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# Two-colour bound–free–bound spectroscopy of the $[^2E_{1/2}]_c$6s Rydberg states of $CH_3I$ and $CD_3I$

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## Abstract

In this resonantly enhanced multiphoton ionization (REMPI) experiment, an extended vibrational progression in the C–I stretching mode ($\nu_3$) of methyl iodide (-$h_3$ and -$d_3$) is observed in the 1 + 1′ excitation of the [1/2]6s; 0 Rydberg state when the pump photon wavelength lies in the bound → free absorption continuum. This is in contrast with one-colour coherent (non-resonant) two-photon excitation, where the $\nu_3$ mode is not excited. By working at several different fixed probe wavelengths and scanning the pump frequency, the relative contributions from the three intermediate repulsive states can be explored through changes in the relative strengths of the $\Omega = 0$ and 1 components of the final Rydberg states. Extensive predissociation in the Rydberg states curtails the vibrational progression.

*Keywords:* $CD_3I$; $CH_3I$; Rydberg states; Two-colour bound–free–bound spectroscopy

## 1. Introduction

Interest in probing the dynamics of molecular dissociative states continues to develop as new techniques come into use [1]. One prominent aspect of the progress made so far involves the use of femtosecond lasers in a pump–probe experiment, where the dissociative dynamics of the intermediate state are probed by varying the time delay between the two lasers. In this experiment, as well as when using a continuous wave excitation laser in a Raman scattering experiment with a dissociative state as a resonant intermediate, the dissociative state is essentially probed under half-collision conditions. It has been demonstrated that, even with nanosecond pulsed lasers in a pump–probe experiment via a shallow-bound state above its dissociation limit, we can still observe the excitation of the final state [2–6]. Previously, we have carried out several experiments on $I_2$ and $Cl_2$ using dissociative intermediates to access ion pair states having geometries different from the ground state [4–6]. The interpretation of the observed vibrational structure of the ion pair states is based essentially on the Franck–Condon principle. This implies a full-collision model for the dissociative intermediate state and builds up a picture similar to that derived by Shapiro [7] when interpreting the continuum Raman excitation profile of $CH_3I$ observed by Galica et al. [8]. In a zero kinetic energy (ZEKE) photoelectron spectroscopy experiment, Strobel et al. [9] used a one-colour two-photon scheme to excite higher overtones ($v' \leq 10$) of the C–I stretching mode ($\nu_3$) in the two spin–orbital components of the ground state of $CH_3I^+$, where the one-photon energy resonantly accesses the strongest continuum absorption band of $CH_3I$.

In this paper, we attempt to extend the bound–free–bound scheme to the observation of higher overtone excitation in some of the low-lying $CH_3I$ Rydberg states. Since the energy required to reach the continuum valence cluster $\tilde{A}$ of $CH_3I$ is considerably greater than half the energy of the final Rydberg states [10–12], a two-colour experiment with two independently tunable lasers was performed. Fig. 1 shows schematically the potential curves along the C–I coordinate of the relevant electronic states of $CH_3I$, illustrating the transition routes of the 1 + 1′ two-colour bound–free–bound excitation and one-colour non-resonant excitation of the [1/2]6s; 0 Rydberg state. The steepness of the three repulsive valence states is based on the width of each absorption maximum determined in the MCD study [10]. In order to explore the role of the repulsive intermediate states, the results of the two-colour experiments are compared with those of the one-colour 2 + 1 resonantly enhanced multiphoton ionization

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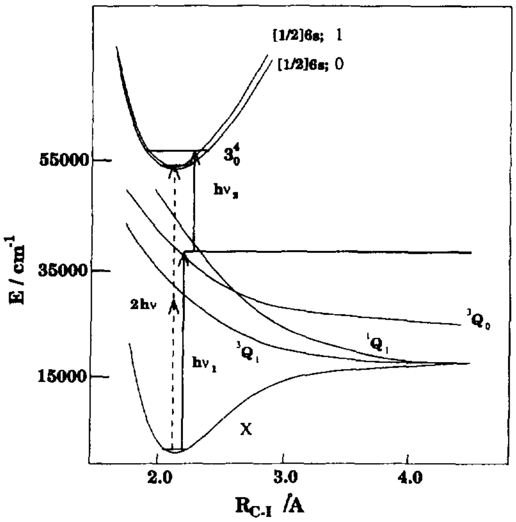

Fig. 1. Schematic diagram showing the potential curves of the ground state, the $^3Q_1$, $^3Q_0$ and $^1Q_1$ continuum valence states and the [1/2]6s; 0 and 1 Rydberg states along the C–I stretching coordinate of $CH_3I$. Both $1+1'$ bound–free–bound (full line) and one-colour two-photon non-resonant excitation (broken line) routes to the [1/2]6s; 0 Rydberg state are indicated.

