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2- and 3-photon excitation of components of the lower Rydberg states of iodomethane (CH_3I) using linearly and circularly polarized light, followed by ionization with one more photon, is used to determine their molecular term symbol, Ω, values as well as quantum defects. These Ω values, together with a detailed theoretical analysis, require a re-assignment of the $7s$ and $8s$ states to various components of the $5d$ and $6d$ states, but there is evidence of $(n+2)s/nd$ hybridization in the pairs of $\Omega = 1$ states. Predissociation sets in for all Rydberg states beyond $6d$ based on the ground ($^2\Pi_{3/2}$) state of the core, but sharp autoionizing resonances based on the $^2\Pi_{1/2}$ core state are assigned to the $9s$, $7d$, and $5f$ states. The dominant effect of the singlet/triplet character of the Rydberg states on their accessibility from the ground state, seen in bromomethane and chloromethane, is again apparent and a concordant interpretation of the Rydberg spectra of CH_3I can now be presented. Evidence for coupling of some $\Omega = 1$ and $\Omega = 0^+$ Rydberg states with a repulsive valence state and an ion-pair state, respectively, is also put forward. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4798972]

I. INTRODUCTION

The electronic spectra of the halomethanes have been widely investigated both in the lower energy valence region of continuous absorption and in the structured Rydberg region. The Rydberg states have been identified using 1-photon, VUV, absorption, (2+1) and (3+1) resonance enhanced multiphoton ionization (REMPI), and 2-photon autoionization (2P-AI) techniques.[1–14] However, iodomethane, both CH_3I and CD_3I, departs from the clear pattern set by bromomethane (CH_3Br) and chloromethane (CH_3Cl), for which various Rydberg series can be followed to ionization using REMPI, in that predissociation sets in relatively early making it harder to identify the Rydberg series without more experimental information than has hitherto been available.

Previous assignments for CH_3I have largely been based on quantum defects[1–5,14] and below we present new assignments based on 2- and 3-photon REMPI spectra obtained with linearly polarized (LP) and circularly polarized (CP) light to determine the electronic angular momentum state, Ω. In addition, we have recorded the highly structured 2P-AI spectrum above the first ionization limit, IE_1, again using LP and CP excitation, from which the relationship to the below-ionization (2+1) REMPI spectrum is established.

The Rydberg state peaks observed are assigned on the basis of their polarization behavior and by comparison with the equivalent spectra of CH_3Br.[9] In many cases this involves changing the assignments given in the most extensive previous ionization[3] and 2P-AI[14] studies in which polarization data were not recorded. The current analysis also involves several re-assignments of the 1-photon absorption spectrum.[4,5]

We also present evidence for coupling of the bound Rydberg states with a repulsive valence state and also the ion-pair (IP) state that correlates with $CH_3^+(X)+I^-(^1S_0)$. These couplings are discussed in the light of the most recent

ab initio study[15] and are compared with equivalent interactions in CH_3Br.[9,16]

II. CLASSIFICATION OF THE RYDBERG STATES OF THE HALOMETHANES

Different ways of labeling the Rydberg states of a C_{3v} molecule can lead to confusion. We will label the Rydberg states CH_3I using the same description as that used for the halogens, and which was described in full for CH_3Br in a previous paper.[9] Briefly, in the diatomic halogens, Ω, the component of total electronic angular momentum about the internuclear axis, **r**, is a good quantum number in Hund's cases a and c. Ω is the sum of the axial component of the electronic angular momentum of the ionic core Ω_c and that of the Rydberg electron ω_{Ryd}. ω_{Ryd}, in turn, is the sum of the axial component of the orbital angular momentum λ_{Ryd} and the spin $m_s = \pm 1/2$ of the Rydberg electron. Ω_c and ω_{Ryd} together provide a useful basis set for the description of the lower Rydberg states. In this basis there is some mixing between states based on different values of Ω_c but with the same Ω and λ_{Ryd} values that arises from electron exchange between the core and Rydberg orbitals. Thus, the labeling scheme adopted here for Rydberg states is $[\Omega_c]nl;\Omega$ where n is the principal quantum number of the Rydberg orbital.

The spin-orbit coupling of the ionic core yields $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states (using $C_{\infty v}$ notation) which will be abbreviated hereafter to [3/2] and [1/2], respectively. In the limit when Ω_c and ω_{Ryd} are good quantum numbers, the overall spin state is not necessarily defined. In the s series, only those states with $\Omega = 1$ are of mixed singlet/triplet character, those with $\Omega = 0^+$ and 2 being pure triplets. In the p series, six states with $\Omega = 0^+$, 1, and 2 have this mixed spin character, three on each of the two core states. Ten members of each nd-cluster

with $\Omega = 0^+$, 1(2), 2, and 3 have singlet character, five associated with each Ω_c. For instance, the two $\Omega = 1$ states in the d series based on $\Omega_c = 3/2$ are $[1^+1^-\underline{1}^+]_c\, 0^-_{\text{Ryd}}$ and $[1^-\underline{1}^+1^-]_c\, 2^+_{\text{Ryd}}$ where 1_c and $\underline{1}_c$ are the m_l states of the core lone pair $5p$ orbitals, 0^-_{Ryd} denotes the d_σ orbital with $m_l = 0$, in 2^+_{Ryd} the Rydberg electron is in the d_δ orbital with $m_l = 2$, and $\pm$ denotes the electron spin $m_s = \pm 1/2$. Subsequently, states having this mixed spin character will be described as "singlet" states and all others as "triplet" states. An example of the latter, of which there are also 5 on each core in the d series, again with $\Omega = 1$, would be $[1^+1^-\underline{1}^+]_c\, 1^+_{\text{Ryd}}$, where 1_{Ryd} could be a p_π or d_π orbital. The singlet states are the only ones that, neglecting spin-orbit coupling in the Rydberg orbital, are strongly accessible from the purely singlet ground state and in 2-photon excitation $\Delta\Omega \leq 2$ making four nd states accessible on each core.

