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Mass-resolved multiphoton ionization spectroscopy of jet-cooled Cl-2- .2. The (2+1) REMPI spectrum between 76000 and 90000 cm(-1)

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Mass-resolved multiphoton ionization spectroscopy of jet-cooled Cl_2.
II. The (2+1) REMPI spectrum between 76 000 and 90 000 cm^{-1}

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The (2+1) resonance-enhanced multiphoton ionization (REMPI) spectrum of Cl_2 has been recorded between 76 000 and 90 000 cm^{-1}. The origins of twenty Rydberg states are located, with the *s* series ($4s-8s$) generally exhibiting four Ω components and the *d* series ($3d-5d$) two components for each value of *n*. Vibronic coupling between the $\beta(1_g)$ ion-pair state and the $3d$ and $4d$ ($\Omega=1$) states is pronounced, necessitating the use of mass-resolved REMPI for the analysis of these vibronically mixed states. © *1996 American Institute of Physics.* [S0021-9606(96)01705-9]

I. INTRODUCTION

While extensive studies of the *ungerade* Rydberg states of Cl_2 have been undertaken, very little information on the *gerade* states is available. Some optically forbidden (single photon) $4s$ Rydberg states were seen in the threshold electron impact excitation of Cl_2 in the 2–14 eV region.[1] Later studies, using electron energy loss spectroscopy,[2,3] identified both the $4s$ $^1\Pi_g$ and the $5s$ $^1\Pi_g$ states. More recently (2+1) resonance enhanced multiphoton ionization (REMPI) spectroscopy has been used to study the $4s$ Rydberg region in more detail.[4,5] In particular, a surprisingly long progression, with $v'=0-15$, in the $[^2\Pi_{1/2}]_c4s$; 1_g state was observed. In the accompanying paper we have reinvestigated this region,[6] using a (1+1) double resonance, bound-free-bound, technique and conventional (2+1) REMPI spectroscopy and have accessed many of the triplet *gerade* ion-pair states. The vibrational spacings in all of the observed progressions are essentially regular, indicating that there are no strong interactions in the energy region up to 78 000 cm^{-1}. In the present paper we extend the (2+1) REMPI data up to 90 000 cm^{-1} and report the observation of many new *gerade* Rydberg states, together with some examples of stronger ion-pair/Rydberg interactions.

II. EXPERIMENT

The experimental arrangement is described in detail in Ref. 6. The frequency doubled output of the Coumarin dyes 307, 102, 47, and 120 covered the one-photon wavelength range 263–222.5 nm (i.e., equivalent to a two-photon energy range of 76 000–90 000 cm^{-1}). The spectra were recorded by collecting $^{35}Cl_2^+$, $^{35}Cl^{37}Cl^+$, $^{35}Cl^+$, and $^{37}Cl^+$, and normalized to the square of the laser power.

III. RESULTS AND DISCUSSION

The mass-resolved (2+1) REMPI spectra of jet-cooled $^{35}Cl_2$ between 79 600 and 89 900 cm^{-1} are shown in Figs. 1 and 2. These spectra were recorded using the $^{35}Cl_2^+$ mass channel which is the most intense in the mass spectrum observed for most Rydberg state resonances. By contrast, the molecular ions contribute <5% to the total ion signal for any of the resonances below 75 000 cm^{-1}. Power dependence

measurements on the Rydberg bands above 80 000 cm^{-1} show a quadratic behavior as expected for a coherent two-photon absorption *via* virtual intermediate states. Thus the spectra in Figs. 1 and 2 are normalized to the square of the laser power.

The spectra in Figs. 1 and 2 are dominated by Rydberg progressions whose band positions are listed in Table I. Individual progressions are readily identified from their vibrational spacings which are similar to those of the X $^2\Pi_g$ ionic ground state, to which the Rydberg series converge. The lowest energy band in each progression is assigned as the electronic origin and the vibrational numbering is confirmed by the observed shifts between the bands of the $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ isotopomers.

