Vibronic dependence of the B̃ state lifetimes of CH 3 I and CD 3 I using femtosecond photoionization spectroscopy

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Vibronic dependence of the $\tilde{B}$ state lifetimes of CH₃I and CD₃I using femtosecond photoionization spectroscopy

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Tunable deep UV femtosecond photoionization spectroscopy with single photon excitation and wavelengths longer than 192 nm has been used to determine predissociation-mediated excited state lifetimes for many vibronic levels of the $\widetilde{B}$ (6s[2] Rydberg) state of CH₃I and CD₃I. These include states with vibrational excitation in the ν_1, ν_2, ν_3, and ν_6 modes. We have previously reported lifetime measurements for the origin bands [Chem. Phys. Lett. **222**, 335 (1994)]. The vibronic and isotopic dependences presented here qualitatively agree with various aspects of results from two indirect measurements. Our results corroborate the counterintuitive result from the resonance Raman work by Wang and Ziegler [J. Chem. Phys. **95**, 288 (1991)] that the level singly excited in the C–I stretching mode (3^1) dissociates more slowly (we measure ∼4.0 ps for both CH₃I and CD₃I) than the vibrationless levels (1.38 and 1.90 ps, respectively). In contrast to the resonance Raman results and similar to those from resonance enhanced multiphoton ionization linewidth studies by Syage [Chem. Phys. Lett. **212**, 124 (1993)], we find a faster predissociation rate upon excitation in the ν_6 mode. The lifetimes are considerably longer than those measured for the higher lying 6p and 7s Rydberg states by femtosecond mass-resolved photoionization studies by Janssen *et al.* [Chem. Phys. Lett. **214**, 281 (1994)]. In that case, a faster dissociation rate was measured for the 3^1 compared to the vibrationless level. This work provides further evidence of the multidimensional nature of the $\widetilde{B}$ state predissociation mechanism and an opportunity to critically test high level calculations of the Rydberg state photodissociation dynamics. © *1998 American Institute of Physics.* [S0021-9606(98)01009-5]

I. INTRODUCTION

The photochemistry of methyl iodide has been extensively studied, not only under collisionless gas phase conditions, but also in a wide range of molecular environments, including high pressure gases,[1] clusters,[2–4] solution,[5] and as surface adsorbates.[6] Much of the gas phase work has been concentrated on the directly dissociative $\widetilde{A}$ state, which has been investigated by a variety of methods[7] including elegant emission studies by the Kinsey[8] and Butler[9] groups. More recently, the spectroscopy and dynamics of the higher lying and predissociative Rydberg states have been attracting attention.

The directly dissociative valence levels that form the $\widetilde{A}$ state exhibit a broad absorption band with no observed vibronic structure.[10–12] The first Rydberg levels ($\widetilde{B}$ state: 6s [1] and [2] near 200 nm, $\widetilde{C}$ state: 6s [3] and [4] near 180 nm, 6p and 7s near 150 nm), on the other hand, exhibit vibronically resolved structure[2,3,13–17] in which the rotational structure is obscured due to lifetime broadening. For the $\widetilde{A}$ state and lower lying Rydberg levels, the two available dissociation channels are $CH_3 + I\,^2P_{3/2}(I)$ and $CH_3 + I\,^2P_{1/2}$ (I*). One or more of the states contributing to the $\widetilde{A}$ state is thought to intersect the $\widetilde{B}$ state and induce its predissociation.[18,19]

Photon absorption spectra for the $\widetilde{B}$–$\widetilde{X}$ band of CH₃I and CD₃I occur in the region 190–205 nm as shown in Figs. 1

and 2. The strongest vibronic bands are the origin bands and progressions in the ν_2 mode, but transitions involving excitation of other modes (ν_1, ν_3, and ν_6) can also be seen. The vibronic assignments indicated in Fig. 1 were previously established by Dobber *et al.*[17] and others.[13–16] The bands appear surprisingly sharp for a perpendicular transition.[15,16,20–22] The $\widetilde{B}$–$\widetilde{X}$ origin band (and other A-type vibronic bands) is a $\Pi \leftarrow \Sigma^+$ (E←A) transition considered in $C_{\infty v}$ (C_{3v}) symmetry and is therefore a perpendicular transition. But the effective internal angular momentum parameter (ζ_{eff}) virtually eliminates the K dependence, so that it resembles a parallel band. The nomenclature follows that of Felps *et al.*[13] and refers to the 6s Rydberg level of E symmetry in C_{3v}.

