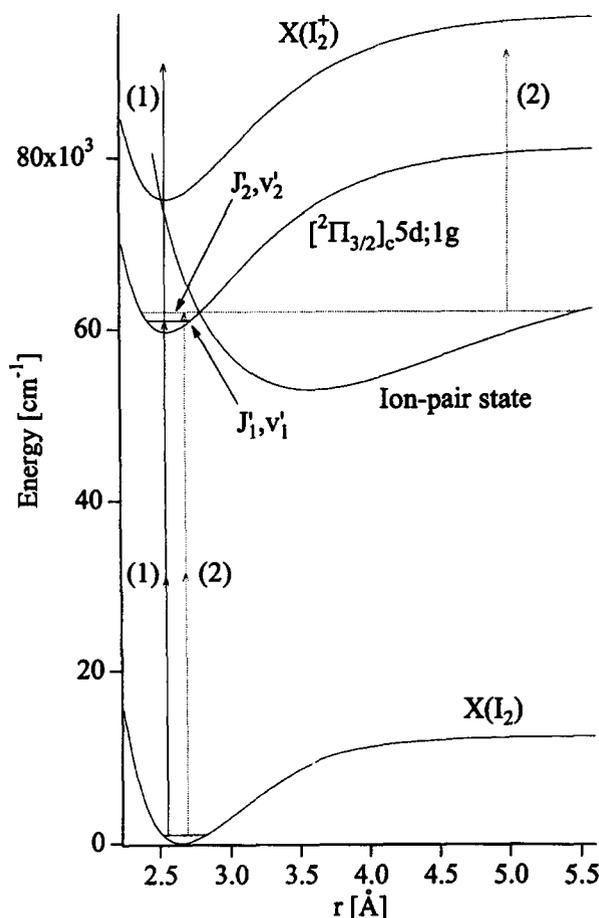


Fig. 5. Semi-schematic figure of potential energy curves showing (2 + 1) REMPI transitions for a nonperturbed (1) and a perturbed (by an ion-pair state) rovibrational level in the resonantly excited Rydberg state.

that near resonance rotational interaction between the Rydberg state and an ion-pair state for  $J' \approx J'_{ip}$  is indeed occurring. In the case of heterogeneous perturbation ( $\Delta\Omega = \pm 1$ )  $\Delta J = \pm 1$  is to be expected, while in the case of homogeneous perturbation ( $\Delta\Omega = 0$ ),  $\Delta J = 0$  will hold. For  $v' = 2$  and 3 on the other hand such a simple correlation is not found (Fig. 4b). Hence off resonance interaction must be involved for  $v' = 2$  and 3, and the limit of two-level interaction cannot be a valid assumption in these cases.

$\bar{B}'_e$  and  $\alpha'_e$  for the Rydberg state were evaluated from a plot of  $\bar{B}'_{v'}$  values versus  $v' + 1/2$  for  $v' = 0, 1, 2$ , to give  $\bar{B}'_e = 0.04047 \pm 0.00010 \text{ cm}^{-1}$  and  $\alpha'_e = (1.3 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$ .  $\bar{B}'_{v'=3}$  was ignored due to its abnormally low value.  $r'_e$  was then evaluated from  $\bar{B}'_e$  based on the rigid rotor approximation.  $r'_e = 2.562 \pm 0.003 \text{ \AA}$ .

Evaluation of band origins,  $\bar{\nu}_{2hv}^0$ , by comparison of calculated and experimental rotational contours was used before as a basis for evaluating  $T'_e$ ,  $\omega'_e$  and  $\omega_e x'_e$  for the Rydberg state [10]. Although improved rotational parameters were obtained by the analysis described here no changes in  $\bar{\nu}_{2hv}^0$  values, within experimental uncertainty, were observed. Values of  $T'_e = 59683.9 \pm 1.5 \text{ cm}^{-1}$ ,  $\omega'_e = 248.5 \pm 0.6 \text{ cm}^{-1}$  and  $\omega_e x'_e = 1.96 \pm 0.15 \text{ cm}^{-1}$  were obtained by least squares fit analyses. These values are in agreement with earlier results.

### 3.4. Discussion

Perturbation in the resonantly excited Rydberg state at the two-photon level due to an ion-pair state detected by (2 + 1) REMPI can be viewed in the following ways, with reference to Fig. 5 and Eqs. (1) and (2). Fig. 5 is a semi-schematic figure showing potential curves and transitions which may occur in the two cases where state interactions (1) *do not occur* and (2) *do occur*. The product of  $f_{J',v'}$  and  $C_{v',v''}$  in Eqs. (3) and (4) can be expressed as [2,9]

$$f_{J',v',v''} = KF(J',v';J'',v'')P'\sigma(J',v'), \quad (5)$$

where  $F(J',v';J'',v'')$  is the Franck–Condon factor for the transition  $J',v' \leftarrow J'',v''$ .  $\sigma(J',v')$  is a factor which accounts for possible variations in the efficiency of photoionization from the excited state.  $P$

is the laser power and  $n \leq 3$ , while  $K$  is an additional parameter dependent on the electronic structure of the molecule, geometric factors and sample concentrations. In the case of *no state interactions* (1),  $F(J',v';J'',v'')$  and  $\sigma(J',v')$  can be assumed to be independent of  $J'$  and  $J''$  as a first approximation ( $F(v';v'')$ ;  $\sigma(v')$ ), hence  $f_{J',v'}$  will be constant ( $f_{J',v'} = 1$ ). In the case of *state interaction* (2) on the other hand, both  $F(J',v';J'',v'')$  and  $\sigma(J',v')$  can vary with  $J'$ , depending on the strength and nature of the interaction.