The assignment of the Rydberg states is based on the effective quantum number ($n-\delta$) which is calculated from the Rydberg equation,

$$T([\Omega_c]nl) = IP(\Omega_c) - R/[n-\delta(l)]^2,$$

where $T([\Omega_c]nl)$ is the term value of the electronic state origin, R is the Rydberg constant (109 737.1 cm^{-1}), δ is the quantum defect, and $IP(\Omega_c)$ is the ionization potential associated with the ion core to which the Rydberg series converge. The ($n-\delta$) values calculated using the ionization potentials corresponding with the $[^2\Pi_{3/2}]_g$ and $[^2\Pi_{1/2}]_g$ ionic cores of 92 616 and 93 366 cm^{-1}, respectively,[7] are presented in Table II. From the equivalent spectra of Br_2 and I_2 it was ascertained that the quantum defect (δ) of an electron in a particular Rydberg orbital is essentially the same irrespective of whether the ionic core is molecular or atomic.[8,9] Hence, the assignments are made from a comparison of the ($n-\delta$) values obtained in the present studies with those of atomic chlorine.[10] As the lowest Rydberg states must have a *gerade* core, the final Rydberg states in a two-photon transition from the ground state must be *s* or *d* in order to maintain the overall symmetry in the homonuclear case.

It can be seen from Table II that the spectrum is dominated by ns Rydberg series built on both $[^2\Pi_{3/2}]_g$ and $[^2\Pi_{1/2}]_g$ cores. Previously, it was shown that the Rydberg series observed in the equivalent Br_2 and I_2 spectra could be classified by considering the coupling of the spin of the Rydberg ns electron with the core angular momentum.[8,9] This
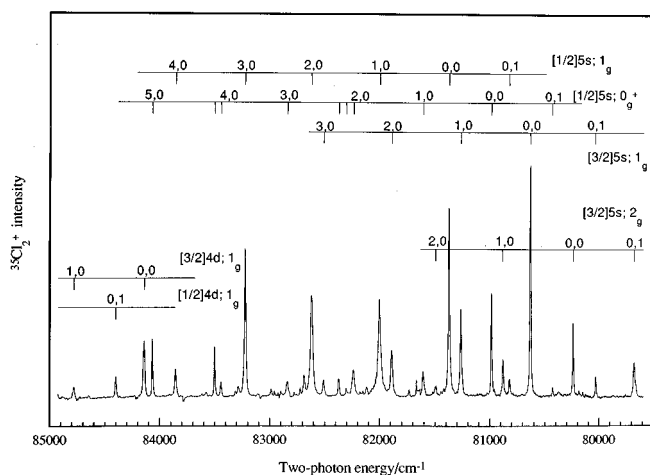
FIG. 1. The (2+1) REMPI spectrum of jet-cooled ^{35}Cl$_2$, recorded on the ^{35}Cl$_2^+$ mass channel between 79 600 and 84 800 cm^{-1}.

coupling gives rise to $[^2\Pi_{3/2}]_c ns$; 2_g, $[^2\Pi_{3/2}]_c ns$; 1_g, $[^2\Pi_{1/2}]_c ns$; 1_g, and $[^2\Pi_{1/2}]_c ns$; 0_g sub-states. In both Br$_2$ and I$_2$, transitions to all of these were observed where, apart from the lowest value of n, the 1_g states were 2–3 times more intense than their 2_g or 0_g partners and also occurred at higher energy (for the same core state). The same pattern is observed here in Cl$_2$ and the overall assignments are given in Table II.

