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Resonance enhanced multiphoton ionization photoelectron spectroscopy on nanosecond and picosecond time scales of Rydberg states of methyl iodide

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Rydberg states of methyl iodide have been investigated using resonance enhanced multiphoton ionization in combination with photoelectron spectroscopy with nanosecond and picosecond laser pulses. The study of the ns ($6 \leq n \leq 10$) Rydberg states in two-, three-, and four-photon excitations has resulted in an unambiguous identification of state [1] in the $7s$ and $8s$ Rydberg states. As a consequence, it is concluded that the transition to $6s[1]$ in two- and three-photon excitations is anomalously weak. The application of photoelectron spectroscopy to identify the electronic and vibrational nature of a resonance has led to a major reinterpretation of the excitation spectrum of the $6p$ Rydberg state in two-photon excitation. In many of the recorded photoelectron spectra anomalous electrons are observed, which derive from a one-photon ionization process. This process is suggested to find its origin in the mixing of $6p$ and $7s$ character into higher-lying Rydberg states. The major difference between resonance enhanced multiphoton ionization photoelectron spectroscopy with nanosecond and picosecond lasers is found in a less effective dissociation of the molecule in the picosecond experiments.

I. INTRODUCTION

The excited states of methyl iodide have since long attracted considerable interest, both from an experimental and a theoretical point of view.¹⁻³¹ Investigations of the dissociation occurring in the lowest excited dissociative states, the A band,¹⁻²² and the predissociation of higher-lying excited states to the A band²³⁻³⁰ have served as benchmark studies of the dissociation of an isolated molecule. Spectroscopic studies of the Rydberg states of methyl iodide, on the other hand, have allowed for a detailed characterization of properties such as the influence of spin-orbit coupling and vibronic interactions,³²⁻³⁵ and the study of analogies of the quantum defects in molecules and rare gas atoms.³⁶⁻³⁹

Methyl iodide is a molecule of C_{3v} symmetry with a ground state electronic configuration $\cdots a_1^2 e^4 ({}^1A_1)$. In the following we will, for reasons of convenience, sometimes use the symmetry labels appropriate for $C_{\infty v}$ as well. The vibrational modes of methyl iodide can be divided into three totally symmetric ones [the C-H stretch (ν_1), the umbrella mode (ν_2), and the C-I stretch (ν_3)] and three vibrational modes of e symmetry [the antisymmetric C-H stretch (ν_4), the CH_3 deformation mode (ν_5), and the H_3C -I bending mode (ν_6)].⁴⁰ In Table I the frequencies of these vibrations in the ground state are given.³² Since the ground state is totally symmetric, the Franck-Condon principle allows only transitions to the a_1 vibrational modes in the excited states. The vibrational modes of e symmetry can only be excited in one-photon absorption as a result of vibronic coupling.

The first excited states of methyl iodide arise from the excitation of a nonbonding $5p\pi$ iodine electron to a C-I antibonding orbital ($5p\pi \rightarrow \sigma^*$). If the molecule for the mo-

ment is considered as being of $C_{\infty v}$ symmetry, then the five states resulting from this excitation are of Δ , Π , (Σ^+ , Σ^-) and Π symmetry. The Σ^+ and Σ^- states are degenerate as indicated by the parentheses. These five states are collectively designated as the A band and form a broad, featureless absorption band beginning at approximately $32\,000\text{ cm}^{-1}$ with its maximum at about $38\,000\text{ cm}^{-1}$.⁴¹ One-photon excitation to the A band results in a rapid direct dissociation yielding methyl radicals ($X\,{}^2A_2''$) and iodine atoms in their electronic ground state (${}^2P_{3/2}$) as well as in the spin-orbit excited state (${}^2P_{1/2}$). Studies of the dissociation of the molecule upon excitation into the A band have elucidated the time scale on which the dissociation occurs ($< 100\text{ fs}$)¹⁻⁴ and the final-state distribution of the fragment species.^{2,5-15}

The next transitions to states higher in energy are known as the B and C bands. They result from the transitions to states which arise from the excitation of a nonbonding $5p\pi$ iodine electron to a $6s$ molecular Rydberg orbital ($5p\pi \rightarrow \sigma$). The three remaining $5p\pi$ electrons are subject to a strong spin-orbit coupling yielding a ${}^2\Pi_{3/2}({}^2E_{3/2})$ and a ${}^2\Pi_{1/2}({}^2E_{1/2})$ ionic core in $C_{\infty v}(C_{3v})$ symmetry. Coupling of the spin of the Rydberg electron with these ionic cores subsequently leads to states of Δ (E) and Π (E) symmetry with a ${}^2\Pi_{3/2}({}^2E_{3/2})$ ionic core and states of (Σ^+ , Σ^-) (A_1, A_2) and Π (E) symmetry with a ${}^2\Pi_{1/2}({}^2E_{1/2})$ ionic core. These states are also known in literature as states [1], [2] (the B band) and [3], [4] (the C band).³²⁻³⁵ States [1], [2] and states [3], [4] are separated by approximately 5000 cm^{-1} , the spin-orbit splitting observed in $CH(D)_3I^+$. The spectroscopy of the $6s$ states has been extensively investigated using one-photon absorption techniques^{32-34,42} as well as resonantly enhanced multipho-

TABLE I. Vibrational frequencies in the ground (1A_1) and $6s[2]$ Rydberg state of CH_3I and CD_3I and the $^2E_{3/2}$ state of CH_3I^+ and CD_3I^+ . The frequencies in the ground and $6s[2]$ Rydberg state are given in cm^{-1} , those in the ionic state in eV.

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
CH_3I (1A_1) ^a	2970	1250	535	3060	1440	880
CD_3I (1A_1) ^a	2155	950	500	2300	1050	660
CH_3I ($6s[2]$) ^b	2647	1095	487	2892	1257	835
CD_3I ($6s[2]$) ^b	1985	835	480	2200	955	630
CH_3I^+ ^c	0.368	0.157	0.061	0.379	0.18 ^d	0.114
CD_3I^+ ^c	0.267	0.119	0.057	0.285	0.13	0.086

^aAdopted from Ref. 32.

^bAdopted from Refs. 32 and 43.

^cAdopted from Ref. 50.

^dCalculated on the basis of the ratio ν_5/ν_2 in the $6s[2]$ Rydberg state.

^eCalculated on the basis of the ratio $\nu_i(\text{CD}_3\text{I})/\nu_i(\text{CH}_3\text{I})$ in the ground state.

ton ionization (REMPI) spectroscopy with one-^{24,25} and two-photon excitation.^{25,35,43,44} On symmetry arguments the transitions to state [2], [3], and [4] are allowed in one-photon excitation, but experimentally it is observed that the perpendicular transitions to states [2] and [4] dominate the excitation spectrum. The one-photon transition to state [1] is forbidden in $C_{\infty v}$ symmetry. In C_{3v} symmetry this state can mix with state [2], however, thus making the transition to state [1] slightly allowed. Experimentally, a very weak band has been observed in absorption experiments at the expected position of the 0–0 transition to state [1]. Assignment of this band to $[1]0_0^0$ has been substantiated by magnetic circular dichroism (MCD) studies³³ and by simulation of the rotational bandstructure.³⁴ In one- and two-color (1+1) REMPI spectroscopy this band has, however, not been seen.²⁴ In this respect it is interesting to note that the $[1]6_0^1$ transition can clearly be observed in one-photon absorption and (1+1) REMPI spectroscopy. The selection rules for two-photon transitions allow transitions to all states of the $6s$ manifold, except the $\Sigma^-(A_2)$ state. Strong two-photon transitions to the $\Sigma^+(A_1)$ state of [3] have indeed been observed but, unexpectedly, the 0–0 transition to state [1] can not be identified in two-photon absorption. The only observed two-photon transition to state [1] is the 6_0^1 transition.²⁵ Both in one- and two-photon excitations all vibrational modes have been identified, though the ν_2 mode dominates the vibrational progressions of the excitation spectra. The frequencies of the vibrational modes in the $6s$ Rydberg states^{32,43} are given in Table I.

Transitions to the manifold arising from the excitation of a $5p\pi$ electron to the molecular Rydberg $6p$ orbital are observed at slightly higher energies. This manifold has been studied systematically for the first time by Gedanken *et al.* using (2+1) REMPI spectroscopy.⁴⁵ Though 16 states, 8 with a $^2E_{3/2}$ and 8 with a $^2E_{1/2}$ ionic core, can arise from the $5p\pi \rightarrow 6p$ excitation, only one state with a $^2E_{3/2}$ core and one state with a $^2E_{1/2}$ core have been assigned. Tsukiyama *et al.*⁴⁶ have obtained an excitation spectrum of the $6p$ region very similar to that of Gedanken *et al.* by monitoring the fluorescence. This fluorescence has been attributed to highly excited neutral fragments that are created by a dissociation process at the three-photon level, which competes effectively with ionization.

The remaining part of the Rydberg spectrum of methyl iodide has only been investigated with low-resolution one-photon vuv absorption measurements.^{36–39} In these studies, ns , np , and nd Rydberg series converging to the lowest $^2E_{3/2}$ and $^2E_{1/2}$ ionic limits have been identified, but many absorption features have also been left unaccounted for. Also, the individual states within one ns , np , or nd manifold have not been identified, but assignments have only been made to the manifold with a $^2E_{3/2}$ or a $^2E_{1/2}$ ionic core as a whole. REMPI studies of these higher-lying Rydberg states are hindered by the fact that photon energies have to be used that excite the A band at the one-photon level. The two-photon excitation to a Rydberg state consequently has to compete with the high dissociation rate of the A band. In spite of this unfavorable competition, several groups have shown that it is possible to pump through the A band with a high-power pulsed laser and excite higher-lying Rydberg states of methyl iodide, which subsequently may be ionized.^{4,19–22} However, no systematic assignment of Rydberg states has been arrived at in such studies.