The relative magnitude of the interaction strength between the Rydberg state and the ion-pair state as a function of  $v'$  is given by the  $F$  values evaluated from Eq. (3), which vary as  $v' = 0 < v' = 1 < v' = 2 \sim v' = 3$ . The relative magnitude of the perturbation effects between vibrational levels in the Rydberg state and vibrational levels in the ion-pair state will be determined by the vibrational contribution to the matrix element ( $H_{Ry,ip}$ ) of the perturbing function ( $H'$ ) hence the overlap between the vibrational wavefunctions. Thus the interaction strength will be determined by the distance between the outer turning points of vibrational levels in the Rydberg state and inner turning points of vibrational levels in the ion-pair state for energy levels with similar energies. The observed sequence of interaction strength suggests that the crossing of the interacting ion-pair state and the Rydberg state occurs between  $v'_{Ry} = 2$  and 3.

The three gerade ion-pair states which correlate with the ground state ions ( $D'(2g)$ ,  $\beta(1g)$  and  $E(0_g^+)$ ) [29], are all expected to cross the Rydberg state in this energy region [10]. The weak rotational coupling observed here differs from the homogeneous one due to interaction with  $\beta(1g)$  which is believed to cross the Rydberg state between  $v'_{Ry} = 3$  and 4 [10], hence only couplings due to interactions with  $D'(2g)$  and/or  $E(0_g^+)$  need to be considered here. The inner wall potential energies in the energy region of concern has been found to differ as  $E(D') < E(\beta) < E(E)$  [27,28], hence the most likely candidate for the heterogeneously interacting ion-pair state is the  $D'(2g)$  state. An effect of a heterogeneous coupling from the higher energy  $E(0_g^+)$  state could of course also be involved. The regularity in the correlation between interactions of rovibrational levels in a *single* ion-pair state and the Rydberg state and crossing of energy level curves, for  $v' = 0$  and  $v' = 1$ , as

presented in Fig. 4a, on the other hand, does not suggest that interaction from two ion-pair states is important for these vibrational levels. Simultaneous interaction effects of both the D' and E states on  $v' = 2$  and 3 cannot be ruled out on the other hand.

As described above, the simulation analyses involved insignificant shifts of energy levels. This is what one might expect for weak near resonance interactions, such as we believe is occurring for  $v' = 0$  and 1. For  $v' = 2$  and 3, on the other hand, the interactions are stronger and must involve multilevel off resonance interactions. The quality of the simulations for the (2,0) and (3,0) bands by this method are quite high. This makes us confident in the rotational line intensities and positions obtained this way. Hence the relative transition probabilities  $f_{J'}$  are well represented within experimental error. It could be that in cases of near resonance interactions (for  $v' = 2$  and 3), where the largest shifts are to be expected, lines are negligible in intensity due to relatively large mixing of states. On the other hand for weaker off resonance interactions, effects on rovibrational levels in the Rydberg state from higher energy levels in the ion-pair state could roughly equal those from lower energy levels, to cause negligible overall shift of levels.

Rotational perturbations such as are observed and interpreted here have not been seen before for iodine, nor for any other halogen or interhalogen molecules. Recently Gordon et al. published work on rotational perturbations observed in the (2 + 1) REMPI spectrum of HCl, which bears some resemblance to our observation [32]. Decrease in rotational line intensities, but negligible line shifts are observed in the (2 + 1) REMPI spectrum of the (0,0) band for the  $F(^1\Delta) \leftarrow X$  transition in HCl. These are interpreted as being due to coupling of the F state with a bound state, which then predissociates. A similar effect could hold for iodine. Also indirect predissociation of ion-pair states of iodine and other halogens and interhalogens, via coupling with Rydberg states, which then predissociate is a well known fact [33–35]. However, we favor the interpretation of two different ionization mechanisms depending on whether *no interaction* (1) or *interaction* (2) between the Rydberg state and an ion-pair state is involved as given above.

#### 4. Conclusions

Analyses of the rotational contours of the (2 + 1) REMPI spectrum for the  $[^2\Pi_{3/2}]_c 5d;1g$  Rydberg state of iodine have been performed. The structure of the rotational contours indicates that rotational perturbations, the magnitudes of which change with vibrational quantum numbers, are occurring. The spectra were simulated by assuming that the energies of the rotational levels involved can be formulated in the simple form  $E(J) = BJ(J + 1) - DJ^2(J + 1)^2$ , while deviations from the explicit forms of line strengths as determined by Bray and Hochstrasser [24] for  $\Delta\Omega = 1$  transitions needed to be assumed. The analysis allowed evaluations of rotational constants,  $B_{v'}$  and  $B_e$  as well as internuclear distance values,  $r_{v'}$  and  $r_e$  for the Rydberg state. Band origins were evaluated from comparison of experimental and calculated spectra based on the rotational parameters to derive the vibrational parameters,  $\omega'_e$  and  $\omega_e x'_e$  as well as  $T_e$  for the Rydberg state. The rotational perturbations are interpreted as being due to heterogeneous coupling between the Rydberg state and an ion-pair state of gerade symmetry, which belongs to the first cluster of ion-pair states which correlate with  $I^+(^3P_2) + I^-(^1S)$ . Arguments are presented suggesting that the perturbing state may be the D'(2g) state.

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