A. The *ns* Rydberg states

In most respects the *ns* states with $n \geqslant 5$ are very regular. Firstly, the ω_e values for all states are 635 ± 5 cm^{-1} and most of the vibrational spacings decrease smoothly, within the accuracy of our measurements (± 2 cm^{-1}), as v' increases. Secondly, the ionic core spin–orbit splittings, as indicated by the $[^2\Pi_{3/2}]_c ns$; 1_g to $[^2\Pi_{1/2}]_c ns$; 1_g separations, range from 748 to 712 cm^{-1} for $n=5$–7: the measured splitting of the ground state of the molecular ion is 750 cm^{-1}.[7] Thirdly, the
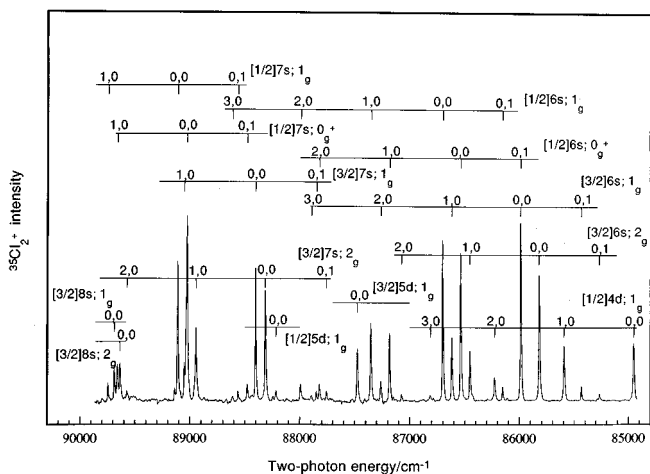

FIG. 2. The (2+1) REMPI spectrum of jet-cooled ^{35}Cl$_2$, recorded on the ^{35}Cl$_2^+$ mass channel between 84 800 and 89 900 cm^{-1}.

$[3/2]_c ns 2_g - 1_g$ and $[1/2]_c ns 0_g - 1_g$ splittings are the same, to within ± 5 cm^{-1}, and decrease smoothly from 387 to 52 cm^{-1} as n increases from 5 to 8. Finally, the vibrational envelopes of most progressions conform to the Franck–Condon factors expected for an unperturbed Rydberg state, in that transitions with $v'=0$–3 are the strongest. However, the $[1/2]_c 5s$ states both have unusual vibrational envelopes and will be discussed in more detail late.

B. The *nd* Rydberg states

In addition to the *ns* series, a few weaker *nd* series are also observed in Figs. 1 and 2. These *nd* states can be seen much more clearly in the spectra recorded in the ^{35}Cl$^+$ mass channel shown in Fig. 3. This is a consequence of the absolute intensities of all of the *nd* bands being greater in the spectrum recorded on the ^{35}Cl$^+$ channel compared with the ^{35}Cl$_2^+$ channel, while those of the *ns* bands are smaller. Furthermore, the (2,0) band of the $[^2\Pi_{1/2}]_c 4d$ progression shown in Fig. 3 is anomalously intense. An explanation for both of these observations will be given in Sec. III C.

Two $3d$ states, one based on each core, have also been observed (Fig. 4) and will be discussed in detail in Sec. III C. Both of these $3d$ states undergo a strong homogeneous interaction, most likely with the $\beta 1_g (^3P_2)$ ion-pair state, and are labeled accordingly as having 1_g symmetry. The quantum defects of the $4d$ and $5d$ states are consistent with those for the observed $3d$ states. However, there is no additional information with which to confirm the 1_g assignments and these must remain provisional.

C. Rydberg/ion-pair state interactions

The (2+1) REMPI spectrum between 71 000 and 77 000 cm^{-1} is dominated by a long vibrational progression in the $\beta(1_g)$ ion-pair state. In an accompanying paper[6] we report that over this range there are no significant perturbations in the band positions and that any interaction with the $4s$ Rydberg states must be very weak.

Evidence for much stronger interactions appears in the (2+1) REMPI spectrum of ^{35}Cl$_2$ between 76 000 and 80 000 cm^{-1}, recorded in the ^{35}Cl$^+$ mass channel and shown in the lower trace of Fig. 4. In this energy region the inner walls of the $^3P_2$ ion-pair states, including the $\beta(1_g)$ state, cross the $3d$ Rydberg states near to their potential minima. Previous work on I$_2$ and ICl has shown that such crossings can result in an enhancement of the intensities of the ion-pair bands and significant shifts in the positions of both ion-pair and Rydberg bands.[11,12] The same phenomena are observed here for Cl$_2$. Most of the ion-pair bands above $v'=135$ have enhanced intensity, but particularly $v'=138$, 151, and 162. Adjacent to each of these there is an additional strong band and these are assigned as $3d$ Rydberg bands. The ion-pair/Rydberg interaction is strong and so is presumably homogeneous, the Rydberg states having 1_g symmetry.