(REMPI) study of the same Rydberg states when the first photon energy lies below the onset of continuous absorption.

## 2. Experimental details

A molecular beam of $CH_3I$ in helium was crossed at 90° by two counterpropagating laser beams. These were generated by a Lambda Physik EMG201 MSC excimer laser which simultaneously pumped two Lambda Physik dye lasers, an FL3002 (pump) and an FL2002 (probe). The lasers were directed via 5 cm focal length lenses into the molecular beam, both lenses being slightly defocused from the ionization region in order to minimize one-colour photoionization signals.

The molecular beam was generated by pulsing a mixture of 150 Torr of $CH_3I$ and 400 Torr of helium through a General Valve nozzle 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 molecular and laser beams. The mass-resolved ion signals were processed by a Stanford Instruments SR250 boxcar integrator and stored on a PC.

In all of the spectra shown, $CH_3^+$, $I^+$ and $CH_3I^+$ signals have the same order of magnitude. However, the relative strengths of the three signals are dependent on the power of the pump photon, which varies significantly with wavelength. Thus a good approximation of a power normalized spectrum could only be obtained by simultaneously monitoring the total ion signal together with the laser power. Since, experimentally, this option is not open to us and since, as discussed later, the number of photons involved in the initial ionization step is not certain, none of the spectra are power normalized. All spectra were collected in the $CH_3/CD_3$ mass channel.

## 3. Spectroscopic notation for valence and Rydberg states

The three valence states which can be reached in a one-photon transition from the ground state were denoted $^1Q_1$, $^3Q_0$ and $^3Q_1$ by Mulliken [13]. These are the symmetry species $3E$, $2A_1$ and $2E$ in a $C_{3v}$ molecule [14]. By analogy with linear molecules in Hund's case (c), these states can also be denoted as $\Omega=0$ or 1, and in Hund's case (a) the correlation is with $^1\Pi_1$, $^3\Pi_0$ and $^3\Pi_1$ respectively. In the heavier methyl halides, the halogen spin–orbit coupling is sufficiently greater than the exchange energy between the halogen lone pair orbitals and the lowest Rydberg orbitals [15] for the axial component of the electronic angular momentum of the core ($\omega_c$) to be a fairly good quantum number. Since the total $\Omega$ ($\omega_c+\omega_{Ry}$) is always good, we can also describe Rydberg states using the ($\omega_c$, $\omega_{Ry}$) coupling scheme: $[\omega_c]nl$; $\Omega$. The five substates of the 6s Rydberg cluster are then [3/2]6s; 2, [3/2]6s; 1, [1/2]6s:0$^\pm$ and [1/2]6s:1 in ascending order of energy. The first two are based on the $^2E_{3/2}$ state of the molecular ion and the other three on the $^2E_{1/2}$ core. The $\Omega=2$, 0 states are pure triplets and the two $\Omega=1$ states have both singlet and triplet character (an equal admixture in the limit of pure $\omega_c$, $\omega_{Ry}$ coupling).

## 4. Results and discussion

Fig. 2(a) shows the one-colour 2+1 REMPI spectrum recorded in the $CH_3^+$ mass channel over the 54 000–57 000 cm$^{-1}$ excitation energy range. Such multiphoton ionization studies in the same energy range have been reported previously [16–18], and our observed [1/2]6s; 0 and 1 Rydberg states reproduce the previous results. The one-photon wavelength (350–370 nm) does not access any of the three repulsive valence states. It can be seen that the only strong two-photon transitions from the ground state terminate on the electronic origins and $v'=1$ of $\nu_2$, the umbrella mode, of each Rydberg state. Fig. 2(b) shows the $1+1'$ excitation spectrum of the same two-photon energy region recorded with a probe photon fixed at 570 nm and a pump photon scanned between 274 and 253 nm. Over this region, the pump photon is in resonance with the $^3Q_0$ continuum valence state which has the strongest absorption cross-section of the three continuum valence states $^3Q_1$, $^3Q_0$ and $^1Q_1$. The electric planes of the pump and probe photons were set parallel to each other to reproduce the polarization conditions in the 2+1 REMPI experiment. Since the addition of a further probe photon cannot reach either the $^2E_{3/2}$ (76 930 cm$^{-1}$) or $^2E_{1/2}$ (81 979 cm$^{-1}$) ionic state of $CH_3I$ [9], a further pump photon or two probe photons are required to ionize the $1+1'$ excited Rydberg states. It is not known which ionization route is more favourable, but for brevity the overall excitation scheme will be labelled as $1+1'+1$ throughout. The difference between the spectra in Fig. 2(a) and Fig. 2(b) is obvious; an extensive vibrational progression up to $3_0^5$ of the $\nu_3$ mode in the [1/2]6s; 0 state is identified, as well as a combination overtone progression with the $CH_3$ umbrella mode $\nu_2$, e.g. $2_0^1 3_0^1$, $2_0^1 3_0^2$ and $2_0^1 3_0^3$, in Fig. 2(b), whereas in Fig. 2(a) only the vibronic origin $0_0^0$ and one- and weak two-quantum excitation of the $\nu_2$ mode, $2_0^1$ and $2_0^2$, are observed. The band positions are given in Table 1.