Much of our understanding concerning photodissociation processes in CH₃I has been derived from asymptotic product state distribution studies. For example, dissociation of CH₃I via the $\widetilde{A}$ state results in CH₃ products excited almost exclusively in the ν_2 umbrella mode,[23] suggesting the process can be well described in terms of a linear pseudotriatomic system as indicated by Shapiro and Bersohn.[24] Excited state lifetimes derived from photodissociation studies provide valuable information for determining appropriate models for the predissociation mechanism, i.e., the nature and complexity of the nonadiabatic coupling. Results for various isotopes and vibronic levels are particularly useful in this regard. Such information helps determine whether the dissociation is relatively simple, involving primarily the dis-
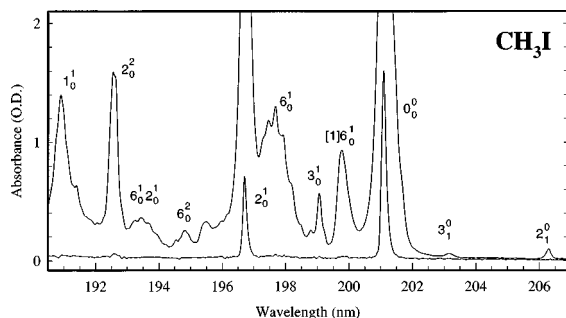
FIG. 1. Absorption spectra for CH_3I in the region of the $\widetilde{B}$–$\widetilde{X}$ band using a 10 cm path length and sample pressures of ~0.05 and ~1.3 Torr.

sociation coordinate (as assumed in a pseudotriatomic framework), or is more complicated with many of the available modes being involved. Various indirect methods, such as absorption linewidths, product angular distributions, and Raman polarization methods, yield estimates or lower limits, but direct time-resolved measurements are more straightforward and less ambiguous. Furthermore, single photon excitation is desirable since it avoids complications due to intermediate state dynamics and provides direct comparison with most previous work. Only recently has it been possible to investigate the dissociation dynamics in the time domain over an entire band in the deep UV with tunable femtosecond spectroscopy.[25]

We have previously reported[25] excited state lifetime measurements based on time-resolved photoionization studies using single photon tunable deep UV excitation of the $\widetilde{B}$–$\widetilde{X}$ origin bands of CH_3I and CD_3I. In this study we extend that to include five additional vibronic bands for each isotope. There have been indirect studies of the $\widetilde{B}$ state lifetimes[26–29] as well as direct time-resolved measurements for higher lying Rydberg states of CH_3I.[30–32]

In nanosecond photodissociation studies using 193 excitation, van Veen et al.[18] detected only I* and found CH_3 products vibrationally excited only in the ν_2 mode. Subsequent studies at 193 nm by Continetti et al.[33] revealed a detectable amount of ν_1 excitation in the products as well as a minor (3%) CH_2I+H dissociation channel. The product angular distribution anisotropy measured by van Veen et al.[18] demonstrates that the absorption is due to a perpendicular transition. The anisotropy is high but less than maximum.
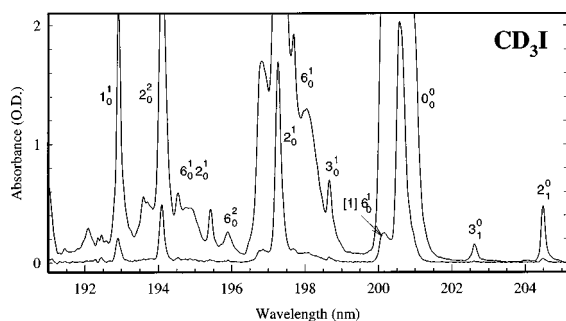

FIG. 2. Absorption spectra for CD_3I in the region of the $\widetilde{B}$–$\widetilde{X}$ band using a 10 cm path length and sample pressures of ~0.05 and ~1.3 Torr.

This is ascribed to the excited state lifetime being 150 fs for the $2\nu_2$ state, which was inferred from the absorption linewidth measured by Felps et al.[13] In their absorption and resonantly enhanced multiphoton ionization (REMPI) spectra measured for the $\widetilde{B}$–$\widetilde{X}$ system, Sapers and Donaldson and co-workers[2,34] observed the origin but not the 3_0^1 band. They concluded that the 3_0^1 band was broadened by stronger nonadiabatic coupling than for the vibrationless level, indicating faster dissociation for the ν_3 state. This conclusion was qualitatively confirmed in the emission studies carried out at 193 nm by Lao et al.[35] They also reassigned the vibronic state for CH_3I excited at 193 nm to the $3^2 2^1$ and reported 100 fs as the lower limit of the lifetime. Donaldson and workers[2,19] interpreted the fast ν_3 dissociation rate to establish the crossing point with the predissociating ($\widetilde{A}$ state) state to be between the $\nu_3=1$ and $\nu_3=0$ levels of the $\widetilde{B}$ state. In contrast to the monomer, they detected the 3_0^1 band for CH_3I dimer, suggesting that the curves cross at a higher position (above the $\nu_3=1$ level) in the cluster.