It was shown in the (2+1) REMPI spectrum of I$_2$ how mass resolution could aid an understanding of such interactions.[11] Ionization of all of the vibronic bands of I$_2$ produces I$^+$, while I$_2^+$ is only observed from vibronic bands

TABLE I. Vibronic assignments of the *gerade* Rydberg states of ^{35}Cl$_2$.

(v',v'')	(0,1)	(0,0)	(1,0)	(2,0)	(3,0)	(4,0)	(5,0)
$[\Omega_c]nl;\ (\Omega)$							
$[3/2]4s;^a$				64 290[b]	64 942[b]		66 233[b]
$[1/2]4s;\ (1_g)^a$	63 469[b]	64 026[b]	64 678	65 340	65 992[b]	66 637[b]	67 277[b]
$[3/2]3d;\ (1_g)$		75 922	76 627			78 570[b]	79 180[b]
$[1/2]3d;\ (1_g)$		76 781	77 474	78 201	78 839	78 483	
$[3/2]5s:\ (2_g)$	79 678	80 228	80 860	81 484			
$[3/2]5s;\ (1_g)$	80 044	80 610	81 248	81 875	82 497[b]		
$[1/2]5s;\ (0_g^+)$		80 966	81 600	82 220	82 840	83 448	84 058
$[1/2]5s;\ (1_g)$		81 358	81 980	82 608	83 232	83 850	84 483[b]
$[3/2]4d;\ (1_g)$		84 133	84 772				
$[1/2]4d;\ (1_g)$		84 941	85 590	86 228	86 832		
$[3/2]6s;\ (2_g)$	85 263	85 817	86 454	87 085			
$[3/2]6s;\ (1_g)$	85 431	85 986	86 623	87 254	87 888		
$[1/2]6s;\ (0_g^+)$		86 540	87 177	87 814			
$[1/2]6s;\ (1_g)$	86 151	86 706	87 342	87 974			
$[3/2]5d;\ (1_g)$		87 464	88 096[b]				
$[1/2]5d;\ (1_g)$		88 200	88 833[b]				
$[3/2]7s;\ (2_g)$	87 749	88 298	88 934	89 570			
$[3/2]7s;\ (1_g)$	87 840	88 387	89 025				
$[1/2]7s;\ (0_g^+)$	88 463	89 016	89 654				
$[1/2]7s;\ (1_g)$	88 548	89 099	89 740				
$[3/2]8s;\ (2_g)$	89 070	89 630					
$[3/2]8s;\ (1_g)$	89 128	89 682					

[a]From Ref. 6.
[b]Bands observed in the ^{35}Cl$^+$ spectrum only.

having a large Rydberg component. It was proposed that the general appearance of regions where Rydberg/ion-pair interactions are important can be understood in terms of three factors; the two-photon oscillator strength is usually carried by the Rydberg state, both states can have favourable Frank–

Condon factors and, ionization occurs most efficiently from the ion-pair state. Ionization of ion-pair states is believed to take place predominantly from their outer wall, and to go *via* unbound states generating mainly atomic ions.

The upper trace in Fig. 4 shows part of the $(2+1)$ REMPI spectrum of ^{35}Cl$_2$ recorded in the ^{35}Cl$_2^+$ mass channel. Two electronic state origins, confirmed by their isotopic shifts, are observed at 75 922 and 76 781 cm^{-1}. The splitting of ca. 800 cm^{-1} is close to that of the $[^2\Pi_{3/2}]_g$ and $[^2\Pi_{1/2}]_g$ ionic cores. The effective quantum number $(n-\delta)$ of the state origins is 2.56. The 3d Rydberg states of atomic chlo-

TABLE II. Assignments of the origins of the *gerade* Rydberg states of ^{35}Cl$_2$.