Rydberg states of methyl iodide are furthermore expected to be subject to predissociation to the A band. The $6s$ Rydberg states have been the focus of several studies investigating the rate of such a predissociation.^{23–26} From these studies it is concluded that the lifetime of the $6s$ Rydberg states is about 500 fs in CH_3I and 1.2 ps in CD_3I .²⁶ A real-time study of the $6p$ Rydberg state has determined the lifetime of this state as 175 fs and 325 fs in CH_3I and CD_3I , respectively.³⁰

The majority of the REMPI studies on the states of methyl iodide have been performed on the basis of ion detection. In such a detection scheme the ionization step merely serves as a means to detect resonances at the intermediate level, but in itself does not provide any further information about the resonance. Resonance enhanced multiphoton ionization in combination with photoelectron spectroscopy (REMPI-PES), on the other hand, allows for the determination of the electronic and vibrational states in which the ions are created. It is clear that this final ionic state distribution is to a large extent determined by the nature of the state responsible for the resonance and, vice versa, offers valuable information on the electronic and vibrational character of the resonant state. Apart from the

advantages REMPI-PES offers for spectroscopic studies, it can also be of considerable importance in elucidating dynamical processes occurring in excited states. Often ionic fragment species are created in REMPI experiments. With ion detection it is difficult to determine at which level these fragments are created, i.e., whether they derive from the ionization of neutral fragments or from the dissociation of the molecular ion into ionic fragments. Such problems are circumvented in REMPI-PES where ionization of neutral fragments generates photoelectrons, which can subsequently be identified. Furthermore, dynamical processes such as the decay and (pre)dissociation of excited states on a time scale within reach of the experimental possibilities are expected to have a profound influence on the photoelectron spectrum. REMPI-PES thus can lead to the identification of the mechanisms underlying these processes.

In the present study we have investigated the Rydberg states of methyl iodide with REMPI-PES using nanosecond and picosecond laser pulses. The application of nanosecond REMPI-PES has enabled the identification of the ns ($6 \leq n \leq 10$) Rydberg states in two-, three-, and four-photon excitation. Of special interest is state [1], which has unambiguously been identified in the $7s$ and $8s$ Rydberg states but coincides with state [2] in the $9s$ and $10s$ Rydberg states. The study of the $6p$ Rydberg manifold with two-photon excitation has led to the conclusion that the assignments of previous studies^{45,46} need to be revised. In particular, the excitation spectrum of the $6p$ Rydberg manifold turns out to have contributions from more than the two states originally assigned. For many of the photon energies employed in the present study the photoelectron spectrum shows electrons with kinetic energies that do not correspond to an $(n+m)$ ionization but derive from a one-photon ionization. The combination of the results obtained with nanosecond REMPI-PES and those obtained with picosecond REMPI-PES leads to the tentative proposal that a significant mixing of the $6p$ and $7s$ Rydberg states into higher-lying Rydberg states occurs. The influence of shortening the laser pulses from nanoseconds to picoseconds is shown to manifest itself primarily in a smaller yield of fragment species. The photoelectron spectra, however, do not demonstrate significant changes. Finally, pump-probe experiments on a picosecond time scale with REMPI-PES will be considered. These experiments show good agreement with previous results.

II. EXPERIMENT

The experimental setup has been described in detail before.⁴⁷ Briefly, laser light from either a nanosecond or picosecond laser system is focused into a magnetic bottle spectrometer through a quartz lens with a focal length of 25 mm. Another laser beam, counterpropagating to the first one, can be introduced through a similar lens mounted on the other side of the spectrometer. Electrons produced in the ionization region of the spectrometer are spatially and temporally separated according to their kinetic energies in a 50 cm time-of-flight tube, and subsequently detected by a pair of microchannel plates. This signal is amplified by a home-built fast preamplifier and recorded by a

transient digitizer which is connected to a microcomputer. A negative bias of the repeller grid in the flight tube enables an energy resolution of ≈ 10 meV at all electron kinetic energies. An absolute energy calibration is obtained by calibrating the system with the lower spin-orbit ionic states of the rare gas atoms xenon or krypton, depending on the laser wavelength range.

In some spectral regions iodine atom resonances interfere heavily with the molecular resonances. In order to resolve the much weaker molecular resonances use has been made of two strategies. First, in regions where the kinetic energies of electrons originating from atomic and molecular resonances are distinctly different only molecular electrons have been selected to be monitored. Second, in regions where this is not possible mass-resolved ion detection has been applied. Although the magnetic bottle spectrometer has been designed purely for electron detection, mass-resolved ion detection is possible as well, albeit with a lower detection efficiency. In order to allow for ion detection positive voltages of 250 and 180 V are applied to the two grids surrounding the ionization region, while the repeller grid in the flight tube is grounded. In such a configuration a mass resolution of 150 at the mass of CH_3I (142 amu) is achieved.

The nanosecond laser system consists of a XeCl excimer laser (Lumonics HyperEx-460), working at a repetition rate of 30 Hz, which pumps a dye laser (Lumonics HyperDye-300). Frequency doubling is achieved using angle-tuned BBO and KD*P crystals in a frequency-doubling unit (Lumonics HyperTrak-1000). The peak power of the resulting pulses with a 10 ns temporal width and 0.08 cm^{-1} energy width was kept at such a level that space charge effects in the ionization region were minimal. In practice this meant that pulse energies up to 0.2 and 2 mJ/pulse were used for the frequency-doubled and fundamental wavelengths, respectively.

The picosecond laser system starts from a cw mode locked Nd:YLF laser (Coherent Antares 76) producing 18 W average output power at a wavelength of 1055 nm in pulses with a pulsewidth of 50 ps at a repetition rate of 76 MHz. This infrared beam is doubled in a KTP crystal giving a maximum of 2 W output power at 527.5 nm with a pulsewidth of 35 ps. Of the laser light at 527.5 nm 800 mW is used to synchronously pump a dye laser (Coherent CR-590) operating on rhodamine 6G dissolved in ethylene glycol. Wavelength selection in the range of 560 to 640 nm is possible by rotating a three-plate birefringent filter with a dc motor with encoder operated from a computer. Dye laser pulses with a transform limited bandwidth of 5 cm^{-1} and a pulse width of 3 ps are obtained at an average output power of 320 mW. The dye laser is calibrated using the optogalvanic effect in Ne.

Amplification of the dye laser pulses is done by a combination of a regenerative amplifier (Continuum Nd:YLF RGA 47-30) and a longitudinally pumped three-stage picosecond tunable dye amplifier (Continuum PTA 60) operating on rhodamine 6G dissolved in methanol. The regenerative amplifier, consisting of an unstable resonator and a double-pass amplifier, is seeded with 700 mW of the

infrared beam from the Nd:YLF laser and produces a 20 mJ Gaussian infrared pulse with a pulsewidth of 50 ps at a repetition rate of 30 Hz. Frequency doubling in a 10 mm long KD*P crystal results in pulses of 35 ps with an energy of 10 mJ. This energy can be adjusted by varying the voltage on the flashlamps of the double-pass amplifier stage. Recombination of the amplified 527.5 nm pulses with the dye laser pulses in the tunable dye amplifier then produces pulses with a pulsewidth of 3 ps and an energy of up to 0.5 mJ. Due to the short pump pulses the amplified dye laser pulses have an ASE contribution of less than 1%. The amplified dye laser pulses are frequency doubled in an angle-tuned KDP crystal which is driven by a dc motor with encoder controlled by the computer. To avoid space charge effects in the ionization region the final uv pulse energy is kept below 1 μ J in the present experiments.

In some of the ps experiments a second laser beam has been used. This beam is generated from a small part of the 527.5 nm output of the regenerative amplifier which is frequency doubled in a KDP crystal to a 263.8 nm pulse with an energy of 10 μ J and a pulsewidth of 25 ps. The timing of this laser pulse with respect to the dye laser pulse is adjustable by moving a retroreflector mounted on a stepper motor translational stage.

CH₃I and CD₃I (99%) have been purchased from Merck and Aldrich, respectively. Samples have been purified by vacuum-freeze-thaw cycles. During the experiments the sample was cooled down to 0 °C and introduced into the ionization chamber via an effusive inlet. Typical operating pressures were 10⁻⁴ mbar in the ionization chamber and 10⁻⁶ mbar in the flight tube.

III. RESULTS AND DISCUSSION

A. REMPI-PES experiments on nanosecond time scale

1. Spectroscopy of the *ns* Rydberg states

In this section we shall first consider the *ns* Rydberg states resulting from the excitation of a 5p π iodine lone pair electron to the molecular *ns* Rydberg orbitals and concentrate on the spectroscopy of these states. The excitation spectra of the 6s to 10s Rydberg states of methyl iodide have been obtained using two-, three-, and four-photon excitations combined with photoelectron or photoion detection and will be discussed in the following. Table II summarizes all observed molecular *ns* Rydberg resonances at various excitation levels in CH₃I and CD₃I together with their assignments. Though the excitation spectra to be shown allow for an accurate determination of the various resonances, which is our prime interest, caution should be taken with respect to their intensities. Since we are not using a one-photon excitation scheme, it would have been necessary to perform wavelength scans under constant-intensity conditions in order to determine the relative intensities of the resonances. In our present setup such wavelength scans are not possible as yet. Consequently, the peak intensities in the excitation spectra can

TABLE II. Observed molecular methyl iodide resonances to the *ns* ($6 < n < 10$) Rydberg states in CH₃I and CD₃I using two-, three-, and four-photon excitations. Frequencies are given in cm⁻¹. The uncertainty in the one-photon frequency is about 5 cm⁻¹.

$h\nu_{\text{fund}}$	$n h\nu_{\text{fund}}$	$h\nu_{\text{fund}}$	$n h\nu_{\text{fund}}$	Assignment
CH ₃ I		CD ₃ I		
16 057	64 230	16 063	64 254	7s[1]0 ₀ ⁰
16 180	64 720	16 192	64 766	7s[2]0 ₀ ⁰
16 582	49 746	16 623	49 868	6s[2]0 ₀ ⁰
16 685	50 055			6s[1]6 ₀ ¹
16 745	50 235	16 776	50 329	6s[2]3 ₀ ¹
16 975	50 924	16 902	50 707	6s[2]2 ₀ ¹
		17 028	51 084	6s[2]6 ₀ ²
17 338	52 014	17 173	51 520	6s[2]2 ₀ ²
17 419	69 676	17 426	69 702	7s[4]0 ₀ ⁰
17 484	69 935	17 495	69 981	8s[1]0 ₀ ⁰
17 543	70 174	17 558	70 232	8s[2]0 ₀ ⁰
17 718	53 154			6s[2]2 ₀ ³
17 866	71 465			8s[2]2 ₀ ¹ or 5 ₀ ¹
18 158	72 631	18 166	72 665	9s[1,2]0 ₀ ⁰
18 241	54 724	18 279	54 838	6s[4]0 ₀ ⁰
18 387	55 162			6s[4]3 ₀ ¹
18 495	73 979			9s[1,2]2 ₀ ¹ or 5 ₀ ¹
18 595	55 786	18 554	55 662	6s[4]2 ₀ ¹
18 815	75 260	18 825	75 300	8s[4]0 ₀ ⁰
18 959	56 876	18 825	56 475	6s[4]2 ₀ ²
21 410	64 230	21 414	64 242	7s[1]0 ₀ ⁰
21 573	64 718	21 586	64 757	7s[2]0 ₀ ⁰
		21 737	65 211	7s[1]2 ₀ ¹ or 5 ₀ ¹
21 912	65 736	21 916	65 749	See the text
23 369	70 106	23 375	70 125	8s[1]0 ₀ ⁰
23 422	70 265	23 428	70 284	8s[2]0 ₀ ⁰
24 232	48 464	24 455	48 910	6s[2]2 ₀ ¹
24 614	49 228	24 675	49 350	6s[2]3 ₀ ⁰
24 853	49 706	24 919	49 838	6s[2]0 ₀ ⁰
32 097	64 194	32 107	64 213	7s[1]0 ₀ ⁰
32 339	64 678	32 362	64 723	7s[2]0 ₀ ⁰
32 415	64 830	32 340	64 680	7s[1]6 ₀ ¹
		32 619	65 237	7s[1]2 ₀ ¹ or 5 ₀ ¹
32 968	65 937			7s[2]2 ₀ ¹ or 5 ₀ ¹
34 562	69 125	34 569	69 139	7s[3]0 ₀ ⁰
34 774	69 548	34 788	69 575	7s[4]0 ₀ ⁰
35 037	70 074	35 048	70 096	8s[1]0 ₀ ⁰
35 110	70 219	35 121	70 242	8s[2]0 ₀ ⁰
36 322	72 644	36 336	72 672	9s[1,2]0 ₀ ⁰
36 977	73 954	36 988	73 976	10s[1,2]0 ₀ ⁰