In the one-colour two-photon ZEKE photoelectron spectrum of $CH_3I$, a smoothly converging progression in $\nu_3$ up to $v' = 10$, with $\omega_e = 484$ cm$^{-1}$ and an anharmonicity constant of $-3.41$ cm$^{-1}$, was observed for the $^2E_{3/2}$ state of the ion [9]. A similar progression up to $v' = 6$ with $\omega_e = 463$ cm$^{-1}$ was observed for the $^2E_{1/2}$ state of the ion. In the present study, a progression up to $v' = 5$ is observed with $\omega_e = 485$ cm$^{-1}$ for $CH_3I$. It should be stressed that the termination of the progression at $v' = 5$ is not due to a loss of dye power, nor does it reflect a decrease in the absorption strength at the pump stage. This was confirmed by carrying out equivalent scans with various, lower wavelength, fixed probe photons, none of which showed any extension of the progression in $\nu_3$ above $v' = 5$. As discussed below, it is believed that the termination of the progression is due to some form of predissociation of the higher vibrational levels.

One-photon transitions to three valence states have been observed between 215 and 320 nm [10]: absorption to the $^3Q_1$ state occurs between 275 and 320 nm, to the $^3Q_0$ state between 230 and 310 nm and to the $^1Q_1$ state between 215 and 280 nm. The relative oscillator strengths are approximately 1 : 100 : 30. Thus the pump photon used to record the spectrum in Fig. 2(b) (253–274 nm) excites predominantly the $^3Q_0$ state. Since the [1/2]6s; 0 component is much more efficiently excited than the $\Omega = 1$ component (Fig. 2(a)), parallel ($\Delta\Omega = 0$) probe transition seems more favourable than perpendicular.

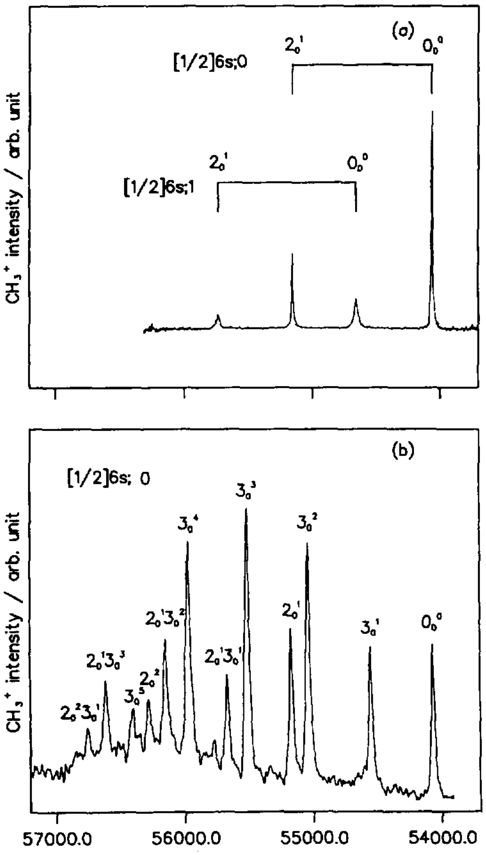

Fig. 2. (a) One-colour non-resonant 2 + 1 REMPI spectrum of $CH_3I$. (b) The 1 + 1′ + 1 bound–free–bound multiphoton ionization spectrum with the probe photon fixed at 570 nm.