The binding energies, $E_{n,l} = \text{IE}(\Omega_c) - T_{n,l}$, of a Rydberg series converging on the state Ω_c of the ion core for which the ionization energy is $\text{IE}(\Omega_c)$, where $T_{n,l}$ are transition energies, are given to a good approximation by the formula

$$E_{n,l} = R/(n^*)^2 \tag{1}$$

where $n^* = n - \delta_l$ and δ_l is the quantum defect for the l series. Values of 76 934 and 81 983 cm^{-1} are used for IE_1 and IE_2.[17]

The Ω value of a state can be unambiguously determined from a comparison of 2-photon and 3-photon polarization data. Any peak in the 2- or 3-photon spectrum whose intensity in the spectrum recorded with CP light, I_{CP}, is significantly less than in the spectrum recorded with LP light, I_{LP}, will be described as "$\mathcal{P}_-$". Any $\mathcal{P}_-$ band in the 2-photon spectrum can be unambiguously identified as being that of an $\Omega = 0^+$ state. Polarization cannot distinguish between $\Omega = 1$ and $\Omega = 2$ states in 2-photon spectra where $I_{\text{CP}}/I_{\text{LP}} = 3/2$, a "$\mathcal{P}_+$" band. Similarly, any peak in the 3-photon spectrum whose $I_{\text{CP}}/I_{\text{LP}} = 5/2$ can be identified as being that of an $\Omega = 2$ (or 3) state. Finally, a band that is $\mathcal{P}_+$ in the 2-photon spectrum and is $\mathcal{P}_-$ in the 3-photon spectrum can be identified as being due to an $\Omega = 1$ state. Only transitions to $\Omega = 0^+$ and $\Omega = 1$ states are allowed in the 1-photon absorption spectrum and this fact will be used to provide further confirmation of the assignments.

III. EXPERIMENTAL

The molecular beam was generated by passing mixtures of 15–100 Torr of CH_3I and $\sim$400 Torr of helium through a pulsed nozzle (General Valve, Iota One) with a 250 μm diameter aperture, into the ionization region of a linear time-of-flight mass spectrometer. Ions were collected at 90° to both the molecular and laser beams. Mass-resolved ion signals were processed by a Stanford Research SR250 boxcar integrator and stored on a PC.

The radiation, provided by a Lambda Physik FL3002 dye laser pumped by a Lambda Physik EMG201MSC XeCl excimer laser, was focused by a 6 cm focal length lens into the interaction region with the molecular beam. The (2+1) REMPI and 2-P AI spectra were recorded using the fundamental of the dye PTP and the frequency-doubled outputs

of the dyes R101, RB, R6G, C153, and C307. The (3+1) REMPI spectra were recorded using the fundamentals of the dyes C307, C47, and S3. Circular polarization was achieved by passing the linearly polarized laser beam through a Soleil Babinet prism. None of the spectra have been power normalized.

The laser wavelengths were calibrated to an accuracy of ± 2 cm^{-1} using Ne optogalvanic lines. However, the uncertainties attached to the transition energies (band maxima) presented in Table I vary with the width of the bands and are $\leq \pm 10$ cm^{-1}. In addition, the rotational contour of a particular band in the 2-photon spectrum can be significantly different from that of the same band in the 3-photon spectrum and hence the positions of the observed maxima may also differ slightly.

IV. RESULTS

A. The (2+1) and (3+1) REMPI spectra

1. Assignments

The (2+1) and (3+1) REMPI spectra of CH_3I up to 74 000 cm^{-1} were reported in a previous paper.[3] We have re-recorded these spectra by simultaneously collecting two of the three ions, CH_3I^+, CH_3^+, or I^+; the choice of ions collected varied from region to region. The ions were chosen to ensure that there were no signals due to resonances in the fragments. This was possible in every case with one exception that will be highlighted in the text. The two ion signals were then added to improve the signal-to-noise. We could not identify any bands above 72 000 cm^{-1}, although two extremely weak bands at slightly higher energy had been reported previously.[3] The loss of signal between this energy and IE_1 had been attributed to either the lifetimes of the Rydberg states being too short for efficient ionization or to the influence of an unbound valence state(s) at the intermediate level(s). We will discuss these factors in Sec. V below. The spectra are shown in Figs. 1–3.

In a previous paper[9] we assigned the bands observed in the 2-photon spectrum of CH_3Br, by analogy with the equivalent spectrum of Br_2.[18] The CH_3Br spectrum is surprisingly simple in that it is dominated by transitions to $[3/2]nd;2,0^+$ and $[1/2]nd;2,0^+$ Rydberg series with $nd \leq 17$ and 6, respectively. Transitions to one $np;0^+$ series based on both ionic cores with $n \leq 10$ were also observed.[9] The only ns states observed were the $[3/2, 1/2]5s$ states. The low-energy region of the CH_3I spectrum is entirely analogous to that of CH_3Br but the nd series are only seen with $n \leq 8$. This analysis involves the re-assignment of all the bands previously assigned as ns state bands,[3] with the exception of those of the $6s$ states, to nd states with $\Omega = 2$ or 0^+. The assignments of the np states remain unchanged.