not be compared reliably. To emphasize this, the boundaries between different scans have been marked with vertical bars in the figures.

In the (2+1) ionization scheme the first photon may excite ground state methyl iodide molecules into the dissociative *A* band which results in extremely fast (< 100 fs)^{2,3} direct dissociation of the molecule into methyl radicals in the electronic ground state and iodine atoms in the ground state [*I*(²P_{3/2})] or in the spin-orbit excited state [*I**(²P_{1/2})]. Despite this dissociation it is observed that with the intensities used in the present experiments it is still possible to pump through the *A* band and excite molecular Rydberg states at the two-photon level. A consequence of the dissociation is that excitation spectra may not only show molecular resonances, but also resonances deriving from the fragments, in particular of the iodine atom. A total number of 95 atomic iodine resonances in the one-

photon energy region of 32 000–38 000 cm^{-1} have been observed. These lines could easily be assigned on the basis of previous studies^{10,20,45,48} and the tables of Minnhagen.⁴⁹ Most of these atomic resonances are an order of magnitude larger than the molecular resonances. Since our main interest is in the much broader molecular resonances, wavelength steps as large as 3 cm^{-1} have been used while recording the excitation spectra. These spectra therefore do not give an accurate representation of the relative intensities of the atomic resonances. Within some of the other ionization schemes it is in principle also possible to excite the molecule into the *A* band, albeit with two photons. In agreement with previous results, however, no fragment resonances have been observed under these circumstances.⁴⁵

The intense atomic iodine resonances interfere in the (2+1) experiments with the methyl iodide resonances of interest. Electrons arising from these resonances have kinetic energies $E_{\text{kin}} = (2+1)h\nu - I_{\alpha} + E_{\text{SO}}$. E_{SO} determines whether the resonance stems from $\text{I}(^2P_{3/2})$ for which its value is 0 eV or from $\text{I}^*(^2P_{1/2})$ for which it is 0.943 eV.⁴⁹ I_{α} is one of the ionization energies of the iodine atom, which in the present study can be limited to those of the 3P_2 , 3P_0 , 3P_1 , and 1D_2 states. The interference of electrons deriving from atomic resonances can in principle be minimized by setting gates on the methyl iodide $^2E_{3/2}$ and/or $^2E_{1/2}$ photoelectron peaks. However, under the conditions that a reasonable molecular signal was present, the number of iodine electrons often drove the detection system into severe overload. Also, the 3P_2 ionization limit for $\text{I}^*(^2P_{1/2})$ atoms is 9.509 eV,⁴⁹ whereas the $^2E_{3/2}$ ionization limit of methyl iodide is 9.538 eV.³⁹ The difference between these two energies is too small to set different gates in an excitation spectrum and, consequently, does not allow selective monitoring in cases where electrons resulting from ionization to these two limits are generated. Under the circumstances that molecular and atomic resonances nearly coincided we have therefore also employed mass-selective ion detection. As an example where such a strategy worked especially well we show in Fig. 1 the excitation spectra of the $7s[1]$ and $7s[2]$ states in CD_3I (*vide infra*), measured with both electron detection and with mass-resolved ion detection. In the electron-detected spectrum it is seen that the sharp atomic resonance at 32 103 cm^{-1} [$(^3P_0)6p[1] 1/2 \leftarrow \text{I}^*(^2P_{1/2})$] dominates the underlying broad resonance of the $7s[1]$ 0–0 transition. In contrast, the ion-detected spectrum at the mass of CD_3I beautifully reveals the presence of the molecular transition at 32 107 cm^{-1} .

The assignments in Table II have been made on the basis of the following considerations. In contrast to ion-detected REMPI spectroscopy, the ionization step in REMPI-PES provides information about the state in which the ion is produced. From the photoelectron spectrum obtained at a particular resonance information on the ionic core and the vibrational level of the excited Rydberg state can be extracted. First, the photoelectron spectrum shows whether ions are generated with a $^2E_{3/2}$ or $^2E_{1/2}$ core. Under the reasonable assumption of a predominant core conservation in the ionization step, we can consequently deduce whether the resonance arises from a Ryd-

FIG. 1. Two-photon excitation spectrum of the $7s[1]$ and $7s[2]$ Rydberg states in CD_3I using (a) electron detection and (b) mass-resolved ion detection at the mass of CD_3I . At 31 769 cm^{-1} the 0–0 transition to $6p[4]$ is also observed, while in (a) the narrow resonances derive from atomic iodine.

berg state with a $^2E_{3/2}$ or $^2E_{1/2}$ ionic core. Second, in the present study we are investigating Rydberg states whose potential energy surface is very similar to that of the ionic state to which they converge. In the absence of perturbing effects such as autoionization, it is to be expected that removal of the Rydberg electron will not influence the vibrational state of the ionic core, i.e., $\Delta v=0$ propensity should be valid. The vibrational state in which the generated ions are found is therefore a signature of the vibrational level of the Rydberg state which has been excited. The vibrational state of the methyl iodide ion can easily be determined using its known vibrational frequencies⁵⁰ (see Table I). On the basis of the photoelectron spectrum one can thus in principle reach a reliable assignment of a resonance in the excitation spectrum. Such assignments have been carefully checked with the results of previous studies which give information on isotope shifts and vibrational frequencies. It has been shown that upon complete deuteration vibrationless origin bands of Rydberg states in CH_3I are shifted by +110 cm^{-1} in the $6s$ Rydberg state^{32,43} to about +20 cm^{-1} in the higher-lying Rydberg states.²⁰ Additionally, the studies of Felps *et al.*³² and Parker *et al.*⁴³ on the $6s$ Rydberg state in methyl iodide have given an indication of

FIG. 2. Three-photon REMPI-PES excitation spectrum of the 6s Rydberg state in CD_3I . Apart from the 6s resonances, transitions to higher-lying Rydberg states located at the four-photon level are also observed. The assignments of the resonances are given in Table II.

the vibrational frequencies in the Rydberg states of CH_3I and CD_3I .

The 6s Rydberg state examined with (3+2) REMPI-PES may serve as an example of how our assignments in Table II have been arrived at. In Fig. 2 the three-photon excitation spectrum of the 6s Rydberg state in CD_3I is shown (*vide infra*). Previously this state has been investigated systematically using one-photon^{32–34} as well as two-photon excitations.^{35,43} The assignments that we find on the basis of the photoelectron spectra of the resonances can consequently be compared with these previous assignments, and validate our assumptions concerning core conservation and Franck–Condon behavior. In Fig. 3 the photoelectron spectra taken at 18 279 (18 241) and 18 554 (18 595) cm^{-1} in CD_3I (CH_3I), previously assigned to the origin and the ν_2 vibration of 6s[4] are shown. The peaks observed in these photoelectron spectra are summarized in Table III, together with the theoretically predicted positions. The photoelectron spectrum obtained at 18 279 (18 241) cm^{-1} in CD_3I (CH_3I) is dominated by the ionic origin of the $^2E_{1/2}$ core. From this we would conclude that the resonance corresponds to the vibrationless origin of a state with a $^2E_{1/2}$ ionic core. This is in agreement with previous studies using one- and two-photon excitations which have assigned this resonance to the origin of the 6s[4] state. The photoelectron spectrum at 18 554 (18 595) cm^{-1} in CD_3I (CH_3I), on the other hand, shows the largest intensity in the $\nu_2=1$ vibration of the $^2E_{1/2}$ ionic state. Our conclusion that these resonances derive from the $\nu_2=1$ vibration of a state with a $^2E_{1/2}$ ionic core agrees with previous assignments of these bands as the 6s[4] 2_0^1 bands.

We have studied the 6s Rydberg state using two- and three-photon excitations. At this point we will consider only states [2], [3], and [4] and postpone the discussion of state [1] since, as will become clear, the excitation behavior of this state is rather peculiar. Our results on states [2], [3], and [4] using two-photon excitation are in good agreement

FIG. 3. Photoelectron spectra obtained at the (a) $6s[4]0_0^0$ and (c) $6s[4]2_0^1$ transitions in CH_3I using three-photon excitation. In (b) and (d) the photoelectron spectra of the analogous transitions in CD_3I are depicted. The assignment of the photoelectron peaks is given in Table III.

with the previous study of Parker *et al.*,⁴³ who have investigated these states using two-photon excitation as well, albeit with ion rather than with electron detection. In Fig. 2 the three-photon excitation spectrum of the 6s states in CD_3I has been depicted. In this spectrum additional resonances can be observed that occur at the four-photon level. If we consider for the moment only the 6s resonances, it can be concluded that at the three-photon excitation level the results show satisfactory agreement with the results obtained at the one- and two-photon excitation level. The major difference encountered with three-photon excitation concerns the intensity of the 6s[3] state. In one-photon excitation this state is extremely weak. This can be understood from group theoretical considerations, which indicate a parallel transition to this state. In two-photon excitation, on the other hand, the transition is of comparable strength as the transition to 6s[4]. From our present results it can be observed that in three-photon excitation the transition to 6s[3] is evidently very weak again. One of the possible explanations for its weakness is that the transition might be induced through the *zzz* component of the three-photon hyperpolarizability tensor. A second difference of interest is found in the 6s[2] 3_0^1 band. This band is present in CH_3I but absent in CD_3I using two-photon excitation. Sapers *et al.*²⁵ have concluded from the absence of this band in CD_3I that CD_3I is more effectively predissociated by the *A* band than CH_3I . However, in the present study using three-photon excitation we have identified this band in both isotopes. This can qualitatively be understood on the

TABLE III. Observed peaks in the photoelectron spectra obtained at the $6s[4]0_0^0$ and $6s[4]2_0^1$ transitions in CH_3I and CD_3I using three-photon excitation.