Excitation of the 6s Rydberg states corresponds to the promotion of an electron from the non-bonding iodine 5p orbital to the weakly bonding 6s Rydberg orbital, and therefore the equilibrium C–I bond length of the 6s states may be slightly smaller than that of the ground state [1]. This is confirmed in the observed non-resonant 2 + 1 REMPI spectrum, where only the $0_0^0$ and $2_0^1$ vibronic bands of the [1/2]6s; 0 and 1 states appear, indicating that the equilibrium separation of the C–I coordinate in the two Rydberg states is quite close to that of the ground state.

Bound–free–bound excitation in diatomics [4–6] has produced very long vibrational progressions in the final state, and resonant Raman scattering of $CH_3I$ via the $^3Q_0$ continuum state results in progressions in $\nu_3$ up to $v'' = 29$ in the ground state [19]. We must therefore look for the factors causing the relatively short extension to the vibrational progression observed here. In the diatomic halogens, the envelope of the vibrational progression is found to be oscillatory, a consequence of two interfering branches [20] contributing to the integral in the Franck–Condon factor for bound–free overlap at the probe stage, which is in turn a consequence of a double-valued Mulliken difference potential between the intermediate and final states. The present group of five $v'$ levels might therefore be just the first lobe in a much more extended progression. However, the Mulliken difference potential between the $^{1,3}Q^{\Omega}$ states and the Rydberg states is now monotonic, as is the difference potential between the same repulsive states and the ground state [21]. Direct computation of the bound–free Franck–Condon factors does not reveal a modulation of the vibrational envelope anywhere near the required periodicity. Experimentally, there is no evidence from changing $\lambda_{\text{probe}}$ for any resumption of the vibrational progression beyond $v' = 5$. We therefore conclude that the cessation of the REMPI signal is due to a fairly sudden onset of rapid predissociation around $v' = 5$.

Some spectra of $CD_3I$ were also recorded and these are illustrated in Fig. 3(a) and Fig. 3(b). The 1 + 1′ spectrum (Fig. 3(b)) was recorded with a pump photon fixed at 265 nm and a probe photon scanned between 525 and 610 nm. Termination of the $v'$ progression at $3_0^5$ was also observed. The $\nu_3$ mode is only weakly affected by isotopic substitution and the vibrational amplitudes in the C–I coordinate should be roughly the same for the two isotopomers at each value of

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[1] The radius of the Rydberg orbital in the lowest members of an s Rydberg series is typically about 3 Å, and thus there is still some repulsion between the promoted electron and the filled valence orbitals of the core, which perhaps offsets the expected bond contraction.

Table 1
Positions and assignments of the observed vibronic bands of the [1/2]6s; 0 Rydberg state of $CH_3I$ and $CD_3I$

| Vibronic band | $CH_3I$ | | $CD_3I$ | |
|---|---|---|---|---|
| | Band position ($cm^{-1}$) | Energy separation ($cm^{-1}$) | Band position ($cm^{-1}$) | Energy separation ($cm^{-1}$) |
| $0_0^0$ | 54052 | 0 | 54159 | 0 |
| $3_0^1$ | 54537 | 485 | 54628 | 469 |
| $3_0^2$ | 55015 | 963 | 55091 | 932 |
| $2_0^1$ | 55146 | 1094 | 54985 | 826 |
| $3_0^3$ | 55482 | 1430 | 55544 | 1385 |
| $2_0^1 3_0^1$ | 55633 | 1581 | 55452 | 1293 |
| $3_0^4$ | 55930 | 1878 | 55987 | 1828 |
| $2_0^1 3_0^2$ | 56103 | 2051 | 55913 | 1754 |
| $2_0^2$ | 56237 | 2185 | 55807 | 1648 |
| $3_0^5$ | 56360 | 2308 | 56427 | 2268 |
| $2_0^1 3_0^3$ | 56570 | 2518 | 56389 | 2230 |
| $2_0^2 3_0^1$ | 56709 | 2657 | 56275 | 2116 |

$v'$. We therefore conclude that the predissociation occurs in the C–I rather than the C–H stretch.