In a series of papers, Zeigler and co-workers report the most comprehensive study of the $\widetilde{B}$ state dynamics to date using measurements of the Raman and hyper Raman excitation profiles and depolarization dispersions.[26–28] They measured lifetimes of both CH_3I and CD_3I for vibronic levels throughout the band. They originally reported a lifetime of 0.5 ps for the vibrationless level of CH_3I. A revised analysis has recently been reported yielding a value of 0.8 ps.[1,36] They find the counterintuitive result that excitation of the $\nu_3=1$, C–I stretching mode, nominally the dissociation coordinate, increases the lifetime by a factor of 3. This clearly contradicts the conclusions from the previous spectroscopic studies.[2,19,34] In addition, Wang and Zeigler[28] report that the rate is nine times faster following excitation to the ν_1 C–H stretching vibronic level. These observations clearly indicate the multidimensional nature of the $\widetilde{B}$ state predissociation mechanism. The lifetimes for the ν_2 and ν_6 states were found to be the same as for the vibrationless level and measurements on the 3_1^2 hot band indicated that the $2\nu_3$ level rate is also the same as for the vibrationless level. For the deuterated species, they found a similar pattern of relative rates for various vibronic modes, but the overall rates are slower by more than a factor of 2. The most striking difference for CD_3I is that the dissociation rate is accelerated by only a factor of 2 following excitation to the ν_1 level.

Campbell and Zeigler[37] have used resonance hyper Raman band shape and depolarization ratio dispersion measurements to investigate the $\widetilde{C}$ state and found a shorter lifetime (180 fs) for the vibrationless level than for that of the $\widetilde{B}$ state. A longer lifetime was also measured for the ν_3 state (440 fs) (compared to the $\widetilde{C}$ state vibrationless level). The $\widetilde{B}$ state ν_3 mode lifetime dependence was modeled based on the Franck–Condon (FC) overlap between wave functions for the quasibound level and for a predissociating state associated with the $\widetilde{A}$ state.[28,38] The nonadiabatic interaction FC factor was parameterized in terms of the relative displacement of the curves, and satisfactory agreement for the $\nu_3=1$ and $\nu_3=2$ relative rates was found using a crossing

point on the outer turning point of the $\widetilde{B}$ state potential. It was also recognized that a very (and unrealistically) steep repulsive state would be needed to describe the ν_3 dependence for both the $\widetilde{B}$ and $\widetilde{C}$ state lifetimes.

Syage[29] has reported jet cooled absorption linewidths for several $\widetilde{B}-\widetilde{X}$ bands of CH_3I. His results provide lower limits to the lifetimes since there may be additional broadening, such as residual rotational structure. Measurements were carried out for the 2_0^1 (0.83 ps), 3_0^1 (0.92 ps), and 6_0^1 (0.67 ps) bands in addition to the band origin (0.87 ps). These results indicate that, of the modes investigated, only excitation of the ν_6 substantially affects the lifetime. This study also included a measurement for the $\widetilde{C}$ state for which the lifetime was found to be 0.25 fs, close to the value reported by Campbell and Zeigler.[37]

Zewail and co-workers have reported time- and mass-resolved femtosecond studies of CH_3I. They have investigated the $\widetilde{A}$ state dynamics[39,40] and most recently determined the dissociation to occur in 166 fs.[40] Janssen et al.[30,31] used the same method for studies of the $6p$ and $7s$ Rydberg states using two photon excitation near 310 nm followed by multiphoton ionization. Dissociation times were measured for several vibronic bands and both CH_3I and CD_3I. The lifetimes for the $6p$ [4] vibrationless levels for CH_3I and CD_3I are 166 and 331 fs, respectively, and 131 and 415 fs for the $7s$ [2]. Unlike the case for the $\widetilde{B}$ and $\widetilde{C}$ states, the 141 fs lifetime measured for the $6p$ [4] 3^1 state indicates that the dissociation rate increases upon excitation of the C–I stretching mode in the higher Rydberg state.