The 2-photon spectrum of CH_3I shown in Fig. 3 serves as an illustration of the current re-assignments. For example, the band at 70 210 cm^{-1} was previously assigned[3] as the $8s[2]$ band, $[3/2]8s;1$ in our nomenclature. However, it is clearly a $\mathcal{P}_-$ band, i.e., has $\Omega = 0^+$, but there are no $[3/2]8s$ states with this symmetry, only one with $\Omega = 2$ and one with $\Omega = 1$. Similarly, the band at 69 540 cm^{-1}, previously

TABLE I. Transition energies, T, effective quantum numbers, n^*, and assignments of the Rydberg states converging on the $^2\Pi_{3/2}$, [3/2], and $^2\Pi_{1/2}$, [1/2], states of the ion observed in the 1-, 2-, and 3-photon excitation spectra of CH_3I.

$nl;\Omega$	n^*	T (1-photon)/cm^{-1}	Previous assignment[a]	Previous assignment[b]	T (2-photon)/cm^{-1}	T (3-photon)/cm^{-1}
			[3/2]			
6s;1	2.01	49 724[a]	[3/2]6s	[3/2]6s;1	49 734	49 746[c]
6p;0⁺/1[d]	2.41	58 052[a]	Unassigned	Not reported		58 045
2	2.43				58 333	58 338
0⁺	2.47	58 927[a]	[3/2]6p	[3/2]6p;1	58 927	58 927
1	2.51	59 555[a]	Unassigned	[3/2]6p;0⁺	59 554	59 554
5d;0⁺[d]	2.60	60 673[a]	Unassigned	Not reported	60 682	
1[d]	2.71	61 996[a]	Unassigned	Not reported		
1	2.81	63 072[a]	[3/2]5d	[3/2]5d;1	63 036	
2	2.94				64 194	64 204
1	2.97	64 492[a]	[1/2]6p	[1/2]6p;0⁺		64 497
0⁺	2.99	64 701[a]	[3/2]7s	[3/2]7s;1	64 679	64 679
7s;1	3.13	65 697[a]	Vibrational band	Not reported		65 717
7p;2	3.47				67 800	
0⁺	3.48	67 984[a]	[3/2]7p	[3/2]7p;0⁺		
1	3.50				67 924	
6d;1	3.85	69 444[a]	[3/2]6d	[3/2]6d;1	69 451	
2	4.00				70 071	
0⁺	4.04	70 251[a]	[3/2]8s	[1/2]5d;0⁺	70 210	
7d;2/0⁺	5.06	72 646[a]	[3/2]9s	[3/2]7d;0⁺	72 644[c]	
8d;2/0⁺	6.07	73 956[a]	[3/2]10s	[3/2]8d;0⁺	73 954[c]	
			[1/2]			
6s;0⁺[d]	1.98				54 055	54 062
1	2.00	54 660[a]	[1/2]6s	[1/2]6s;1	54 654	54 656
6p;0⁺/1[d]	2.43	63 391[a]	Unassigned	Not reported		
2	2.44				63 493	63 502
0⁺	2.52	64 701[a]	[3/2]7s	[3/2]7s;1	64 679	64 679
1	2.59	65 568[a]	Vibrational band	[3/2]5d;0⁺		65 585
5d;1	2.79	67 871[b]	Not reported	[3/2]7p;1	67 871	
2	2.91				69 044	
1	2.93				69 172	
0⁺	2.97	69 517[b]	Not reported	[3/2]6d;1	69 540	
7d;1	4.80	77 228[b]	Not reported	[1/2]7d;1	77 232	
2+1	4.99	77 582[b]	Not reported	[1/2]9s;1	77 579	
0⁺	5.04	77 689[b]	[1/2]9s	[1/2]7d;0⁺	77 670	
5f;1	4.92	77 458[b]	Not reported	[1/2]5f;0⁺/1	77 445	
2+1	5.01	77 582[b]	Not reported	[1/2]9s;1	77 611	
0⁺	5.04	77 689[b]	Not reported	[1/2]7d;0⁺	77 670	
9s;1	5.16		Not reported	Not reported	77 863	

Effective quantum numbers are calculated from values of IE_1 and IE_2 of 76 934 and 81 983 cm^{-1}, respectively.[15]

[a]Reference 4.

[b]Reference 5.

[c]Reference 3.

[d]Triplet state.

assigned as the 7s[4] band, [1/2]7s;1 in our nomenclature, also has $\Omega = 0^+$. While there is a [1/2]7s state with $\Omega = 0^+$, this lies below the [1/2]7s;1 state and would be labeled 7s[3]. Thus, the observed polarization behavior of the two bands at 69 540 and 70 210 cm^{-1}, in which their intensities decrease in the CP spectrum, is the reverse of that expected from previous assignments. Thus, we can unambiguously say that these two bands are due to $\Omega = 0^+$ states and, by analogy with CH_3Br, are assigned to [1/2]5d;0⁺ and [3/2]6d;0⁺ states, respectively. Again, by analogy with CH_3Br, the origins at 69 042 and 70 071 cm^{-1} are assigned to [1/2]5d;2 and [3/2]6d;2 states, respectively, although on the grounds

of n^* values alone, the bands at 70 071 and 70 210 cm^{-1} can equally well be assigned as [3/2]4f;2 and 0⁺ states, respectively. The intense peak at 69 853 cm^{-1} and the four sharp, weak lines to higher and lower energy in Fig. 3 are due to the $4p^2 A''_2 \leftarrow X^2 A''_2$ transition in CH_3.[19] No Rydberg state origins were observed in the 3-photon spectrum in this region.