Observed electron energy (eV)	Calculated electron energy (eV)	Ionic state
$6s[4]0_0^0(\text{CH}_3\text{I})$ $h\nu = 18\,241\text{ cm}^{-1}$		
1.150	1.144	$\text{CH}_3\text{I}^+(^2E_{1/2})$
1.774	1.770	$\text{CH}_3\text{I}^+(^2E_{3/2})$
$6s[4]0_0^0(\text{CD}_3\text{I})$ $h\nu = 18\,279\text{ cm}^{-1}$		
0.882	0.880	$\text{I}^+(^3P_2) \leftarrow \text{I}^+(^2P_{3/2})$
1.164	1.168	$\text{CD}_3\text{I}^+(^2E_{1/2})$
$6s[4]2_0^1(\text{CH}_3\text{I})$ $h\nu = 18\,595\text{ cm}^{-1}$		
1.213	1.207	$\text{CH}_3\text{I}^+(^2E_{1/2})\ \nu_2=1$
1.258	1.250	$\text{CH}_3\text{I}^+(^2E_{1/2})\ \nu_6=1$
1.369	1.364	$\text{CH}_3\text{I}^+(^2E_{1/2})$
1.468		
1.669	1.685	CH_3^+
1.882	1.876	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_6=1$
1.990	1.990	$\text{CH}_3\text{I}^+(^2E_{3/2})$
$6s[4]2_0^1(\text{CD}_3\text{I})$ $h\nu = 18\,556\text{ cm}^{-1}$		
1.230	1.220	$\text{CD}_3\text{I}^+(^2E_{1/2})\ \nu_2=1$
1.341	1.339	$\text{CD}_3\text{I}^+(^2E_{1/2})$
1.652	1.660	CD_3^+
1.763		
1.811	1.835	$\text{CD}_3\text{I}^+(^2E_{3/2})\ \nu_5=1$
1.848	1.846	$\text{CD}_3\text{I}^+(^2E_{3/2})\ \nu_2=1$
1.985	1.965	$\text{CD}_3\text{I}^+(^2E_{3/2})$

basis of intensity arguments. In three-photon excitation higher laser intensities are employed than in two-photon excitation. The up-pumping rate will consequently be larger in three-photon excitation. Although CD_3I seems to be more effectively predissociated, we can conclude that at the intensities used in three-photon excitation the absorption of ionizing photons competes effectively with the predissociation occurring in the 3_0^1 band.

The next member of the ns Rydberg series, the $7s$ state, has been observed in the present study using two-, three-, and four-photon excitations (see Table II and Figs. 1, 2, 5, and 6). Previously, states [2] and [4] have been assigned in a vuv absorption study of CH_3I .^{36,37} Resonances have also been observed at approximately these energies with $(2+1)$ REMPI spectroscopy,^{20,45} but no clear consensus exists concerning their assignments. The two-photon excitation spectrum of $7s[1]$ and $7s[2]$ measured in the present study using ion and electron detection has been shown before in Fig. 1. Gedanken *et al.*,⁴⁵ in their REMPI study of the $6p$ Rydberg state, assigned the resonance corresponding to state [2] to the $\nu_5=1$ vibration of one of the states of the $6p$ Rydberg state with a $^2E_{1/2}$ ionic core. When the photoelectron spectrum taken at this energy [see Fig. 4(b) and Table IV] is considered, it is clear that the resonant state is a state with a $^2E_{3/2}$ rather than a $^2E_{1/2}$ core as should have been the case if the assignment of Gedanken *et al.* were correct. Moreover, ions are predominantly created in the vibrationless ionic state, demonstrating that the resonance corresponds to a 0–0 transition. In agreement with the previous

FIG. 4. Photoelectron spectra obtained in CH_3I at the 0–0 transitions to the (a) $7s[1]$ and (b) $7s[2]$ states using two-photon excitation. The assignment of the photoelectron peaks is given in Table IV.

vuv work we have therefore assigned this resonance to the $7s[2]$ state. Assignment of the $7s[1]$ state is a little more problematic since this state has not been observed before. On the basis of previous considerations made for the $6s$ state,^{32,51} it can be expected that this state is lower than state [2] by a few hundred wave numbers. Inspection of the photoelectron spectra taken at resonances close to state [2] reveals that there is indeed a resonance at $64\,194$ ($64\,213$) cm^{-1} in CH_3I (CD_3I) whose photoelectron spectrum shows that it belongs to the 0–0 transition of a state with a $^2E_{3/2}$ core [see Fig. 4(a) and Table IV]. We notice that Gedanken *et al.*⁴⁵ have assigned this resonance to the $\nu_6=1$ band of a $6p$ state with a $^2E_{1/2}$ core, but our REMPI-PES results show that it actually should be assigned to the $7s[1]$ state. States [3] and [4] have as yet not been directly assigned in multiphoton experiments. Black and Powis have observed in their $(2+1)$ REMPI studies of CD_3I a resonant feature consisting of a rotational contour around the energy of state [4], but left this resonance unassigned.²⁰ In our study we have observed this resonance as well. Our REMPI-PES results show that this feature derives from a state with a $^2E_{1/2}$ ionic core. In line with the assignments of the vuv study^{36,37} it has been assigned to the $7s[4]$ state. At

TABLE IV. Observed peaks in the photoelectron spectra obtained at the $7s[1]0_0^0$ and $7s[2]0_0^0$ transitions in CH_3I using two-photon excitation.

Observed electron energy (eV)	Calculated electron energy (eV)	Ionic state
$7s[1]0_0^0(\text{CH}_3\text{I})$ $h\nu = 32\,097\text{ cm}^{-1}$		
1.548	1.551	$\text{I}^+(^3P_1) \leftarrow \text{I}^*(^2P_{1/2})$
1.654		peak 1 (see the text)
2.022	2.022	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_4=1$
2.402	2.401	$\text{CH}_3\text{I}^+(^2E_{3/2})$
$7s[2]0_0^0(\text{CH}_3\text{I})$ $h\nu = 32\,339\text{ cm}^{-1}$		
1.700		peak 1 (see the text)
1.745	1.751	$\text{CH}_3\text{I}^+(^2E_{1/2})\ \nu_6=1$
1.864	1.865	$\text{CH}_3\text{I}^+(^2E_{1/2})$
1.942		
2.108	2.112	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_4=1$
2.489	2.491	$\text{CH}_3\text{I}^+(^2E_{3/2})$

FIG. 5. Three-photon REMPI-PES excitation spectrum of the $7s[1]$ and $7s[2]$ states in CD_3I . The assignment of the resonances is given in Table II.

a slightly lower energy (see Table II) a resonance can be observed in two-photon excitation whose photoelectron spectrum indicates that it corresponds to a vibrationless origin of a state with a $^2E_{1/2}$ core. This resonance can consequently be assigned to the $7s[3]$ state.

One of our main interests in the present study concerns the assignment of state [1] in the ns Rydberg states. In the $(2+1)$ REMPI-PES analysis of the spectrum has been somewhat complicated by the presence of atomic iodine resonances, which result from direct dissociation in the A band reached with the first photon. In order to confirm our assignment of the $7s[1]$ state with two-photon excitation we have therefore employed three- and four-photon excitations as well. Such excitation schemes have the advantage that the A band cannot be excited, and thus that no atomic fragments are formed by direct dissociation. Additionally, the wavelengths employed in these experiments are such that ionization of fragments formed by predissociation of the Rydberg state is considerably less probable. In Fig. 5 the three-photon excitation spectrum of the $7s(^2E_{3/2})$ Rydberg states in CD_3I is depicted, while the four-photon excitation spectrum is part of Fig. 2. It can be concluded from Table II that the energies at which the $7s$ Rydberg state is observed in three- and four-photon excitations are in good agreement with the results of the $(2+1)$ experiments.

Up until now we have seen that the assignment of a band in the excitation spectrum could be obtained reliably from its photoelectron spectrum. An exception to this is found in the assignment of the strong peak in the three-photon excitation spectra at $65\,736\text{ cm}^{-1}$ in CH_3I and at $65\,749\text{ cm}^{-1}$ in CD_3I . Mass-resolved ion spectroscopy has positively identified methyl iodide as the carrier of this resonance. In view of the proximity of these resonances to the $0-0$ transitions of the $7s[1]$ and $7s[2]$ states, a first guess for their assignment would be that these peaks belong to the vibrational progression of either one of these states. The photoelectron spectrum in CH_3I is dominated by two equally intense peaks, the $^2E_{3/2}$ origin and a $^2E_{3/2}$ peak with 0.17 eV vibrational energy. In CD_3I the same kind of

FIG. 6. Two-photon REMPI-PES excitation spectrum of the $8s[1]$ and $8s[2]$ states in CD_3I . Apart from the $0-0$ transitions to these two states resonances are also observed of the fragments, i.e., the methyl radical and iodine atoms.

photoelectron spectrum is observed, although the second peak now has a vibrational energy of 0.12 eV . The value of 0.12 eV corresponds well with the $\nu_2=1$ vibration of the ion, but the value of 0.17 eV in CH_3I is significantly larger than the $\nu_2=1$ vibration of the ion (0.157 eV), and seems rather small to be correlated with the $\nu_5=1$ vibration of the ion ($\approx 0.18\text{ eV}$). The photoelectron spectra thus do not offer an unambiguous identification of this band. One of the possible assignments could be that the resonance in CH_3I corresponds to $7s[1]5_0^1$ and in CD_3I to $7s[2]2_0^1$, implying frequencies for ν_5 and ν_2 of 1506 and 992 cm^{-1} , respectively. Such frequencies are in line with the values expected for these vibrations. The obvious argument against such an assignment is, however, that it is not clear why ν_5 is observed in CH_3I and not in CD_3I , and vice versa for ν_2 . The other possible assignment of this resonance is that it would be the $0-0$ transition to another Rydberg state. Such an assignment would be corroborated by the small positive isotope shift ($+13\text{ cm}^{-1}$) of the band. In this respect it is interesting to note that the resonance is only very weakly observed in two- and four-photon excitation where it shows the same kind of photoelectron spectrum as in three-photon excitation. This near-absence might be due to different selection rules implying as well that the band derives from a Rydberg state other than the $7s$ state. However, no suitable candidates for such a state can be found in this energy region.^{36,37}

The study of the $8s$, $9s$, and $10s$ Rydberg states has been limited to states [1] and [2]. Of these Rydberg states only the $8s$ state has previously been observed with $(2+1)$ REMPI spectroscopy in the study of Black and Powis,²⁰ though no specific assignment to state [1] and/or [2] was made. Our REMPI-PES results show that the resonances observed in their study are readily reproduced (Fig. 6) and can be assigned to the $8s[1]$ and $8s[2]$ states. We notice that the assignment of $8s[2]$ is in good agreement with the vuv assignments.^{36,37} In the study of the $8s$ Rydberg state the same problem is encountered as before in the study of the

FIG. 7. Two-photon REMPI-PES excitation spectrum of the $9s[1,2]$ states in CH_3I . The magnified part of the spectrum, showing the 0-0 transition to these two states, has been obtained collecting only those electrons that derive from molecular ionization.