We have previously reported excited state lifetime measurements for the vibrationless level for both CH_3I and CD_3I (Ref. 25) and for the 3_0^1 and [1] 6_0^1 bands of CH_3I.[41] In this paper, we report direct measurements of lifetimes for five vibronic levels of the $\widetilde{B}$ state of both CH_3I and CD_3I using tunable deep UV femtosecond excitation. The Ti:sapphire-based laser system permits generation of excitation pulses at shorter wavelengths (>192 nm) than was possible with our previous dye laser system. Consequently, we have been able to measure lifetimes throughout most of the $\widetilde{B}$ state. Since the ionization potential of methyl iodide is 9.53 eV, single photon ionization from the $\widetilde{B}$ state is possible for probe wavelengths shorter than 350 nm.

II. EXPERIMENT

The technique employed closely resembles the approach in our previous work,[25] except that the laser system is based on Ti:sapphire, so that shorter wavelength excitation pulses can be generated (compared to our previous dye laser system). In the experiment, photoionization current is measured as a function of delay time between tunable deep UV pump pulses and near UV probe pulses. A schematic diagram of the experimental apparatus, which has been described elsewhere,[42] is shown in Fig. 3. The laser system consists of a Ti:sapphire oscillator (Clark NJA-5) which is pumped by an intracavity doubled, diode-pumped $Nd:VO_4$ laser (Spectra Physics Millenia). The $\sim$70 fs pulses are tunable near 800 nm at a 100 MHz repetition rate and are used to seed a

regenerative amplifier (Positive Light Spitfire) employing chirped pulse amplification. It is pumped by an intracavity doubled Nd:YLF laser (Positive Light Merlin). This system is operated at 3 kHz and yields pulses that are $\sim$120 fs in duration with an energy of 0.5 mJ.

The near UV probe ($\lambda_{NUV}=256-273$ nm) and deep UV pump ($\lambda_{DUV}=192-205$ nm) pulses are generated by third harmonic generation and then sum frequency generation of that with the fundamental, respectively. A 0.2 mm long type I beta barium borate (BBO) crystal is used for each nonlinear mixing step. The amplified Ti:sapphire pulse is frequency doubled. The $\sim$400 nm second harmonic and fundamental beams are separated, the polarization of the latter is rotated, and they are colinearly and temporally recombined and directed into a second crystal for third harmonic generation (THG) to $\sim$265 nm. A third crystal is placed directly behind the second and rotated 45° for sum frequency generation (SFG) between the third harmonic and the fundamental. The pulse energies in the near and deep UV after separating them with a pair of dichroic mirrors are 6–10 and 0.5–2 μJ, respectively. The pulse width for the third harmonic beam was found to be $\sim$270 fs by cross correlation with the fundamental (120 fs) via sum frequency generation in BBO.

The instrument response time was estimated using photoionization for rapidly dissociating molecules (i.e., excitation to repulsive states via 260 or 195 nm excitation). Gases used for this purpose include CH_3I and $(CH_3)_2CO$ away from the Rydberg state resonances ($\lambda>202$ nm), dichloroethylene (DCE) and benzene. These curves are considered as effective cross correlations between the deep UV and near UV pulses, yielding observed cross correlation (Gaussian) widths which are typically symmetric and consistently 350 ± 30 fs.

The angle between the pump and probe polarizations was typically 45°. Some scans were collected using a half wave plate for the probe (270 nm) beam to check for a polarization dependence.

Most of the data were collected by measuring the photoionization current using biased parallel plates. The pump and probe beams propagate colinearly through a 2.54 cm diameter, 50 cm focal length fused silica lens, and come to a common focus in the center of a six way, 10 cm diameter stainless steel cross. Sample pressures ranged from 500 to 700 mTorr. The electrodes for multiphonon ionization (MPI) detection are 2.54 cm diameter parallel plates separated by 1 cm. Typical voltages on the plates range from 400 to 600 V. The signal is measured using a lock-in amplifier (Stanford Research Systems SR530) referenced to the repetition rate of the laser (3 kHz). The output of the lock-in is sent to a PC, which controls the data acquisition, optical delay stepper motor, and data acquisition.