The present results have a bearing on the previously reported 2 + 1 REMPI spectra of $CH_3I$ [22,23]. In these, strong transitions to the 6s, 6p and 7s Rydberg states have been seen, while above this only the 8s, 9s and 10s states have been observed and these only very weakly. It was proposed that the rapid drop in intensity above the 7s level was due to absorption and subsequent dissociation at the one-photon level. Although this process must take place, we have shown that not only is it possible to pump through the dissociative states, even with two independent photons, but that such an excitation scheme can result in significant enhancement of the two-photon signal. It seems unlikely in a one-colour single laser experiment, with the improved spatial and temporal overlap that exists, that similar signal enhancements would not accompany an intermediate resonance. Thus a more probable explanation for the low intensities in any but the origin band of the higher Rydberg states is that it is the Rydberg states themselves which undergo extensive predissociation even at $v' = 1$.

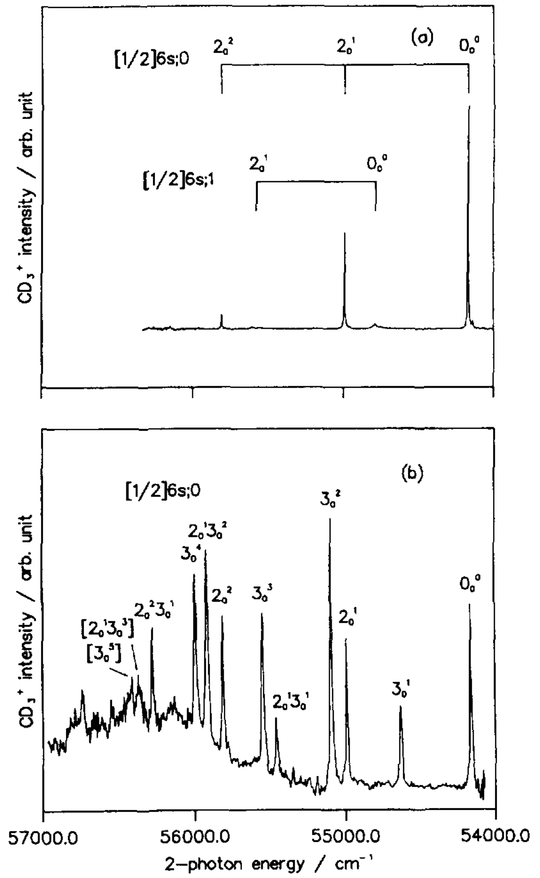

Fig. 3. (a) One-colour non-resonant 2 + 1 REMPI spectrum of $CD_3I$. (b) The 1 + 1′ + 1 bound–free–bound multiphoton ionization spectrum with the pump photon fixed at 265 nm. The assignments in brackets are tentative.

Lastly, we carried out some experiments to probe the relative contributions of the three repulsive intermediate states $^3Q_1$, $^3Q_0$ and $^1Q_1$. In the 2 + 1 REMPI spectrum (Fig. 2(a)), the vibronic band intensities of the two Rydberg states, [1/2]6s; 0 and [1/2]6s; 1, are comparable with each other, whereas the latter state cannot be observed in the two-colour spectrum recorded with a probe photon of 570 nm (Fig. 2(b)). We also scanned the same two-photon energy range with fixed probe wavelengths of 620 nm (Fig. 4(a)) and 520 nm (Fig. 4(c)). The two strongest vibronic bands, $0_0^0$ and $2_0^1$, of the [1/2]6s; 1 state are observed at these new probe wavelengths. In the first of these excitation schemes, the longer wavelength pump photons with $\lambda_{probe} = 520$ nm can access the $^3Q_1$ valence state as well as the $^3Q_0$ state, and the pump photons with $\lambda_{probe} = 620$ nm lie near the maximum of the $^1Q_1$ absorption continuum. Hence it appears that, in spite of the small oscillator strengths of the $^3Q_1 \leftarrow X$ and $^1Q_1 \leftarrow X$ transitions, an $\Omega = 1$ intermediate state is necessary if the [1/2]6s; 1 state is to be observed in a two-colour experiment, i.e. a parallel transition at the probe stage.

In Fig. 4(a) and Fig. 4(c), it is not possible to identify a progression in $\nu_3$ in the [1/2]6s; 1 state because one quantum of $\nu_3$ based on the [1/2]6s; 1 state origin is essentially coincident with one quantum of $\nu_2$ built on the [1/2]6s; 0 state origin. Assuming that the [1/2]6s; 1 state can only be excited