In the 3-photon spectrum of CH_3Br, strong transitions to $\Omega = 1$ states were observed as well as to the $\Omega = 2$ and 0⁺ states observed in the 2-photon spectrum.[9] The same picture emerges from the 3-photon spectra of CH_3I shown in Figs. 1 and 2; a typical example, the [3/2]6p region, is shown
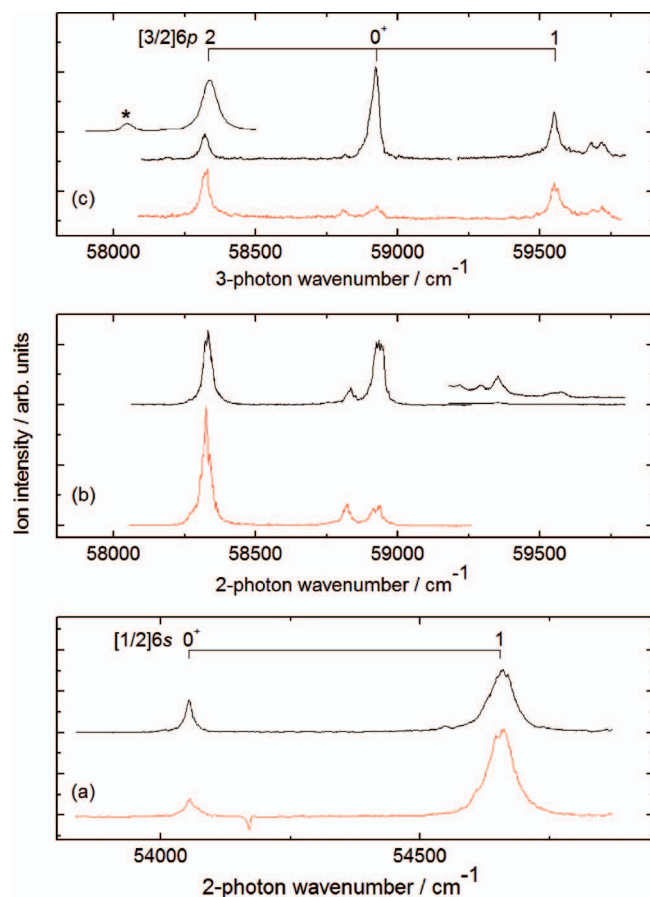
FIG. 1. REMPI spectra of CH_3I; (2+1) in the range 53 800–54 800 cm^{-1}, (a), and (2+1), (b), and (3+1), (c), in the range 58 000–59 800 cm^{-1}. The spectra recorded with CP and LP light are shown in the lower and upper traces, respectively. The labels above the ladders show the Ω value of the Rydberg states. The * in (c) indicates the origin of a triplet [3/2]6p;0$^+$ or 1 state.

FIG. 2. The (2+1), (a), and (3+1), (b), REMPI spectra of CH_3I in the range 62 500–66 000 cm^{-1}. See also caption to Fig. 1.

in Fig. 1(c). The $\Omega = 2$ and 0$^+$ states are observed as strong bands at 58 333 and 58 926 cm^{-1} in the both the 2- and 3-photon spectrum. An additional strong $\mathcal{P}_-$ band at 59 527 cm^{-1} is observed in the 3-photon spectrum and is assigned as the singlet [3/2]6p;1 state; it is only observed as a very weak band in the 2-photon spectrum. The 58 926 and 59 527 cm^{-1} bands are also observed in the 1-photon absorption spectrum,[4,5] in which only transitions to $\Omega = 0^+$ and 1 are allowed, whereas the 58 333 cm^{-1} band is not. These observations support the assignments of the bands to $\Omega = 0^+$, 1, and 2 states, respectively.

Assignments for most of the bands observed in the 2- and 3-photon spectra of CH_3I have been derived using the criteria outlined above and are presented in Table I. Previously, Dobber *et al.*[3] presented photoelectron spectra (PES) following multiphoton excitation of many of the Rydberg states. All of the assignments presented here are consistent with the PES and in the cases of a strong 3-photon band at 65 736 cm^{-1} and two weak 2-photon bands at 60 682 and 63 074 cm^{-1} offer explanations for anomalies that the authors highlighted.

Table I also includes the transition energies of bands observed in the 1-photon absorption spectrum, together with their previous assignments.[4,5] In many cases the present assignments involve changes to the ionic core, nl and, where

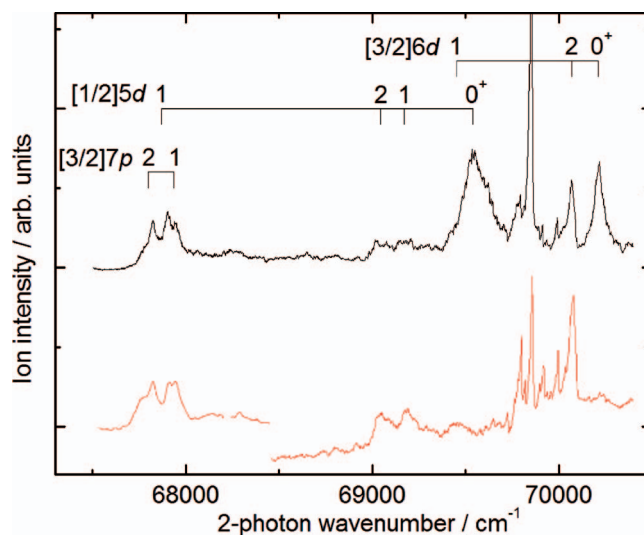FIG. 3. The (2+1) REMPI spectrum of CH_3I in the range 67 500–70 400 cm^{-1}. See also caption to Fig. 1. The intense peak at 69 853 cm^{-1} and the four sharp, weak lines to higher and lower energy are due to the $4p^2 A''_2 \leftarrow X^2 A''_2$ transition in CH_3.[19]