Some of the data were collected using a quadrupole mass analyzer (UTI 100C) to provide mass-resolved detection of the photoions. The arrangement is described in more detail elsewhere.[42] Briefly, a slowly flowing gas sample at a pressure of $2-6\times10^{-5}$ Torr is used with the laser beams directed through the ionizer region of the mass spectrometer. The decay times measured using mass-resolved and parallel plate detection were the same within the experimental uncer-
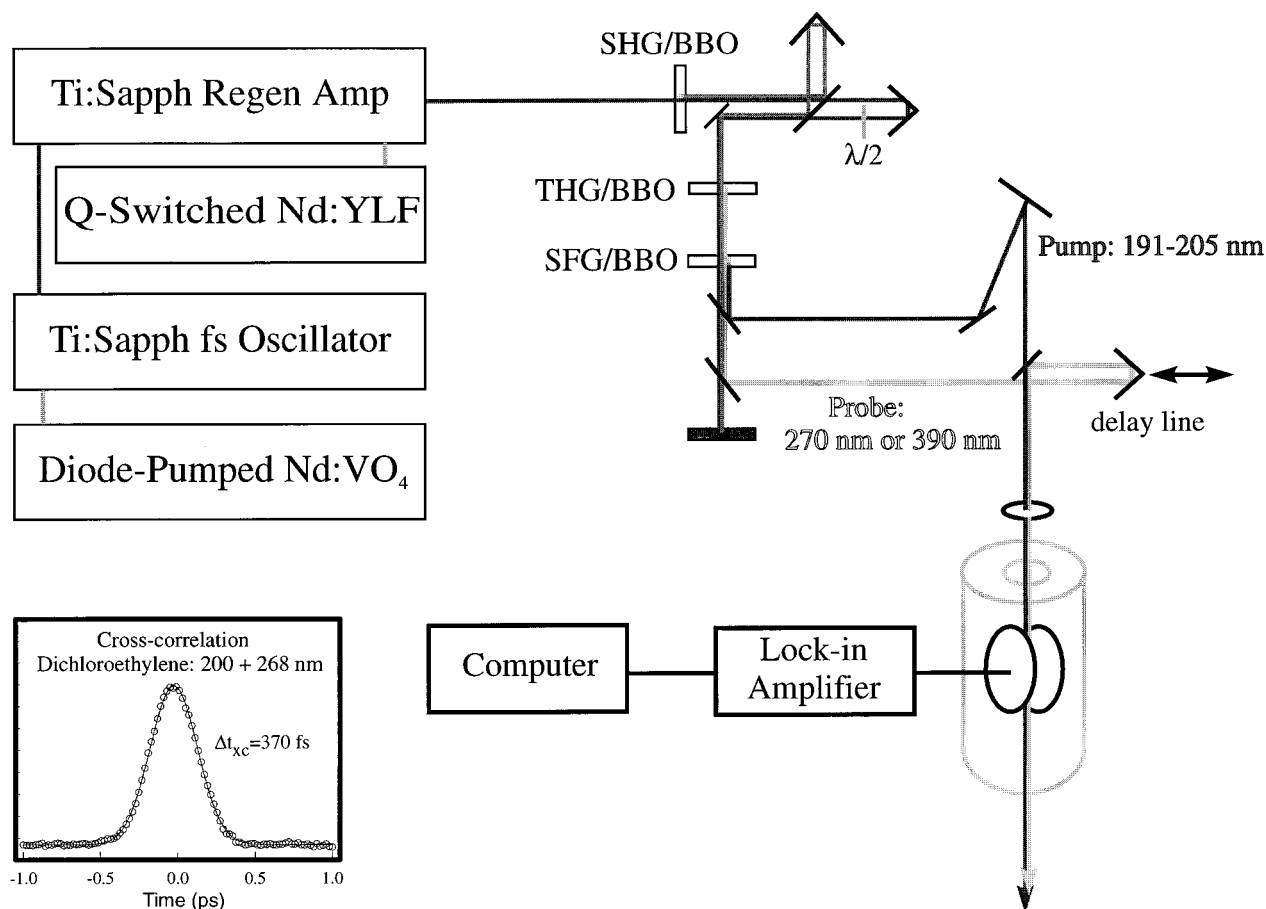
FIG. 3. Schematic diagram of the experimental apparatus. The inset shows a time-resolved signal for dichloroethylene, which provides an upper limit and a good approximation to the instrument response function.

tainty. CH_3I was obtained from Sigma Chemicals and CD_3I (98 at. %) was obtained from Cambridge Labs. Both were used after repeated freeze-pump-thaw cycles.