ν (cm^{-1})	n-δ [3/2] core	Assignment nl (Ω)	n-δ [1/2] core	Assignment nl (Ω)
62 970[a]	1.92	4s		
64 026			1.93	4$s(1_g)$
75 922	2.56	3$d(1_g)$		
76 781			2.57	3$d(1_g)$
80 228	2.98	5$s(2_g)$		
80 610	3.02	5$s(1_g)$		
80 966			2.97	5$s(0_g^+)$
81 358			3.02	5$s(1_g)$
84 133	3.59	4$d(1_g)$		
84 949			3.61	4$d(1_g)$
85 817	4.02	6$s(2_g)$		
85 986	4.07	6$s(1_g)$		
86 540			4.01	6$s(0_g^+)$
86 706			4.06	6$s(1_g)$
87 464	4.62	5$d(1_g)$		
88 200			4.61	5$d(1_g)$
88 298	5.04	7$s(2_g)$		
88 387	5.09	7$s(1_g)$		
89 016			5.02	7$s(0_g^+)$
89 099			5.07	7$s(1_g)$
89 630	6.06	8$s(2_g)$		
89 682	6.11	8$s(1_g)$		

[a]Estimated value (Ref. 6).
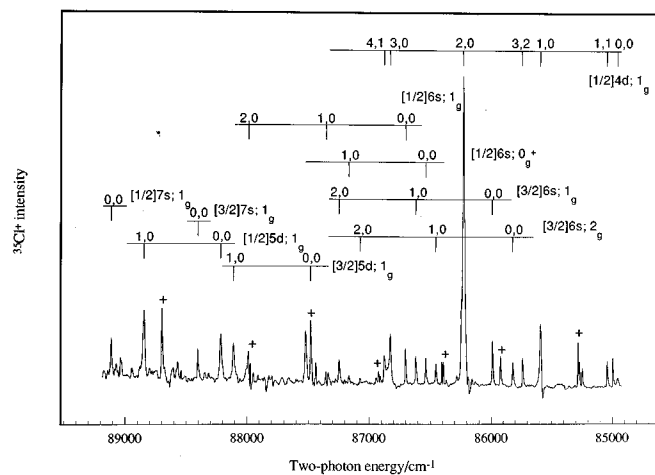
FIG. 3. The $(2+1)$ REMPI spectrum of jet-cooled ^{35}Cl$_2$, recorded on the ^{35}Cl$^+$ mass channel, between 84 800 and 89 300 cm^{-1}. +'s denote bands from HCl impurity.
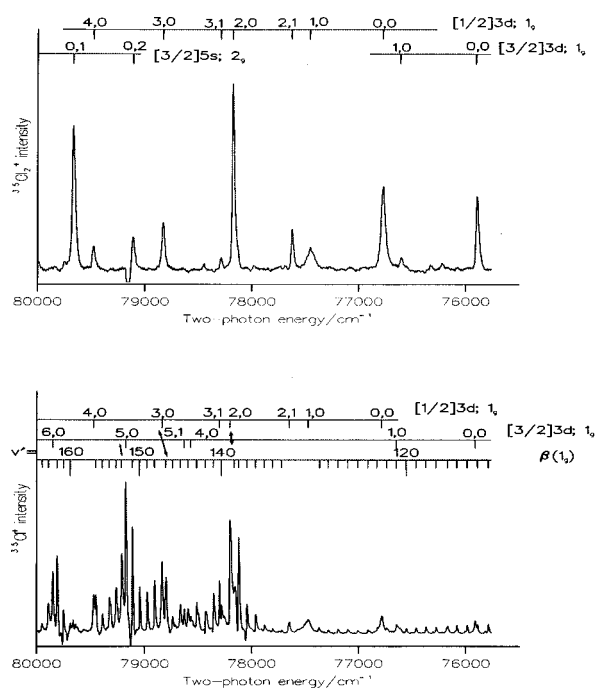
FIG. 4. The (2+1) REMPI spectrum of jet-cooled ^{35}Cl$_2$ between 75 800 and 80 000 cm^{-1}. The upper and lower traces were recorded on the ^{35}Cl$_2^+$ and ^{35}Cl$^+$ mass channels respectively. The arrows in the lower trace indicate regions of strong interaction.