specified, Ω values of the Rydberg state origins. In addition, we assign some previously unassigned or vibrational bands to Rydberg state origins. As examples we will consider the [3/2]6p and [1/2]6p/[3/2]5d regions in more detail.

The origins at 58 333, 58 926, and 59 527 cm^{-1} are unambiguously assigned to the singlet [3/2]6p;2, 0$^+$ and 1 states, respectively. The assignments for the last two reverse those of Locht *et al.*[5] who assigned the 58 926 cm^{-1} band to the a_1 ($\equiv p_\sigma$) Rydberg component, using C$_{3v}$ symmetry, of the [3/2]6p cluster which is equivalent to an $\Omega = 1$ state in our description and the 59 527 cm^{-1} band to the e ($\equiv p_\pi$) component, $\Omega = 0^+$ or 2 in our description. The same reversal of the previous assignments[8] applies for the $\Omega = 0^+$ and 1 components of the [3/2]5p and [1/2]5p states of CH$_3$Br and brings them into agreement with the *ab initio* predictions of Escure *et al.*[16]

Eden *et al.*[4] highlighted several weak bands in the 1-photon absorption spectrum that they could not assign and we tentatively attribute some of these to triplet states. For example, we assign the band at 58 052 cm^{-1} which lies amongst the vibrational structure of the [1/2]6s;1 state to the triplet $\Omega = 0^+$ or 1 component of the [3/2]5p cluster. A very weak $\mathcal{P}_-$ band is seen at this energy in the 3-photon spectrum and is indicated by a star in the upper trace of Fig. 1(c). The other $\Omega = 0^+$ or 1 component of the [3/2]5p cluster may well be one of the other peaks assigned to vibrational structure in the 1-photon spectrum. We have not observed any peak in the 2- or 3-photon spectra that can be assigned to the triplet $\Omega = 2$ component.

The [1/2]6p and [3/2]5d bands overlap as shown in Fig. 2. There is only one $\mathcal{P}_-$ band in the 2-photon spectrum in this region and this is assigned to the unresolved [1/2]6p;0$^+$ and [3/2]5d;0$^+$ components. The assignment is supported by the PES observed when exciting this band in which the origins of both the [3/2] and [1/2] ionic cores are observed in the approximate ratio of 5:1.[3] The remaining bands in the REMPI spectra are assigned on the basis of their polarization behavior and n^* values as outlined above. In addition to these singlet states, we tentatively assign two weak bands observed by Eden *et al.*[4] at 60 673 and 61 996 cm^{-1} in the 1-photon spectrum as triplet [3/2]5d;0$^+$ and 1 states, respectively, with the Ω value of the former being confirmed by its 2-photon polarization behavior.

2. Intensities

The relative intensities of the $\Omega = 0^+$, 1 and 2 state bands in the 2-photon spectrum vary with energy. In the range 58 000–67 000 cm^{-1} the $\Omega = 1$ state bands are vanishingly small; in the range 67 000–70 500 cm^{-1} some $\Omega = 1$ bands are observed while the $\Omega = 0^+$ bands are either missing, [3/2]7p;0$^+$, or very broad, [1/2]5d;0$^+$; no bands are observed above 70 500 cm^{-1}.

In addition, the band at 64 679 cm^{-1} in the 2-photon spectrum exhibits a power dependency that is very different from those nearby as illustrated in Fig. 4. Three bands are observed in the spectrum at 64 194, 64 679, and 64 724 cm^{-1} and these are assigned as [3/2]5d;2, [3/2]5d;0$^+$/[1/2]6p;0$^+$, and
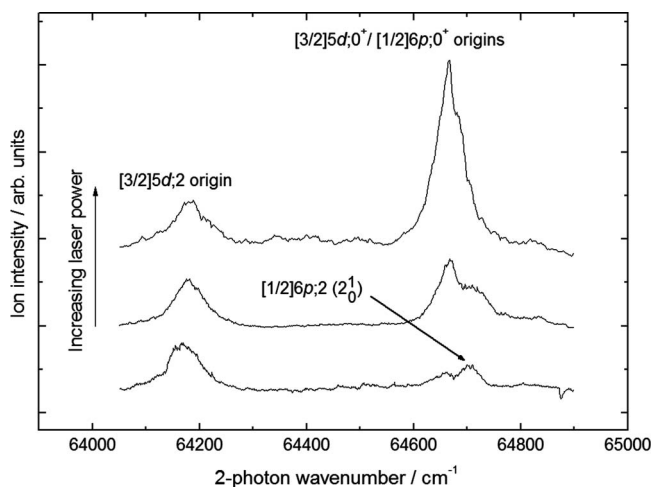

FIG. 4. Part of the (2+1) REMPI spectrum of CH$_3$I recorded with three different laser powers. The spectra are normalized to the intensity of the band at 64 194 cm^{-1}.