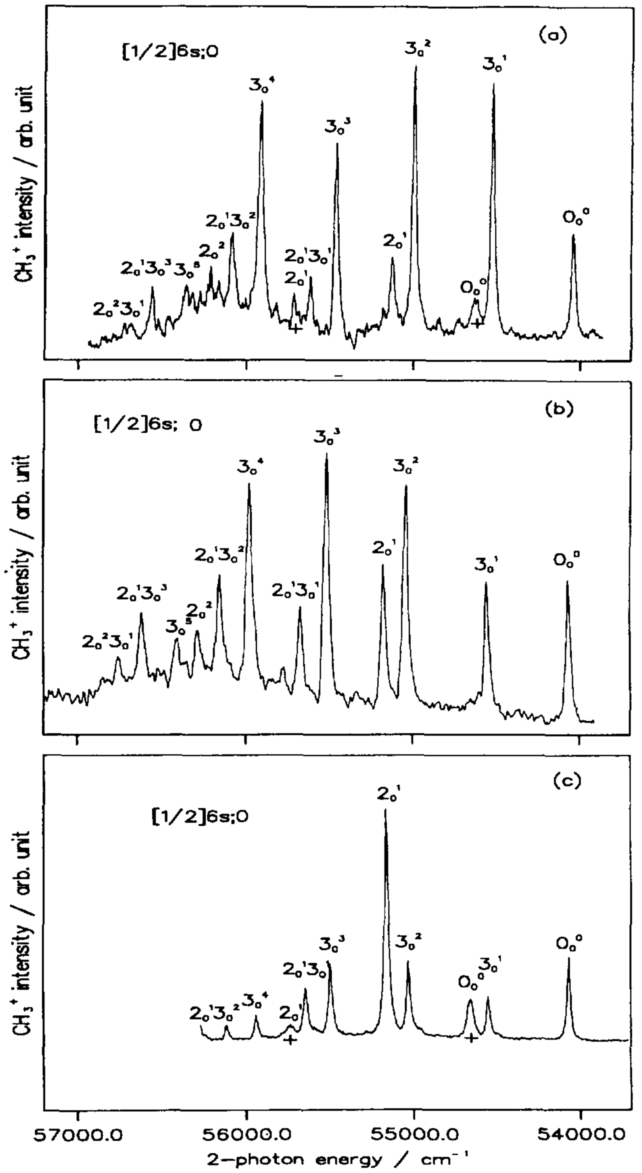

Fig. 4. The $1+1'+1$ REMPI spectrum of CH$_3$I obtained by scanning the pump laser at a fixed $\lambda_{\text{probe}}$: (a) $\lambda_{\text{probe}} = 620$ nm; (b) $\lambda_{\text{probe}} = 570$ nm; (c) $\lambda_{\text{probe}} = 520$ nm. The $0_0^0$ and $2_0^1$ bands marked + belong to the 6s; $\Omega = 1$ Rydberg state.

in a two-colour experiment via a real intermediate state, it is striking that the $^1Q_1$ state, accessed throughout the spectrum shown in Fig. 4(b), does not act as an appropriate intermediate. One possible reason may be that the absorption spectrum by Gedanken and Rowe [10], which they subsequently deconvoluted, was recorded at room temperature while our sample is jet cooled. The wings of a bound → free absorption curve are very sensitive to the vibrational population of the initial state, and it is possible that the absorption from $X(v''=0)$ into the $^1Q_1$ state in the wavelength range 257–271 nm is very weak.

## 5. Conclusions

Extensive vibrational structure with $v' \leq 5$ in the C–I stretching mode $\nu_3$ of the CH$_3$I [1/2]6s; 0 Rydberg state has been observed by pumping through the $^3Q_0$ continuum intermediate state using two independently tunable lasers. The key role played by bond stretching in the real resonant continuum intermediate is confirmed by the absence of vibrational structure in a non-resonant one-colour two-photon experiment. However, the vibrational progressions are rather shorter than might be expected from an unbound intermediate state due to the sudden onset of predissociation in the C–I coordinate above $v' = 5$ in the 6s Rydberg states. The contribution of the resonant intermediate state is confirmed by the observation that, when the pump wavelength is shifted to the peak of the weaker $^1Q_1$ or $^3Q_1$ absorption, the $\Omega = 1$ component of the [1/2]6s pair appears, although not strongly.

Our pump–probe excitation scheme is an alternative way of probing the dissociative valence states of CH$_3$I whereby the Rydberg state is detected rather than the dissociation products CH$_3$ or I($^2P_{1/2}$)/I($^2P_{3/2}$). The deliberate use of repulsive states as resonant intermediate states also opens up more multiphoton pathways to the molecular Rydberg states, with propensity rules for the final state being dictated by the electronic structure of the intermediate state.

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