rine have effective quantum numbers in the range 2.58–2.87 and the molecular states are labeled accordingly. The $[^2\Pi_{3/2}]_c$ and $[^2\Pi_{1/2}]_c$ state progressions extend up to (1,0) and (4,0) respectively. All of these bands are also seen in the ^{35}Cl$^+$ channel. The $[^2\Pi_{1/2}]_c 3d$; 1_g (2,0), (3,0) and (4,0) bands coincide with an enhancement in the intensities of the nearest ion-pair state bands. The Rydberg band and the ion-pair band to which it is coupled most strongly are denoted by arrows in Fig. 4. In each case the band labeled as the Rydberg band is that which is observed in the ^{35}Cl$_2^+$ spectrum. However, all nearby bands will be of mixed ion-pair/Rydberg character so it would be more realistic to describe the "Rydberg" band as being that which has the largest Rydberg component. Enhancement of the ion-pair state band intensities is also observed in three other regions of the spectrum. These regions coincide with the positions of the (4,0), (5,0), and (6,0) bands of the $[^2\Pi_{3/2}]_c 3d$; 1_g state progression, obtained from an extrapolation of the (0,0) and (1,0) bands. It is not known why ^{35}Cl$_2^+$ ions are not produced from the coupled vibronic bands in this progression. The positions and assignments of the bands observed in Fig. 4 are given in Table III. It can be seen from the spacings between adjacent bands, also listed in Table III, that the insertion of a Rydberg level into the ion-pair manifold generally compresses the levels on either side of it.

Reference to the potential energy curves throws further light on the ion-pair/Rydberg interactions observed in both the present and previous studies. The potentials of the most relevant *gerade* ion-pair and Rydberg states are illustrated in Fig. 5 of Ref. 6. An expansion of the curves in the interaction

region is shown in Fig. 5 of the present paper. The mainly singlet $[^2\Pi_{1/2}]_c 4s$; 1_g Rydberg state can be seen to cross the triplet $\beta(1_g)$ ion-pair state at 70 500 cm^{-1} corresponding to $v'_{\text{Ryd}} = 11$ and $v'_{\text{i.p.}} = 67$. The spacings in both progressions are regular throughout this region indicating that, as might be predicted from the singlet and triplet nature of the states involved, there is no significant interaction between the two states. However, such simple multiplicity considerations alone would predict an interaction between the $[^2\Pi_{3/2}]_c 4s$; 1_g Rydberg state and the $\beta(1_g)$ ion-pair state but no shifts in the ion-pair state vibrational levels are observed. This lack of interaction must be a result of the very different electronic configurations; the $\beta(1_g)$ state has a predominantly 2242 configuration which is not related to the $[2430]_c ns$ Rydberg state by a two-electron shift.

The crossings of the $\beta(1_g)$ state with the two triplet $3d$ states, near to $v'=4$ of the Rydberg states, which result in the strong interactions observed in Fig. 4, are illustrated in Fig. 5. Extrapolation of the inner wall of the $\beta(1_g)$ state potential indicates that it will cross the $4d$ Rydberg state potentials around $v'=2$. The very large intensity of the (2,0) band of the $[^2\Pi_{1/2}]_c 4d$; 1_g progression in the spectrum recorded in the ^{35}Cl$^+$ mass channel suggests a fairly strong coupling with the $\beta(1_g)$ state. While no great enhancement in the intensities of any of the individual members of the $[^2\Pi_{3/2}]_c 4d$; 1_g state progression are observed, as a whole this system appears much more strongly in the ^{35}Cl$^+$ spectrum, indicating mixing with the $\beta(1_g)$ ion-pair state. A similar picture occurs in both of the observed $5d$ Rydberg states where the (1,0) bands are only seen in the atomic ion spectrum.