[1/2]6p;2(2$_0^1$) bands, respectively. The intensity of the overlapping $\Omega = 0^+$ states relative to those of the two $\Omega = 2$ states (ν_2 is a totally symmetric vibration) decreases as the power is reduced (by a factor of ∼10 between the top and bottom traces of Fig. 4). In Sec. V below we will attribute these intensity variations to coupling of the Rydberg states with other electronic states.

B. The 2P-AI spectra

The 2P-AI spectrum in the energy region between the two spin-orbit states of the ion is shown in Fig. 5(a). The spectrum was recorded by collecting both CH$_3$I$^+$ and CH$_3^+$ (the latter formed from photofragmentation of the molecular ion) with CH$_3^+$ ion giving the cleanest spectrum. The electric field lowered IE$_1$ is clearly observed around 76 740 cm^{-1}. Extensive structure, assignable to Rydberg series converging on IE$_2$, superimposed on a background continuum is observed to higher energy. The same structure was observed in two previous studies but no polarization data were reported.[13, 14]

An enlargement of the low energy region of the 2P-AI spectrum, in which the 9s, 7d, and 5f Rydberg states lie, is shown in Fig. 5(b); the upper and lower traces show the spectra recorded with LP and CP light, respectively. By extrapolation of the (2+1) REMPI spectrum, the 7d;2 and 7d;0$^+$ bands should be observed. As $\Omega = 2$ and 0$^+$ state bands are generally observed with the greatest intensity in the (2+1) REMPI spectra, we would also expect to see a peak due to each of the lone singlet 5f;2 and 5f;0$^+$ states. There is only one $\mathcal{P}_-$ band observed at 77 670 cm^{-1} and this is assigned to overlapping 7d;0$^+$ and 5f;0$^+$ bands; this coincides with a strong absorption peak in the 1-photon absorption spectrum.[4, 5] The remaining AI bands all show $\mathcal{P}_+$ behavior, i.e., are due to $\Omega = 1$ or 2 states. The two peaks at 77 232 and 77 447 cm^{-1} coincide with strong absorption peaks in the 1-photon absorption spectrum[4, 5] and hence are assigned to $\Omega = 1$ states. By default, the remaining two $\mathcal{P}_+$ AI bands at 77 570 and 77 611 cm^{-1} are assigned to $\Omega = 2$ states. The assignments are presented in Table I.
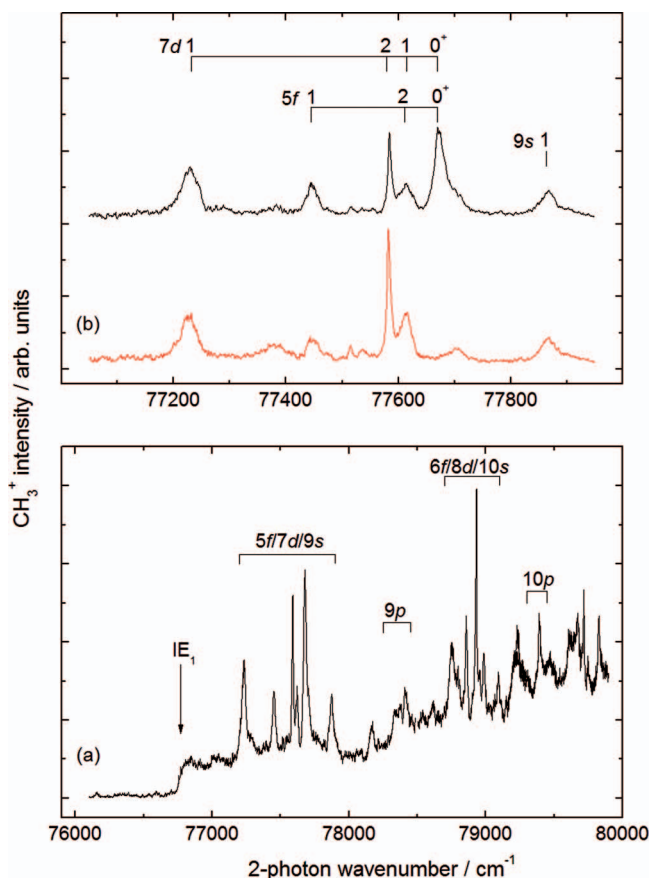
FIG. 5. The 2P-AI spectrum of CH_3I; overview, (a) and the low energy region, (b). See also caption to Fig. 1.

V. DISCUSSION

A. The number of Rydberg states observed in each manifold

The four strong $5d$ components based on each of the two core states in Table I have the Ω values corresponding to the four components with $\Omega \leq 2$ of mixed singlet/triplet character as opposed to pure triplet character, as do the three members of the two $6p$ manifolds. Looking more closely, it is seen that one of the $5d;1$ components is appreciably lowered in energy, the $7s;1$ (again the component with singlet character) is somewhat higher in energy than expected judged from the quantum defect in the $6s;1$ state. First order interaction with

the core is partly responsible for the splitting of the Ω components of d manifold, but we note that the nd and $(n+2)s$ levels for $n > 4$ are very close in energy, with the s states slightly higher. Under these conditions hybridization (a second order effect) takes place allowing the atomic orbitals to adapt to the shape of the core (mixing with the p manifold is less pronounced because of the half-integral values of n^* in the np series). Thus, the unperturbed difference in energy between the $5d$ and $7s$ states, with predicted $n^* \sim 2.95$ and 3.03, respectively, is ~ 700 cm^{-1} and considerable mixing of components with a common Ω value can be expected. More specifically, this mixing will only occur between Rydberg orbitals with the same value of λ_{Ryd}. The two $5d;1$ states have $\lambda_{Ryd} = 0$ and 2, and it is the former that will be lowered in energy with a corresponding raising of the $7s;1$ level. The same situation arises in CH_3Br where the $4d$ and $6s$ states are nearly isoenergetic and two $\Omega = 1$ components mix.[9]