III. RESULTS AND ANALYSIS

The results consist of excited state lifetimes derived from the photoionization decay curves for various excitation wavelengths ($\lambda_{DUV}=192-205$ nm) in the region of the $\widetilde{B}-\widetilde{X}$ band. As noted above, a previous publication[25] describes results for the origin levels (1.38 ps for CH_3I and 1.84 for CD_3I). Preliminary values of 0.98 and 1.80 ps measured for the $[1]6_0^1$ and $[2]3_0^1$ bands of CH_3I were also previously reported.[41] The value for the $[1]6_0^1$ has been confirmed in the present study, but our current result for the $[2]3_0^1$ band is 2.3 times our original value. In the latter case, the shorter time previously measured may have resulted from being slightly detuned from the band center with the pump pulse. We have also investigated the 2_0^1, 2_0^2, and 6_0^1 bands for both isotopes, as well as the 6_0^2 and $2_0^1 6_0^1$ bands of CH_3I and the 3_0^1 and 1_0^1 bands of CD_3I. A summary of the results, including band assignments, excitation wavelengths, and measured lifetimes, are provided in Table I. The results from Wang and Zeigler[28] and Syage[29] are also included. Representative photoionization decays are shown for CH_3I in Fig. 4 and for CD_3I in Fig. 5 for the 2_0^1, 6_0^1, and 2_0^2, bands. Decay curves for 3_0^1 bands for both isotopes are shown in Fig. 6. In all

cases, except the 6_0^2 band of CH_3I, the dynamics are well resolved with our time resolution. We were barely able to resolve the dynamics for the 6_0^2 band of CH_3I and report a lifetime of 200 ± 100 fs for that level.

There are two contributions to our observed signals, which is evident from the decay curves in Figs. 4–6. The signal of interest is photoionization due to excitation of ground state CH_3I to the $\widetilde{B}$ state by the deep UV nominal pump pulse followed by ionization of population in the $\widetilde{B}$ state via the near UV pulse. In addition, the near UV probe pulse is also absorbed due to the $\widetilde{A}-\widetilde{X}$ transition, and photoionization also occurs by deep UV absorption by population in the $\widetilde{A}$ state. The lifetime for the repulsive $\widetilde{A}$ state is very short as demonstrated in studies by Zewail and co-workers,[39,40] in which the most recent results indicate the dissociation time to be 166 fs.[40] With our instrument response function of ~350 fs, this rapid dissociation is difficult to resolve. Therefore our photoionization decay curves are the sum of a rapid $\widetilde{A}$ state response (for near UV pump and deep UV probe, i.e., for negative delay times in Figs. 4–6) and a longer decay for deep UV pump and near UV probe (for positive delay times). The magnitudes of these signals are comparable in our decay curves due to the pulse energies and absorption strengths for excitation to and ionization from the $\widetilde{A}$ and $\widetilde{B}$ states.

TABLE I. $\tilde{B}$ state lifetimes for CH_3I and CD_3I.

			CH₃I				CD₃I	
			Lifetime (ps)				Lifetime (ps)	
Vibronic level		λ (nm)	This work[a]	Wang et al.[b] (RR)	Syage[c] ($\Delta\nu$)	λ (nm)	This work[a]	Wang et al.[b] (RR)
6s[2]	0_0^0	201.2	1.38	0.5[d]	0.87	200.5	1.84	1.2
	2_1^0	206.3	1.38			204.5	1.93	
	3_0^1	199.2	4.1	1.5	0.92	198.6	4.0	4.0
	1_0^1	191.1		0.06		192.8	1.20	0.6
	2_0^1	196.7	1.05	0.5	0.83	197.2	1.65	1.2
	2_0^2	192.7	0.76			194.2	1.30	
	6_0^1	197.8	0.76	0.5	0.67	198.0	1.43	1.2
	6_0^2	194.8	0.20					
	$2_0^1 6_0^1$	193.5	0.91					
6s[1]	6_0^1	199.7	0.98					

[a]Uncertainties are $\pm 10\%$, except for 6_0^2, for which it is ± 0.1 ps.
[b]Reference 28, resonance Raman studies. Uncertainties for CH₃I bands are: ± 0.1 ps for 0_0, 2_0^1, and 6_0^1, ± 0.5 ps for 3_0^1, ± 0.15 ps for 3_0^2, and ± 0.01 for 1_0^1. For CD₃I they are: ± 0.2 ps for 0_0^0 and 6_0^1, ± 2.5 ps for 3_0^1, ± 0.3 ps for 2_0^1, and ± 0.1 for 1_0^1.
[c]Reference 29, linewidth studies. Uncertainties are $+50\%, -10\%$.
[d]An updated value of 0.8 ± 0.1 ps has recently been reported based on a revised analysis (see Ref. 1).