FIG. 9. Two-photon excitation spectrum of the energy region just below the 0-0 transition to $6s[2]$ in CD_3I . The assignment of the resonances is given in Table II.

$7s$ state, i.e., the analysis of the spectrum is complicated by strong fragment resonances. Here too, we have therefore made use of three- and four-photon excitations. The results of these experiments (see Table II) agree satisfactorily with the $(2+1)$ results, albeit that the excitation energy of the $8s[1]$ state in four-photon excitation is somewhat low compared to the two- and three-photon results. Despite that the A band is not excited in the three- and four-photon excitation schemes, atomic iodine resonances are still present in the three-photon excitation spectrum. These resonances at 23 387 and 23 455 cm^{-1} are thought to occur because of predissociation of methyl iodide in the Rydberg states with subsequent $(3+1)$ ionization of ground state iodine atoms via the $(^3P_2)5d[2]5/2$ and $3/2$ states in the JK coupling scheme, respectively.⁴⁹

In Figs. 7 and 8 the two-photon excitation spectra of the $9s(^2E_{3/2})$ and $10s(^2E_{3/2})$ Rydberg states, respectively,

FIG. 8. Two-photon REMPI-PES excitation spectrum of the $10s[1,2]$ states in CH_3I . The magnified part of the spectrum, showing the 0-0 transition to these two states, has been obtained collecting only those electrons that derive from molecular ionization.

are shown for CH_3I . It should be realized that these states are located in an energy region where at the one-photon level the maximum absorption of the A band is found.⁴¹ Moreover, the energy at the two-photon level is close to the 3P_2 ionization limit of $\text{I}^*(^2P_{1/2})$ atoms. The identification of these states is consequently severely hampered by a large number of nearby atomic iodine resonances with an intensity that is almost 2 orders of magnitude larger than those of the molecular resonances. The observation of only one

FIG. 10. Photoelectron spectra obtained at the (a) $6s[2]0^0_0$ and (c) $6s[2]3^0_1$ transitions in CD_3I . The photoelectron spectra obtained at the analogous transitions in CH_3I are depicted in (b) and (d), respectively. The assignment of the peaks is given in Table V.

TABLE V. Observed peaks in the photoelectron spectra obtained at the $6s[2]0_0^0$ and $6s[2]3_1^0$ transitions in CH_3I and CD_3I using two-photon excitation.

Observed electron energy (eV)	Calculated electron energy (eV)	Ionic state
$6s[2]0_0^0(\text{CD}_3\text{I})$ $h\nu=24\,919\text{ cm}^{-1}$		
2.823	2.820	$\text{CD}_3\text{I}^+(^2E_{3/2})$
$6s[2]0_0^0(\text{CH}_3\text{I})$ $h\nu=24\,853\text{ cm}^{-1}$		
1.487		peak 2 (see the text)
1.975	1.982	$\text{CH}_3\text{I}^+(^2E_{1/2})\ v_5=1$
2.039	2.048	$\text{CH}_3\text{I}^+(^2E_{1/2})\ v_6=1$
2.151	2.162	$\text{CH}_3\text{I}^+(^2E_{1/2})$
2.231		
2.411	2.409	$\text{CH}_3\text{I}^+(^2E_{3/2})\ v_4=1$
	2.420	$\text{CH}_3\text{I}^+(^2E_{3/2})\ v_1=1$
2.631	2.631	$\text{CH}_3\text{I}^+(^2E_{3/2})\ v_2=1$
2.679	2.674	$\text{CH}_3\text{I}^+(^2E_{3/2})\ v_6=1$
2.787	2.788	$\text{CH}_3\text{I}^+(^2E_{3/2})$
$6s[2]3_1^0(\text{CD}_3\text{I})$ $h\nu=24\,675\text{ cm}^{-1}$		
1.466		peak 2 (see the text)
1.946	1.959	$\text{CD}_3\text{I}^+(^2E_{1/2})\ v_3=2$
	1.954	$\text{CD}_3\text{I}^+(^2E_{1/2})\ v_2=1$
1.999	2.016	$\text{CD}_3\text{I}^+(^2E_{1/2})\ v_3=1$
2.066	2.073	$\text{CD}_3\text{I}^+(^2E_{1/2})$
2.128	2.135	$\text{CD}_3\text{I}^+(^2E_{1/2}) \leftarrow \text{CD}_3\text{I}(^1A_1)3_1^0$
2.215		
2.402	2.414	$\text{CD}_3\text{I}^+(^2E_{3/2})\ v_4=1$
2.632	2.642	$\text{CD}_3\text{I}^+(^2E_{3/2})\ v_3=1$
2.700	2.699	$\text{CD}_3\text{I}^+(^2E_{3/2})$
2.767	2.761	$\text{CD}_3\text{I}^+(^2E_{3/2}) \leftarrow \text{CD}_3\text{I}(^1A_1)3_1^0$
$6s[2]3_1^0(\text{CH}_3\text{I})$ $h\nu=24\,614\text{ cm}^{-1}$		
0.735		peak 1 (see the text)
1.448		peak 2 (see the text)
1.921	1.929	$\text{CH}_3\text{I}^+(^2E_{1/2})\ v_6=1$
2.035	2.043	$\text{CH}_3\text{I}^+(^2E_{1/2})$
2.514	2.512	$\text{CH}_3\text{I}^+(^2E_{3/2})\ v_2=1$
2.611	2.608	$\text{CH}_3\text{I}^+(^2E_{3/2})\ v_3=1$
2.668	2.669	$\text{CH}_3\text{I}^+(^2E_{3/2})$

band for the $9s(^2E_{3/2})$ and $10s(^2E_{3/2})$ Rydberg states could therefore indicate that either the second origin is hidden under an atomic resonance, or that the two origins of state [1] and [2] overlap. Before we have seen that the energy separation between state [1] and [2] rapidly decreases from 484 (510) cm^{-1} in the $7s$ manifold to 145 (146) cm^{-1} in the $8s$ manifold of CH_3I (CD_3I). Bearing this in mind, and comparing the excitation energies in CH_3I with those in CD_3I leads us to the conclusion that states [1] and [2] overlap in the $9s$ and $10s$ Rydberg states.

We now turn our attention to state [1] of the ns Rydberg states. In previous studies of the $6s$ Rydberg state this state has attracted considerable attention because of its small oscillator strength in one- and two-photon excitations. Let us first consider what is to be expected on group theoretical grounds for the transition probabilities to state [1] in one- and two-photon excitation. Within the $C_{\infty v}$ point group state [1] is of Δ symmetry and consequently cannot be reached in one-photon excitation. The transition to state [2], which is of Π symmetry is, on the other hand, fully allowed. Within the C_{3v} point group states [1] and [2]

are of E symmetry. Consequently, mixing of these two states will introduce some one-photon transition probability to state [1] in one-photon transitions. In one-photon absorption studies^{33,34} of the $6s$ Rydberg state a very weak band has indeed been observed below state [2]. This band consists of four peaks, two of which have been assigned as v_3 hot bands of state [2], and two as arising from the 0–0 transition to state [1].³⁴ However, in a (1+1) REMPI study²⁴ only the $[1]6_0^1$ transition could be observed and not the 0–0 transition to state [1]. Problems arise when the two-photon excitation spectra are considered. Within such an excitation scheme the transition to state [1] is allowed in both $C_{\infty v}$ and C_{3v} and is expected to have about the same intensity as that to state [2]. This is not confirmed by previous⁴³ and our (2+2) REMPI experiments on the $6s$ Rydberg state. In these experiments a very weak band is observed at approximately the energy of the 0–0 transition to state [1] as assigned in the one-photon absorption studies, but this band has previously been assigned to $[2]3_1^0$.⁴³ In previous two-photon excitation studies it has therefore been concluded that if the $6s[1]$ origin is present at all in

the excitation spectrum, it is at least 100 times weaker than the $6s[2]$ origin.

Since there is still some ambiguity in the assignment of the $6s[1]$ origin band using other than one-photon absorption methods, we have investigated by REMPI-PES the energy region in which this transition has been assigned in one-photon absorption studies. The resonances observed using two- and three-photon excitations compare quite well with the work of Parker *et al.*⁴³ In Fig. 9 the energy region just below the $6s[2]$ origin obtained in a two-photon excitation is shown for CD_3I . In order to observe these resonances relatively high laser powers had to be used. The excitation spectrum therefore shows, apart from the resonances of interest at the two-photon level, also resonances at the three-photon level as can be concluded from their small, positive isotope shift. The resonances assigned previously to the $6s[2]2_1^0$ and $6s[2]3_1^0$ hot bands can easily be identified. In one-photon absorption and MCD experiments^{33,34} the $6s[1]$ origin band has been observed to coincide with the $6s[2]3_1^0$ hot band. Such an assignment is in agreement with the following considerations. First, the $6s[1]6_0^1$ vibration has been assigned by Felps *et al.*³² in a one-photon absorption study and has also been observed in several REMPI studies.^{24,25,44} From the position of this band and the vibrational energy of ν_6 in other $6s$ states one can infer that the origin band of $6s[1]$ is close to the 3_1^0 hot band of the much stronger $6s[2]$ state. Second, Mulliken has shown⁵¹ that the energy difference between states [1] and [2] is in first approximation equal to the energy difference between states [3] and [4]. From this argument the origin band of $6s[1]$ can be placed about 600 cm^{-1} below the origin of state [2], again close to $[2]3_1^0$. In Fig. 10 we show for both CH_3I and CD_3I the photoelectron spectra taken at the $6s[2]$ 0-0 transition and the photoelectron spectra taken at what has been assigned before as $6s[2]3_1^0$. An analysis of these spectra is given in Table V. Surprisingly, the photoelectron spectra of CH_3I and CD_3I exhibit a clearly distinct behavior. At the $6s[2]$ origin the spectrum taken for CD_3I shows an unambiguous $^2E_{3/2}$ origin, while in CH_3I several strong vibrations are seen that are not at all indicative of an origin band. Analogous behavior is observed in the photoelectron spectra taken at the $6s[2]3_1^0$ band: the spectrum of CD_3I shows a 0-0 transition character as well as behavior representative of a hot band of ν_3 , the photoelectron spectrum of CH_3I is dominated by the $\nu_2=1$ vibration. These seemingly contradictory spectra can be explained by the observation that the ionization step is a two-photon process. Consequently, the photoelectron spectra taken at resonances at the two-photon level might be influenced by spurious (near-)resonant states at the three-photon level. We conclude that the photoelectron spectra shown here for CH_3I are heavily perturbed by accidental three-photon resonances and do not represent a true reflection of the nature of the resonant state at the two-photon level. The photoelectron spectra taken for CD_3I , on the other hand, are not affected by such resonances and seem representative of the character of the resonance at the two-photon level. The photoelectron spectrum of the $6s[2]3_1^0$ band in CD_3I corroborates an