B. Interactions of the Rydberg states with valence and ion-pair states

The present studies indicate that in the $(2+1)$ REMPI spectra of CH_3I peaks due to $\Omega = 1$ Rydberg states are much weaker than those due to $\Omega = 0^+$ and 2 states in the range 58 000–67 000 cm^{-1}, whereas in the $(3+1)$ REMPI spectra they are of comparable intensity. In a previous paper[9] we showed that the same was true in the equivalent spectrum of CH_3Br and offered two possible explanations. First, it was proposed that if the $\Omega = 1$ states are selectively predissociated, they will be more difficult to ionize with low-power frequency-doubled dye laser photons that are used to record the $(2+1)$ REMPI spectra than with high-power fundamental dye laser photons that are used to record the $(3+1)$ REMPI spectra. Alternatively, it was proposed that the absence of $\Omega = 1$ states may simply be due to low 2-photon transition strengths.

In the 2P-AI spectra shown above, the $\Omega = 1$ states are seen with intensities similar to those of the $\Omega = 0^+$ and 2 states proving that the 2-photon transition strengths to $\Omega = 1$ states are not prohibitively small. Hence, we conclude that the low principle quantum number $\Omega = 1$ states are more strongly predissociated than their $\Omega = 0^+$ and 2 counterparts and require higher laser powers to ionize them; AI, of course, does not require absorption of a third photon. The origins of both $6s;1$ states can be readily observed in the 2-photon spectra either because they are less predissociated or because these spectra are usually recorded using fundamental dye laser photons.[1]

These results suggest that the lifetimes of the $\Omega = 1$ Rydberg states are significantly shorter than those of the $\Omega = 0^+$ and 2 states in the range 58 000–67 000 cm^{-1}. Most previous experimental studies of CH_3I Rydberg state lifetimes have focused on the $[3/2]6s;1$ state and it is now widely accepted that its lifetime is 1.5 ps (see Ref. 20 and references therein). The lifetime of the $[1/2]6s;1$ state is significantly shorter. A value of 250 fs was reported[21] but in the same study the value for the $[3/2]6s;1$ state was $\sim 50\%$ lower than the accepted value; a similar correction for the $[3/2]6s;1$ state will give a lifetime of ~ 400 fs. A recent *ab initio* study appears to show

Assignments of the nl values of the observed Rydberg bands, based on n^* values of observed bands in the REMPI spectra at lower energy, are also proposed, some of which differ to those given previously.[5,14] However, the l labels are somewhat arbitrary, since states with a common Ω are probably coupled to a certain degree. One previous assignment of three peaks in this region as $6f$ states[14] does appear to be in error. This entails a quantum defect for the f states of ~ 1 whereas it is more commonly believed to be ~ 0 (as it is in the I atom) and hence we assign any f states in this region as $5f$ in line with Locht *et al.*[5] The most important observation is that $\Omega = 0^+$, 1, and 2 states are seen with similar intensities in the 2P-AI spectrum.

conclusively that both $6s$;1 states are predissociated by homogeneous coupling with a repulsive valence triplet $\Omega = 1$ state, labeled $^3A_1$, that dissociates to $CH_3(X) + I(^2P_{1/2})$ and crosses the Rydberg state potentials near to their minima.[15] Only $I(^2P_{1/2})$ is observed following predissociation of the origin of the $[3/2]6s$;1 state, i.e., no $I(^2P_{3/2})$, in support of the proposed mechanism.[20,22–24] The *ab initio* study[15] predicts that the only other repulsive valence state that runs parallel to the triplet $\Omega = 1$ state is a triplet $\Omega = 0^-$ state and hence the $\Omega = 0^+$ and 2 Rydberg states are not open to the equivalent predissociation pathway. An obvious consequence of this is that the intensity of the triplet $[1/2]6s$;0^+ state band in the $(2+1)$ REMPI spectrum has a similar magnitude to that of the singlet $[1/2]6s$;1 state as shown in Fig. 1(a).[1,2,11]

We propose that the repulsive valence triplet $\Omega = 1$ ($^3A_1$) state predissociates higher energy $\Omega = 1$ Rydberg states, both singlet and triplet, with varying efficiency as the overlap with the potential minima of the Rydberg state potentials varies. This particular predissociation appears to reach a maximum in the region 58 000–67 000 cm^{-1}, where no $\Omega = 1$ state bands with significant intensity are observed in the $(2+1)$ REMPI spectrum. Lifetimes of the $[1/2]6p$;2, $[3/2]5d$;2, and overlapping $[3/2]5d$;0^+/$[1/2]6p$;0^+ states lying in the range 63 000–65 000 cm^{-1} have been reported by Janssen *et al.*[25] to be 166, 115, and 131 fs, respectively. The fact that all of these are observed as strong bands in the $(2+1)$ REMPI spectrum, implies that the lifetimes of the $\Omega = 1$ states in this region are significantly less than 100 fs.