A final example of Rydberg/ion-pair coupling can be seen from the $[^2\Pi_{1/2}]_c 5s$ state progressions. The (2,0) and (3,0) bands of the 1_g state and (5,0) band of the 0_g^+ state progressions have enhanced intensities in the ^{35}Cl$_2^+$ spectrum and are much more intense than their respective band origins in the ^{35}Cl$^+$ mass spectrum. Figure 5 illustrates that the 1_g state must also be coupling with the $\beta(1_g)$ ion-pair state. It is not known whether the $E0_g^+(^3P_2)$ or $f0_g^+(^3P_0)$ ion-pair states are coupled with the 0_g^+ Rydberg state, as their potential energy curves have not been determined in this region.

It can be seen from Fig. 5 that the $^3\Pi_g$ repulsive valence state could cross the inner wall of the $3d$ Rydberg states in the region of $v'=4$–6. It is believed that there are avoided crossings between these states resulting in a steepening of the bottom of the Rydberg potentials near their minima. The spacings of the vibrational levels supported by these potentials will then be greater than those of an unperturbed state and this is confirmed by the (1,0)−(0,0) separations of the $3d$ states of ca. 700 cm^{-1}, (c.f. 635 cm^{-1} for a typical unperturbed Rydberg state).

In the preceding paper,[6] we accounted for the absence of an interaction between the β state and the $4s$ $\Omega=1$ Rydberg states by pointing out that the preferred dominant configuration of the β state, $\sigma_g^2 \pi_u^2 \pi_g^4 \sigma_u^2$ (2242), cannot mix with the $([2430]ns)$ configuration of the Rydberg states by a simple two-electron shift. The same argument should apply to the d states based on the same $^2\Pi_\omega$ state of the core, but the first members of the progression, the $3d$ states, are observed to

TABLE III. Observed band positions in the (2+1) REMPI spectrum of $^{35}Cl_2$ between 75 000 and 80 100 cm^{-1}.

Vibrational assignment[a]	Band position (cm^{-1})	$\Delta\nu$[b] (cm^{-1})	Vibrational assignment	Band position (cm^{-1})	$\Delta\nu$ (cm^{-1})
110	75 580		$[1/2]_c 3d$ (2,0)	78 201	
111	75 684	104	$[1/2]_c 3d$ (3,1)	78 280	
112	75 782	98	140	78 300	146
113	75 881	99	141	78 357	57
$[3/2]_c 3d$ (0,0)	75 922		142	78 432	75
114	75 981	100	143	78 515	83
115	76 078	97	$[3/2]_c 3d$ (4,0)	78 570	
116	76 175	97	144	78 595	80
117	76 267	92	$[3/2]_c 3d$ (5,1)	78 628	
118	76 365	98	145	78 666	69
119	76 459	94	146	78 738	72
120	76 553	94	147	78 880	62
$[3/2]_c 3d$ (1,0)	76 627		$[1/2]_c 3d$ (3,0)	78 839	
121	76 646	93	148	78 907	107
122	76 737	91	149	78 979	72
$[1/2]_c 3d$ (0,0)	76 781		150	79 048	69
123	76 825	88	151	79 118	70
124	76 919	94	$[3/2]_c 3d$ (5,0)	79 180	
125	77 014	95	152	79 219	101
126	77 103	89	153	79 270	51
127	77 193	90	154	79 335	65
128	77 283	90	155	79 400	65
129	77 365	82	156	79 464	64
$[1/2]_c 3d$ (1,0)	77 474		$[1/2]_c 3d$ (4,0)	79 483	
$[1/2]_c 3d$ (2,1)	77 648		160	79 704	
133	77 712		161	79 768	64
134	77 798	86	162	79 826	58
135	77 875	77	$[3/2]_c 3d$ (6,0)	79 868	
136	77 959	84	163	79 905	77
137	78 039	80	164	79 968	63
138	78 118	79	165	80 034	66
139	78 154	36	166	80 102	68