FIG. 11. Two-photon excitation spectra of the $6p$ Rydberg state in (a) CH_3I and (b) CD_3I . The lower trace in both spectra has been obtained under low laser intensity conditions, the upper trace under high laser intensity conditions. The assignment of the resonances is given in Table VI.

assignment of this band as containing the $6s[2]3_1^0$ band and the origin of the $6s[1]$ state.

The above considerations have shown that the $6s[1]$ state does not show an intensity in two-photon excitation that would be expected on the basis of group theoretical arguments. From our three-photon excitation spectra we can conclude that also in such an excitation scheme the transition to this state is weak. It is therefore worthwhile to consider to what extent higher lying ns Rydberg states resemble the $6s$ Rydberg state. In the present study we have been able to investigate for the first time the $7s$ to $10s$ Rydberg states by multiphoton excitation. These results demonstrate that states [1] and [2] of the $7s$ and $8s$ Rydberg states have a comparable intensity in two-photon excitation, as would be expected. In the $9s$ and $10s$ Rydberg states, on the other hand, the two states overlap. We therefore have to conclude that it is specifically the $6s[1]$ state that deviates from the general behavior of ns states. The most striking difference between the $6s[1]$ state and the other $ns[1]$ states is that state $6s[1]$ is the state closest to the dissociative A band. An explanation for the weakness of

TABLE VI. Observed resonances of the $6p$ Rydberg state of CH_3I and CD_3I using two-photon excitation. Frequencies are given in cm^{-1} . The uncertainty in the frequency is 10 cm^{-1} .

$2h\nu$ (CH_3I)	$2h\nu$ (CD_3I)	Assignment
58 336	58 397	$[1]0_0^0$
58 824	58 869	$[1]3_0^1$
58 918	58 989	$[2]0_0^0$
59 358	59 396	$[2]3_0^0$
59 582	59 343	$[1]2_0^1$
59 716	59 426	$[1]5_0^0$
60 151	59 910	$[2]2_0^1$
60 682		$[3]0_0^0$
61 174		$[3]3_0^0$ and/or $[1]1_0^1$
	60 498	$[1]1_0^1$
61 344		$[2]2_0^2$ and/or $[1]4_0^1$
	60 808	$[2]2_0^2$
	60 647	$[1]4_0^1$
	60 907	$[2]2_0^1 5_0^1$
	60 961	Not assigned
61 748	61 098	$[2]1_0^1$
61 886		$[3]2_0^1$
62 419	61 410	$[1]1_0^2 2_0^1$
62 649	61 858	$[2]4_0^1 6_0^1$
63 074	63 052	See the text
63 493	63 538	$[4]0_0^0$
63 958	63 990	$[4]3_0^1$
	64 467	$[4]3_0^2$

$6s[1]$ might consequently be related to predissociation of $6s[1]$ by the states of the A band.

2. Spectroscopy of the $6p$ Rydberg state

In the previous section we have considered the ns Rydberg series and have identified these states for $6 \leq n \leq 10$. The next states of interest concern the states arising from excitation of a $5p\pi$ lone pair electron of the iodine atom to the $6p$ molecular Rydberg orbital. Group theoretically 16 states are possible, 8 of which have a $^2E_{3/2}$ and 8 a $^2E_{1/2}$ core, but the energy differences between these states are not known. In Fig. 11 the excitation spectra as measured by $(2+1)$ REMPI-PES are shown for CH_3I and CD_3I . These figures consist of two parts: one part is measured using low laser power, and one part using high laser power. The positions of the peaks, together with the assignment as determined from photoelectron spectroscopy, are given in Table VI.

The $6p$ Rydberg states and their vibrational progressions have first been investigated by Gedanken *et al.*⁴⁵ using $(2+1)$ REMPI spectroscopy. In several studies these states have subsequently been investigated as well,^{46,52} but the assignments of the resonances have in most cases been taken from the study of Gedanken *et al.* Our assignments are considerably different, especially when origin bands are considered. In previous studies the strong peak at 58 918 ($58\,989$) cm^{-1} in CH_3I (CD_3I) has been assigned as $6p(^2E_{3/2})6_0^1$. The photoelectron spectrum taken at this resonance is presented in Fig. 12(b) (see also Table VII) and shows that this band cannot be a $\nu_6=1$ band. Rather, it should be assigned as a second $6p(^2E_{3/2})$ origin band, designated here as state $[2]$. An origin has previously been

FIG. 12. Photoelectron spectra obtained at the (a) $6p[1]0_0^0$, (b) $6p[2]0_0^0$, and (c) $6p[3]0_0^0$ transitions in CH_3I using two-photon excitation. The assignment of the peaks is given in Table VII.

reported at this position in one-photon absorption studies,³⁶ so transitions to this state are allowed in both one- and two-photon absorption. The transition to the origin at 58 336 ($58\,397$) cm^{-1} in CH_3I (CD_3I), designated as state $[1]$, on the other hand, is one-photon forbidden but two-photon allowed. In the previous section on the ns Rydberg states we have shown that the peaks, originally assigned to the $6p(^2E_{1/2})6_0^1$ and the $6p(^2E_{1/2})5_0^1$, correspond to transitions to the vibrationless origins of the $7s[1]$ and $7s[2]$

TABLE VII. Observed peaks in the photoelectron spectra obtained at the $6p[1]0_0^0$, $6p[2]0_0^0$, and $6p[3]0_0^0$ transitions in CH_3I using two-photon excitation.

Observed electron energy (eV)	Calculated electron energy (eV)	Ionic state
$6p[1]0_0^0(\text{CH}_3\text{I})$ $h\nu = 29\,168\text{ cm}^{-1}$		
1.256	1.250	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_3=1$
1.312	1.311	$\text{CH}_3\text{I}^+(^2E_{3/2})$
$6p[2]0_0^0(\text{CH}_3\text{I})$ $h\nu = 29\,459\text{ cm}^{-1}$		
0.801	0.793	$\text{CH}_3\text{I}^+(^2E_{1/2})$
1.260	1.262	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_2=1$
1.313	1.305	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_6=1$
1.363	1.358	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_3=1$
1.420	1.419	$\text{CH}_3\text{I}^+(^2E_{3/2})$
$6p[3]0_0^0(\text{CH}_3\text{I})$ $h\nu = 30\,341\text{ cm}^{-1}$		
1.375	1.380	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_1=1$
1.415		
1.459	1.434	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_2=2$
1.579	1.591	$\text{CH}_3\text{I}^+(^2E_{3/2})\ \nu_2=1$
1.743	1.748	$\text{CH}_3\text{I}^+(^2E_{3/2})$

states, respectively. Photoelectron spectroscopy shows that the assignment of the peaks at $63\,493$ ($63\,538$) cm^{-1} to a $6p(^2E_{1/2})$ origin, designated here as state [4], of CH_3I (CD_3I) is correct. It can therefore be concluded that the $(2+1)$ REMPI excitation spectrum is dominated by two origin bands with a $^2E_{3/2}$ ion core and one with a $^2E_{1/2}$ ion core. The vibrational structure belonging to these states is much weaker than the 0–0 transitions and only shows up under high-intensity conditions.

Of the weaker peaks the one at $60\,682\text{ cm}^{-1}$ in CH_3I is of considerable interest. The photoelectron spectrum taken at this energy, shown in Fig. 12(c) (see also Table VII), demonstrates the same kind of behavior as the photoelectron spectra taken at the 0–0 transitions of state [1] and [2] (see Fig. 12 and Table VII), i.e., a strong 0–0 transition to the $^2E_{3/2}$ state of the ion. In CD_3I , however, no such origin can be found. Assignment of this peak to the origin band of another $6p$ state with a $^2E_{3/2}$ ion core, designated as state [3], is corroborated by the following. First, if the peak would be a vibrational band, then the energy difference of this peak with respect to the origin bands of state [1] and [2] should have corresponded to one of the vibrational frequencies or to a combination of vibrational frequencies of CH_3I . Second, peaks are observed at higher energies which on the basis of their photoelectron spectrum and their energy difference with respect to the origin of [3] can be assigned to the $\nu_3=1$ and $\nu_2=1$ vibrations. The vibrational frequencies for ν_3 and ν_2 in state [3] would then be 492 and 1204 cm^{-1} , respectively, in good agreement with the values found for these frequencies in states [1] and [2]. Third, though the vibrational activity is small, it involves mainly ν_2 and ν_3 in states [1] and [2]. The assignment as given above would also imply that the vibrational activity of state [3] is restricted to ν_2 and ν_3 . The reason why state [3] is not observed in CD_3I is not clear. One of the possible explanations might be that the efficiency of predissociation is

isotope dependent, as has been suggested for the $6s$ Rydberg state.²⁵

Another interesting peak is found at $63\,074$ ($63\,052$) cm^{-1} in CH_3I (CD_3I). Gedanken *et al.* have assigned this peak to the $6p[4](^2E_{1/2})3_1^0$ hot band. This would imply a ground-state vibrational frequency of ν_3 of 419 cm^{-1} in CH_3I and 486 cm^{-1} in CD_3I which is at odds with the known ground state-frequencies (see Table I). The photoelectron spectra in both CH_3I and CD_3I show some structure near the $^2E_{1/2}$ 0–0 transition which could indicate that the resonance is a $6p(^2E_{1/2})3_1^0$ hot band, but also an equally strong $^2E_{3/2}$ 0–0 transition. In one-photon absorption experiments a $5d(^2E_{3/2})$ origin has been assigned in this energy region.³⁷ It is consequently possible that the resonance derives from a $5d(^2E_{3/2})$ state. This would imply, however, that the isotope shift of the $5d(^2E_{3/2})$ state would be -22 cm^{-1} , whereas the other methyl iodide states investigated here all show a positive isotope shift.