The widths of the $\Omega = 0^+$ bands in the $(2+1)$ REMPI spectrum vary enormously from ~ 15 cm^{-1} ($[1/2]6s$) up to ~ 150 cm^{-1} ($[1/2]5d$) and back down to 65 cm^{-1} ($[3/2]6d$), with the $[3/2]7p$ state band probably being too broad to be detected. The *ab initio* study by Alekseyev *et al.*[15] predicts the existence of a bound $\Omega = 0^+$ state with a much higher asymptote and a potential minimum at $\sim 46 000$ cm^{-1} with a C–I bond length of ~ 3.7 Å. Extrapolation of the inner wall of this potential, labeled 2^1A_1, will cross the potential minima of Rydberg states $\sim 67 000$ cm^{-1}, consistent with the broadening of the $\Omega = 0^+$ bands. Although Alekseyev *et al.*[15] describe the 2^1A_1 state as a valence state, it is probably more accurate to describe it as the IP state correlating with $CH_3^+(X) + Br^-$, in line with the description of the equivalent state in an *ab initio* study of CH_3Br by Escure *et al.*[16]

It was shown above that the band at 64 679 cm^{-1} in the 2-photon spectrum assigned to the $[3/2]5d$;0^+/$[1/2]6p$;0^+ Rydberg states exhibits an anomalous power dependency (see Fig. 4). If these Rydberg states are coupled to the IP state it is reasonable to expect the ionization efficiencies to be different from those of uncoupled Rydberg states. In the present case the power dependency suggests that the IP state is more difficult to ionize and this seems plausible on two grounds. First, unlike the geometry of the Rydberg states, that of the IP state is very different from that of the ion and hence the vibrational overlap will be much smaller for the ionization step. In addition, ionization will probably be non-diagonal and the resulting PES is likely to exhibit more vibrational structure than observed in the PES following ionization of a Rydberg state. Some of the unexpected vibrational structure in the PES following 2-photon excitation of the singlet

$[3/2]6p$;0^+, the triplet $[3/2]5d$;0^+, and the overlapping singlet $[3/2]5d$;0^+ and $[1/2]6p$;0^+ states[3] might be explained by such Rydberg/IP coupling. Second, if ionization of the IP state goes to the ground state of the molecular ion, it must involve an electronic re-arrangement of the core, in contrast to ionization of a Rydberg state which requires no such re-arrangement. If the overlapping $[3/2]5d$;0^+ and $[1/2]6p$;0^+ Rydberg states are coupled to the IP state, then this may influence the reliability of their measured lifetimes.[25]

In CH_3Br a similar broadening of some $\Omega = 0^+$ Rydberg bands, which was attributed to interaction with the IP state, was observed in the equivalent region of the 2-photon spectrum.[9] It was proposed that below the threshold for free ion formation, this coupling produces a very dense manifold of levels with mixed Rydberg/ion-pair character centered on the position of the uncoupled Rydberg level which is unresolvable and appear as a single broad band. Rydberg/IP coupling in CH_3Br above the threshold for free ion formation results in the production of small concentrations of CH_3^+ and Br^- and the same is true for CH_3Cl.[26–29] However, no equivalent free ion formation has been observed[30] from CH_3I and hence it appears that some other coupling(s) is dominant in this energy region of CH_3I. This strong coupling probably also causes the loss of 2-photon signals for all Ω states between 72 000 cm^{-1} and IE_1, above which AI becomes the dominant process.

VI. CONCLUSIONS

The $(2+1)$ and $(3+1)$ REMPI spectra of jet-cooled CH_3I have been recorded using LP and CP light with mass-resolved ion detection. The analysis involves the re-assignment of all the bands previously assigned as ns state bands,[3] with the exception of those of the $6s$ states, to nd states with $\Omega = 2$ or 0^+, thereby completing the identification of all four components of the $5d$ cluster that have partial singlet character. One of the $\Omega = 1$ components of both the $5d$ and $6d$ clusters is considerably lower in energy than the other $\Omega = 1$ component and this strongly suggests that extensive mixing with the $\Omega = 1$ component of the close-lying $7s$ and $8s$ clusters is responsible and that the d-orbital involved is d_σ. The assignments of the np states remain largely unchanged.

In the range 58 000–67 000 cm^{-1}, transitions to $\Omega = 2$, 1, and 0^+ Rydberg states are seen in the 3-photon spectrum with similar intensities, whereas only transitions to $\Omega = 2$ and 0^+ Rydberg states are seen with large intensities in the part of the 2-photon spectrum that was recorded with frequency doubled laser radiation. It is concluded that the $\Omega = 1$ states are more heavily predissociated and that only the higher power densities achievable with fundamental dye laser photons can compete with this process and efficiently ionize these states. The predissociation is attributed to a repulsive triplet $\Omega = 1$ valence state that dissociates to $CH_3(X) + I(^2P_{1/2})$ in accordance with *ab initio* calculations.[13]

Above 63 000 cm^{-1}, $\Omega = 0^+$ Rydberg state bands are broader than their $\Omega = 2$ and 1 counterparts, reaching a maximum $\sim 68 000$ cm^{-1}. This observation is attributed to homogeneous coupling of the Rydberg states with the IP state correlating with $CH_3^+(X) + I^-$.

No resonances are observed between $72\,000$ cm^{-1} and IE$_1$ in the REMPI spectra as a result of strong coupling, possibly with states correlating with the CH$_3$(X) + I($6s$ $^4P_{5/2}$) asymptote. Above IE$_1$, sharp structure is observed in the 2P-AI spectrum and is assigned to transitions to Rydberg states converging on IE$_2$. It is concluded that AI effectively competes with this strong coupling.

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