[a] v' of the $\beta(1_g)$ state unless stated otherwise.
[b] $\Delta\nu$ for $(v',0) - [(v'-1),0]$.

interact with a first cluster ion-pair state. The T_e values of the nd series correspond to a nearly constant quantum defect of 0.44–0.39 with a characteristic slight decrease with n. Nevertheless, it may be that limited mixing with a $[^2\Pi_u]np$ Ry-
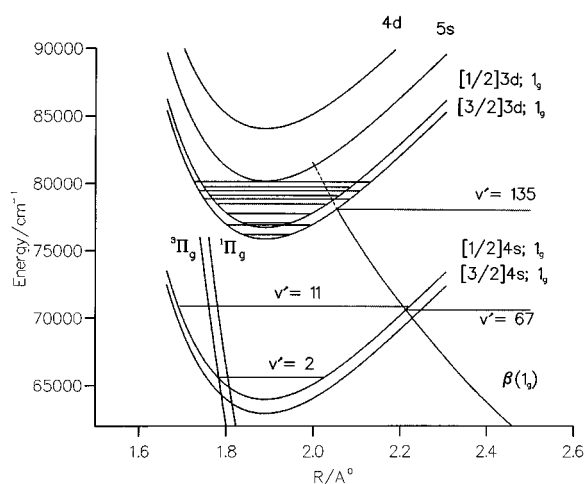

FIG. 5. An expansion of the potential energy curves in the region of interstate crossing.

dberg state (configuration $[2340]np$) is sufficient to give the coupling matrix element $\langle[^2\Pi_\omega 3d|H|\beta(1_g)\rangle$ the small value required without displacing the electronic T_e value by more than ≈ 200 cm^{-1}. This would correspond to a quantum defect change of ≤ 0.01, within the range exhibited by the d series.

Finally, the $D'(2_g)$ ion-pair state which has a 1432 configuration should couple strongly with the $[2430]nl$ Rydberg states. This leaves us with a possible alternative assignment for the interaction observed around 79 000 cm^{-1}, namely that all of the bands between 77 500 and 80 000 cm^{-1} (Fig. 4) have 2_g symmetry. The original assignment that they have 1_g symmetry is based on the positions of the ion-pair bands being consistent with being a continuation of the $\beta(1_g)$ state progression observed below 77 500 cm^{-1}. However, while the spacings in the $D'(2_g)$ are not known in this energy region they are not expected to be largely different from those of the $\beta(1_g)$ state and the 2_g assignment remains a possibility. A strong coupling has been observed between the $[^2\Pi_{3/2}]_c 5d$; 2_g Rydberg state and the $D'2_g(^3P_2)$ ion-pair state in the equivalent spectrum of I_2.[11] It should be emphasized that the $4d$ and $5d$ Rydberg states are assigned as 1_g states only on the assumption that they have the same Ω value as that of the observed $3d$ states. Thus, if the $3d$ states

really have $\Omega=2$, the $4d$ and $5d$ states may have to be reconsidered in this light.

IV. CONCLUSIONS

The spectra of the lower Rydberg states of Cl_2 presented here follows closely those of the other halogens. In particular, each $[^2\Pi_\omega]_c ns$ cluster exhibits the expected four Ω components 2, 1(2), and 0, but only two components of the generally weaker nd series can be detected. All series have very regular vibrational term values in spite of the numerous opportunities for perturbations from close-lying electronic states.

Somewhat unexpectedly, although consistent with the behavior of the other halogens, it is the d series that interact most strongly with the ion-pair states. From the current data, we cannot be sure if this is the $\beta(1_g)$ state or another ion-pair state in the first cluster [i.e., correlating with $Cl^+(^3P_2)$] because the potential wells of such closely related ion-pair states run parallel and have similar T_e values. We have tentatively labeled these d-states as the $\Omega=1$ components based on the two core states $\omega_c=1/2$ and $3/2$.

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