Gedanken *et al.* have found several resonances near the $6p$ Rydberg state at approximately $67\,800\text{ cm}^{-1}$ showing a negative isotope shift.⁴⁵ This was taken as an indication that these states derive from the methyl radical. We have measured these states as well. We confirm the negative isotope shift, but our photoelectron spectra show no sign of electrons deriving from the ionization of the methyl radical. Of these resonances a $^2E_{3/2}$ origin has been found at $67\,932\text{ cm}^{-1}$, which, on the basis of previous one-photon absorption studies,^{36,37} might be assigned to one of the $7p$ Rydberg states, and a $^2E_{1/2}$ origin at $67\,807\text{ cm}^{-1}$ which might be associated with one of the $5d(^2E_{1/2})$ states.³⁷

The $6p$ Rydberg state is known to predissociate with a dissociation time of 175 and 325 fs in CH_3I and CD_3I , respectively.³⁰ It seems therefore peculiar that, using electron detection, no electrons have been observed that arise from ionization of one of the fragments. In particular, no evidence has been found for the ionization of the ground state methyl radical, although it has a strong $3p^2A_2''$ resonance in this wavelength region.^{11–13,53,54} The same results have been obtained when mass-resolved ion detection is employed. In these experiments we have registered the excitation spectra in the $\text{CH}(\text{D})_3$, I, and $\text{CH}(\text{D})_3\text{I}$ mass channels. These excitation spectra all closely resembled the excitation spectrum obtained with electron detection. The fragment ions, that are detected, must consequently be created after ionization of the molecule. It can then be concluded that under the present experimental conditions the rate for ionization from the $6p$ Rydberg state is considerably larger than the predissociation rate to the A band.

3. Anomalous photoelectrons

In the discussion above it has been shown that the peaks in the photoelectron spectra measured in the present study could nearly all be satisfactorily explained by the ionization of methyl iodide or one of its fragments. Still, the photoelectron spectra of both CH_3I and CD_3I contain two peaks that cannot be explained in this way. An example of a photoelectron spectrum, where these peaks are especially evident, is given in Fig. 13. These peaks attract attention because of several reasons. First, they can be

FIG. 13. Photoelectron spectrum obtained at the 8s[1] origin band of CD_3I using two-photon excitation. The peaks labeled 1 and 2 derive from a one-photon ionization process and have widths of about 100 and 50 meV, respectively.

found in almost every photoelectron spectrum that has been measured, irrespective of the excitation scheme employed. The lower limit of the photon energy, for which the peaks could still be observed, has been found to be $21\,414\text{ cm}^{-1}$ for peak 1 and $17\,866\text{ cm}^{-1}$ for peak 2, these energies being the lowest energy resonances at which the peaks have been observed. The upper limit could not be determined, since even at the highest photon energies used in the present experiments ($\approx 37\,000\text{ cm}^{-1}$) the peaks are still present. The relative intensities of these peaks, compared to the larger peaks that dominate each individual photoelectron spectrum, vary with the strength of the resonance whose photoelectron spectrum has been measured. In the majority of the photoelectron spectra, however, the two peaks are an order of magnitude smaller than the dominant peaks. A study of the wavelength dependence of the intensity of the two peaks has shown that their intensities closely follow the methyl iodide resonances, i.e., no resonances different from the methyl iodide resonances could be observed in these channels. A second factor of interest concerns the kinetic energies of these photoelectrons as a function of photon energy. Let us consider electrons deriving from an $(n+m)$ ionization to a specific ionic state at photon energies of $h\nu$ and $h\nu'$. Then, the difference in kinetic energy of these electrons equals $(n+m)h(\nu-\nu')$. If we were therefore to make a graph of the kinetic energies of the electrons deriving from, for example, a $(2+1)$ ionization to the $^2E_{3/2}$ vibrationless origin as a function of the one-photon energy $h\nu$, a line would be found with a slope of 3. When we plot the electron kinetic energies associated with peaks 1 and 2 through the large range of photon

energies in which these anomalous peaks are observed, we obtain the following fits: $E_{\text{kin}}(\text{peak 1}) = -2.34 + 1.01h\nu$; $E_{\text{kin}}(\text{peak 2}) = -1.52 + 0.98h\nu$, in which E_{kin} and $h\nu$ are given in eV. From these fits two important conclusions can be drawn. First, the electrons which give rise to peaks 1 and 2 are created by a one-photon ionization process and second, this ionization takes place from states located 2.34 and 1.52 eV, respectively, below the ionization limit. Another factor, that distinguishes the two peaks from the photoelectron peaks of methyl iodide or its fragments, is found in their widths (about 100 and 50 meV for peak 1 and 2, respectively), which are significantly larger than the widths of the other photoelectron peaks (10–15 meV).

The photoelectrons of peak 1 and 2 derive from the ionization of methyl iodide or one of its fragments. On the basis of the one-photon ionization behavior it can be concluded that ionization takes place from a high-lying state. This conclusion immediately rules out a mechanism in which dissociation in the *A* band results in the production of fragment species, which subsequently are ionized by one photon to yield the photoelectrons of peak 1 and 2. From numerous studies it is known that dissociation in the *A* band results in the fragment species $\text{I}(^2P_{3/2})$, $\text{I}^*(^2P_{1/2})$ and methyl radicals with almost no internal energy.^{2,4,6–13,15,16,19–22,45,46,48,55–57} Ionization of such fragments would require at least three photons in the wavelength range of the present experiments. Also on experimental grounds such a mechanism can be ruled out, since it has been observed that the two peaks are still present in excitation schemes that do not excite the *A* band.

Predissociation of high-lying Rydberg states, on the other hand, could in principle result in excited fragment species that could be ionized with one photon. Several studies have put forward mechanisms in which highly excited fragment species are produced. Danon *et al.* have suggested that excitation of methyl iodide with 266 nm photons excites the $10d(^2E_{3/2})$ state which subsequently dissociates into methyl radicals in their electronic ground state and excited iodine atoms in the $(^3P_2)6s[2]3/2,5/2$ states.¹⁹ Tsukiyama *et al.*, on the other hand, have observed fluorescence from CH/CD radicals in their $A^2\Delta$ and $B^2\Sigma^-$ states and identified the atomic iodine $(^3P_2)6s[2]3/2,5/2$ states after excitation of the $6p$ Rydberg state of methyl iodide.⁴⁶ Their explanation of these fragments was that a superexcited state above the lowest ionization threshold is excited by the absorption of a photon after excitation of the $6p$ Rydberg state. Fotakis *et al.*, in an earlier study using both 193 and 248 nm photons, identified excited CH/CD radicals in the $A^2\Delta$ and $B^2\Sigma^-$ states, as well as the $C^2\Sigma^+$ state.⁵⁸

These examples show that highly excited molecular or atomic species might be created. As concluded before, however, an explanation of the two photoelectron peaks requires also that these species have electronic states that are 1.52 and 2.34 eV below one of their ionization limits. To the extent that highly excited states of possible fragments are known, the most likely candidate for a fragment, which might be the source of the unknown photoelectrons, is found in highly excited iodine atoms. For iodine atoms

some 15 states can be found that, in combination with the 3P_2 , 3P_0 , 3P_1 , and 1D_2 ionization energies, would give electrons with the observed kinetic energies. These states are in the energy range of 72 000–79 000 cm^{-1} .⁴⁹ Creation of such states is unlikely in view of the studies mentioned above, which only report excited iodine atoms in the lower lying excited states around 55 000 cm^{-1} . Another argument against the assignment to iodine atoms concerns the width of the photoelectron peaks. In the present study it has been observed that ionization of $\text{I}(^2P_{3/2})$ and $\text{I}^*(^2P_{1/2})$ atoms produces photoelectron peaks with a FWHM of approximately 10–15 meV. The observed widths of 100 and 50 meV are not consistent with that observation, and need to be explained. When fragment species are created in a dissociation process they might have such a large velocity that Doppler broadening of the photoelectron peaks occurs. This effect plays an important role for light species such as hydrogen atoms, but can safely be assumed to be negligible for atoms like iodine. In order to explain the large width of the photoelectron peaks, it would have to be assumed that iodine is created in a large number of highly excited states. Even then a completely structureless photoelectron peak is not expected. Moreover, considering the large energy range that has been investigated, the shape of the peak should show at least some variation within this energy range. This is contrary to our observations.

The second and preferred possibility that should be considered is that peaks 1 and 2 derive from the ionization of methyl iodide itself, and not from one of its fragments. If we assume that the electrons leave the ion in the $^2E_{3/2}$ state, peak 1 would then arise from a state at 58 380 cm^{-1} and peak 2 from a state at 64 200 cm^{-1} . These energies correspond surprisingly well with the excitation energies of the $6p[1](^2E_{3/2})$ and $7s[1](^2E_{3/2})$ states, respectively, and to a somewhat lesser extent with those of the $6p[2](^2E_{3/2})$ and $7s[2](^2E_{3/2})$ states. On the other hand, if the electrons leave the ion in the $^2E_{1/2}$ state, the states from which ionization takes place are calculated to be at 63 430 and 69 250 cm^{-1} , which agrees well with the excitation energies of the $6p[4](^2E_{1/2})$ and the $7s[3,4](^2E_{1/2})$ states. *A posteriori* the latter agreement is not surprising since the spin–orbit splitting in the Rydberg states is to a good approximation the same as the spin–orbit splitting in the ion. When at a certain resonance peaks 1 and 2 are considered, it is consequently not possible to reach an unambiguous determination of the ionic state.

The above consideration leads to the following picture of the origin of the broad photoelectron peaks. Ground state methyl iodide molecules are first excited to a high-lying Rydberg state. This state can be ionized by one photon, which would give rise to the normal, narrow photoelectron peaks. Another possible ionization path involves the decay of the Rydberg state into the $6p$ and $7s$ Rydberg states. This process is expected to occur with energy conservation since the molecules can be considered as isolated on the time scale of the laser pulse. The decay will therefore occur to highly excited rovibronic levels of the $6p$ and $7s$ states. Molecules created in these states can be ionized with one photon as well, but, since $\Delta v=0$ behavior is ex-

pected, the ions produced by such ionization will be left in a highly excited rovibronic state. Given the state density at such high internal energies the width of the photoelectron peaks is expected to exceed considerably the width measured for direct ionization. The above is a time domain picture. In the frequency domain one would say that the $6p$ and $7s$ Rydberg states are mixed into the higher-lying Rydberg states.