Therefore, the observed decays were fit to the sum of a Gaussian (cross correlation function) and a single exponential decay convoluted with an instrument function. The instrument function was typically fit to the $\tilde{A}$ state signal observed simultaneously. Alternatively, a separate scan with a rapidly dissociating gas could be used to independently determine (set an upper limit to) the instrument function, which was then fixed in the analysis. Despite the high signal-to-noise ratios exhibited in Figs. 4–6, we quote a 10% uncertainty based on ambiguities of the analysis (mostly due to the presence of the instrument-limited signal). The decays observed for the CH₃I and CD₃I vibronic bands were long enough that similar results are also obtained by truncating the signals at early times (0.4–0.8 ps) and fitting the decays without a convolution.

The polarization dependence of the photoionization signal was investigated for the CH₃I 2_0^1 band to confirm that the decay was not due to rotational reorientation-induced anisotropy decay rather than population decay. No difference between the decay curves was observed for relative pump and probe polarizations of 0° and 90°.

IV. DISCUSSION

As indicated in Table I, we obtain lifetimes for the various vibronic states of CH₃I and CD₃I ranging from 0.2–4.1-

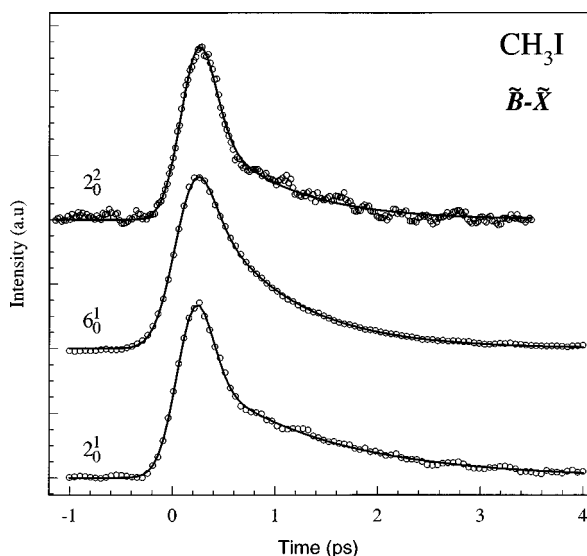FIG. 4. Photoionization decay curves for several $\tilde{B}$–$\tilde{X}$ vibronic bands for CH₃I: 2_0^1, excitation at 196.7 nm, 6_0^1, excitation at 197.8 nm, and 2_0^2, excitation at 192.7 nm.
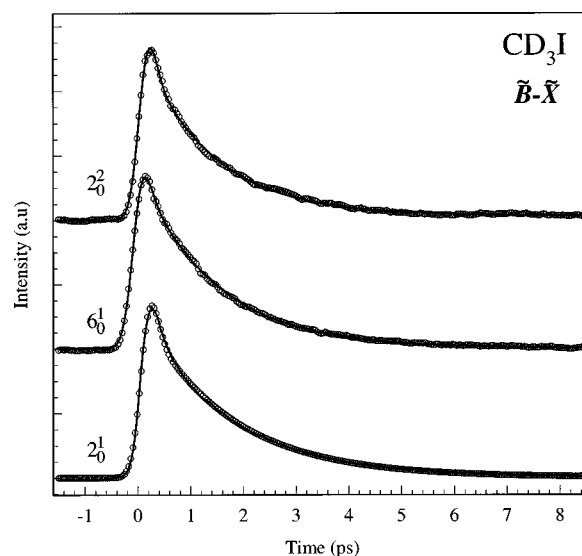
FIG. 5. Photoionization decay curves for several $\tilde{B}$–$\tilde{X}$ vibronic bands for CD₃I: 2_0^1, excitation at 197.2 nm, 6_0^1, excitation at 198.0 nm, and 2_0^2, excitation at 194.2 nm.
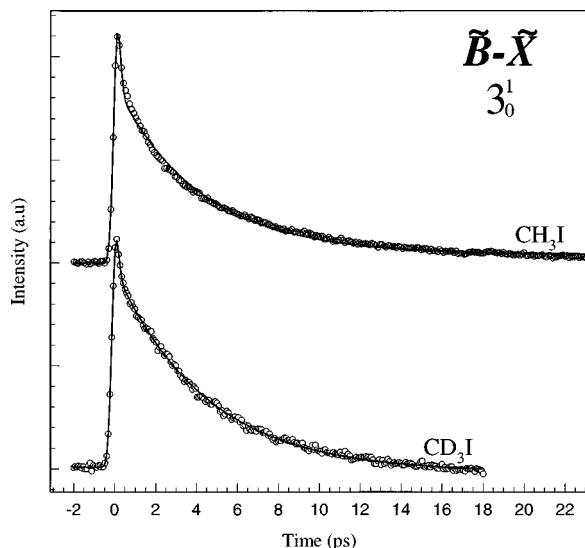
FIG. 6. Photoionization decay curves for $\tilde{A}$–$\tilde{X}$ 3_0^1 bands for CH_3I and CD_3I.