The question that naturally arises is why no other Rydberg states are observed to be mixed in. In particular, it might be expected that the $6s$ state would also be part of the mixing process. A possible explanation for the absence of rovibronically hot ions deriving from $6s$ ionization can be found in the fact that such highly excited rovibronic levels of the $6s$ state would need to be ionized by a two-photon process in order to reach the Franck–Condon region of the ionic state. This is obviously less probable than the one-photon ionization needed for the levels of the $6p$ and $7s$ states.

It is interesting to note that Weber and Thantu have observed similar broad photoelectron peaks in a very recent (1+1) REMPI-PES study of the excited singlet states of azulene using transform limited picosecond laser pulses.⁵⁹ When azulene was ionized, after excitation of the origin of the S_3 and S_4 states, more than 99.9% of the ions were found to be created with a significant amount of rovibronic energy. Under the assumption of $\Delta v=0$ propensity, it was calculated that these ions derive from the ionization of highly excited rovibronic S_2 levels. An explanation was put forward in which a significant mixing of S_2 rovibronic states into S_3 and S_4 takes place, resulting in a distribution of the S_3 character over many molecular eigenstates. Similar conclusions have been drawn in a REMPI-PES study of pyrazine.⁶⁰ Here it was concluded, on the basis of the observation of highly rovibronically excited ions, that the S_1 levels excited in this study contained for more than 96% the character of the lowest triplet state. The major difference between the results on azulene and pyrazine and the present results is that we predominantly observe vibrationally cold ions, with a minor contribution from vibrationally hot ions. This would indicate that the admixture of highly excited $6p$ and $7s$ Rydberg levels into the higher-lying Rydberg states is considerably smaller, in agreement with the lower state density in methyl iodide compared to azulene and pyrazine.

B. REMPI-PES experiments on picosecond time scale

In the previous section we have shown that with a high-power pulsed nanosecond laser it is possible to compete effectively with the rapid direct dissociation occurring in the A band and with the predissociation of Rydberg states to the A band. High-lying ns Rydberg states ($n=7,8,9,10$) have been excited and ionized while at the one-photon level the states of the A band were excited simultaneously. The fragments resulting from the dissociation in the A band have been observed to give rise to signals that in most cases are orders of magnitude larger than the molecular methyl iodide resonances. Furthermore, the predissociation of the Rydberg states of methyl iodide tends to

FIG. 14. Two-photon excitation spectrum of CD_3I using picosecond laser pulses.

decrease the intensity of the molecular resonances as well. In order to examine the influence of a shorter pulse duration and a higher peak power on the competition between (pre)dissociation and the absorption of an additional photon, we have applied a tunable picosecond laser as an excitation source. Additionally, we have investigated the influence of these parameters on the photoelectron spectra taken at various molecular resonances.

In Fig. 14 we show the $(2+1)$ excitation spectrum of CD_3I from 34 400 to 35 550 cm^{-1} as measured with a picosecond excitation laser. The corresponding nanosecond excitation spectrum has been shown before in Fig. 6. Both the nanosecond and picosecond spectrum show methyl iodide resonances assigned to the $7s[3,4]$ and $8s[1,2]$ Rydberg states in the previous section. In the nanosecond excitation spectrum also large fragment resonances can be observed which originate from $\text{I}^*(^2P_{1/2})$ atoms and ground state methyl radicals. The positions of these fragment resonances are in good agreement with previous studies.^{10,20,53,61} The rotationally resolved transition to the $4p^2A_2''$ state of the methyl radical has been investigated in detail before.⁶¹ In the picosecond spectrum, however, the fragment resonances are almost completely absent. The strongest fragment feature in the nanosecond excitation spectrum is the transition to the atomic iodine (1D_2) $6p[3]5/2$ state at 35 497 cm^{-1} , which is even saturated as indicated by its linewidth. In the picosecond excitation spectrum this resonance is at least an order of magnitude smaller than in the nanosecond excitation spectrum, and remains the only fragment resonance that can be confidently observed.

The most prominent difference between the nanosecond and picosecond excitation spectra is thus that the nanosecond spectrum is dominated by fragment resonances while the picosecond spectrum is dominated by molecular resonances. Since the dissociative state responsible for the creation of fragments, the A band, has an estimated lifetime about 30 times shorter than our picosecond laser pulse duration, the amounts of fragments produced in

nanosecond and picosecond pulses of the same energy are expected to be equal. The peak power of the picosecond laser pulse is, however, approximately ten times higher than the peak power of the nanosecond laser pulse. The competition between photon absorption in the A band and dissociation is therefore changed in favor of photon absorption in the picosecond experiment. The results obtained here using electron detection are in agreement with the results of Szaflarski *et al.*,²¹ who have used mass-resolved ion detection. In their study the I^+ production from CH_3I using both a 30 ps laser pulse and a ns laser pulse at 266 nm was examined. It was found that, using a ns laser pulse, only I^+ fragments could be detected, while with a ps laser pulse a significant amount of CH_3I^+ ions was present as well.

The picosecond photoelectron spectra exhibit the same behavior as the excitation spectrum: Apart from the atomic iodine resonance at 35 497 cm^{-1} , no electrons appear in the spectra which derive from the ionization of one of the fragments, not even at those wavelengths where strong fragment resonances are present in the results obtained with nanosecond pulses. The vibrational progressions in the photoelectron spectra are observed to be the same at both timescales. These spectra therefore do not reflect the dissociation occurring in the A band, which is reached with the first photon, or the predissociation occurring in the $7s$ and $8s$ Rydberg states, which are reached at the two-photon level.

In the previous section on the results obtained using nanosecond laser pulses we discussed the origin of the two broad photoelectron peaks. It was tentatively proposed that they reflect the admixture of $6p$ and $7s$ levels into the wave functions of the higher-lying Rydberg states. In the photoelectron spectra obtained with picosecond laser excitation the same two broad peaks are present as well, with an intensity, that is approximately equal to the intensity in the photoelectron spectra obtained with nanosecond laser excitation. Apart from the pulse duration, an important difference between the two types of laser pulses is that the picosecond laser pulse is Fourier-transform limited and the nanosecond laser pulse is not. Following Weber and Thant⁵⁹ we can adopt a description for the origin of the broad peaks in either the time domain or in the frequency domain. In the time domain we would say that a Rydberg state decays into highly excited rovibronic levels of the $6p$ and $7s$ Rydberg states. These levels are subsequently ionized by one photon to yield vibrationally hot ions. However, in such a picture for Fourier-transform limited pulses dephasing cannot proceed faster than the pulse duration. The results of our picosecond experiments therefore indicate that a more appropriate description can be given in the frequency domain picture. In this picture $6p$ and $7s$ character is mixed into the higher-lying Rydberg states and it is the ionization of this admixture that is responsible for the creation of vibrationally hot ions and the production of the broad photoelectron peaks.

For dynamical studies with pump-probe experiments the application of REMPI-PES enables a clear distinction between the various possible ionization processes. To ex-

FIG. 15. (a) Photoelectron spectrum obtained in a picosecond pump-probe experiment on CD_3I using photons of $37\,915$ and $35\,497\text{ cm}^{-1}$ for a delay 0 between both laser pulses. (b) Time dependence of the photoelectrons in (a) with a kinetic energy of 2.29 eV . A negative delay implies that the probe beam arrives prior to the pump beam. (c) Time dependence of the photoelectrons in (a) with a kinetic energy of 1.99 eV .

amine in more detail the effect of the intermediate one-photon resonance of the A band in our present picosecond experiments, we have performed a two-color REMPI-PES experiment in which the fourth harmonic of Nd:YLF ($37\,915\text{ cm}^{-1}$) has been used to excite ground state methyl iodide molecules into the A band. The strong $\text{I}^*(^2P_{1/2}) \rightarrow \text{I}(^1D_2)6p[3]5/2$ transition at $35\,497\text{ cm}^{-1}$ serves as a probe to monitor the fragment production. In Fig. 15(a) the photoelectron spectrum is shown when both laser pulses coincide in time. The electrons with a kinetic energy of 1.99 eV derive from the ionization process

Here ν_1 designates a pump photon ($37\,915\text{ cm}^{-1}$) and ν_2 a probe photon ($35\,497\text{ cm}^{-1}$). The electrons with a kinetic energy of 2.29 eV , on the other hand, derive from the ionization process

By monitoring the dependence of the intensity of these photoelectron peaks on the delay between the two pulses the dynamical processes, which involve either the dissociation via the A band, or the decay of short-lived $\text{I}(^1D_2)6p[3]5/2$ atoms can be investigated. In Fig. 15(b) this time dependence is shown for the electrons with a kinetic energy of 2.29 eV . For negative delays, i.e., the probe pulse arrives prior to the pump pulse, the decay of $\text{I}(^1D_2)6p[3]5/2$, convoluted with the cross correlation between the two laser pulses, is observed. The time dependence of the electrons with a kinetic energy of 1.99 eV is depicted in Fig. 15(c). For this photoelectron peak the signal increases by a factor of 5 within the pump laser

pulse, indicating that the dissociation occurring in the A band is faster than 25 ps , in agreement with previous results.^{3,4}

IV. CONCLUSIONS

REMPI-PES has enabled a detailed study of the Rydberg states of methyl iodide. With nanosecond laser pulses we have identified the ns ($6 \leq n \leq 10$) Rydberg states in various excitation schemes. The transition to state [1], which is very weak in the case of the $6s$ Rydberg state, has been shown to be of equal intensity as the transition to state [2] in the $7s$ and $8s$ Rydberg states, while in the $9s$ and $10s$ Rydberg states the two transitions overlap. It is therefore concluded that the transition to $6s[1]$ is not at all prototypical for the transition to the $ns[1]$ states. Analysis of the excitation spectrum of the $6p$ Rydberg state by means of photoelectron spectroscopy has resulted in assignments of resonances which differ substantially from previous assignments. Interestingly, the photoelectron spectra taken over a large range of photon energies contain contributions from electrons that derive from a one-photon ionization. The presence of these electrons has led to the tentative proposition that $6p$ and $7s$ character is mixed significantly into the higher-lying Rydberg states. Some of the Rydberg states have also been investigated using picosecond laser excitation. The major difference observed between nanosecond and picosecond laser excitation is found in an enhanced molecular ionization.

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