ps. All the vibrationally excited states exhibit lifetimes different from the vibrationless level. The relative mode dependence is quite similar for both isotopes. For each isotope, the only state with a longer lifetime than the vibrationless level is $\nu_3 = 1$. Vibrational excitation in the other modes increases the dissociation rate. These results concerning the vibrational dependence of the predissociation rate are the primary results of this work. A more detailed discussion will follow a brief discussion of the possible influence of rotational effects.

No polarization dependence was observed for the time dependence of the photoionization signals. Furthermore, most of the signals were obtained with a relative polarization angle of 45°, so that polarization anisotropy contributions to the signal should be minimal. A polarization anisotropy might be expected since one of the first indirect estimates of the $\tilde{B}$ state lifetime (2^2 and $2^1 6^1$ states) was based on product anisotropy measurements following 193 nm excitation by van Veen et al.[18] Their work was carried out in a molecular beam where the lower temperature extends the rotation time compared to our studies at room temperature. In our case, the free rotor time is $\leqslant 350$ fs, comparable to the time resolution and faster than most of the reported times.

Rotation could also influence the measured lifetimes if a rotationally induced (e.g., Coriolis or centrifugal) mechanism were operative. A clear demonstration of this can be found for predissociation of the $\tilde{A}$ state of NH_3 and its isotopomers as indicated by the microwave optical double resonance studies of Henck et al.[43] We are unable to resolve the rotational structure, so that we cannot provide evidence for or against a rotationally dependent predissociation rate. In their resonance Raman studies, Wang and Zeigler[28] provide evidence that rotation does not strongly affect the predissociation. They found no variation of the lifetime for different K subbands that were resolved for the $\tilde{B}$–$\tilde{X}$ 6_0^1 band. In related observations using MPI spectroscopy of CH_3I, Zewail and co-workers found no difference between decays measured in a molecular beam and in static cell for the higher lying $6p$ and $7s$ Rydberg states.[31] This again suggests little effect of

rotation either through rotational anisotropy or rotationally mediated predissociation for these states.

The results presented here in combination with our earlier work[25] provide an extensive study of the vibronic mode dependence of the predissociation rates for the $\tilde{B}$ state of CH_3I. The study includes five vibrationally excited levels in addition to the origin level for both CH_3I and CD_3I. These results agree with various aspects of the indirect lifetime measurements for this state from resonance Raman studies by Wang and Ziegler[28] and from the linewidth studies by Syage.[29] However, the vibronic dependences derived from these indirect studies do not agree with one another. The general isotopic variation we observe is well described by Wang and Zeigler[28] who indicate that the vibronic dependence is similar for both isotopes. Relative to the rate for the vibrationless level (0.5 ps for CH_3I and 1.2 ps for CD_3I), Wang and Ziegler[28] report that the ν_3 levels (1.5 ps for CH_3I and 5 ps for CD_3I) predissociate more slowly (and for CH_3I the ν_1 level decay rate is much faster, by a factor of 9). No measurable difference was found for the other levels studied (ν_2, ν_6). Syage,[29] on the other hand, finds similar rates for the ν_3 and origin and a faster rate for the ν_6 level. In addition, the rates originally reported by Wang and Ziegler[28] exceed the upper limits obtained from the linewidths measured by Syage.[29] The recently revised lifetime for the vibrationless level (0.8 ps) from Zeigler and co-workers[1] is 60% longer than their original time and in agreement with the value reported by Syage.[29]

Our results can qualitatively be described as confirming all previously reported vibrational effects. In agreement with Wang and Ziegler,[28] we observe the counterintuitive result that predissociation is slower upon excitation of the ν_3 mode for both isotopes. We also find the relative effect to be comparable in magnitude (2–3 times longer) to the results from Wang and Ziegler.[28] In a one dimensional description, the C–I coordinate is nominally the dissociation coordinate, so that excitation of this mode should promote dissociation and reduce the lifetime. The longer time observed is perhaps the most striking evidence of the multidimensional nature of the dissociation mechanism. The slower dissociation for the ν_3 level contradicts the conclusions from the studies of Sapers and Donaldson and co-workers.[2,34]

The complicated nature of the dissociation mechanism is also indicated by the sensitivity of the predissociation rate to excitation of other vibrational modes. Our result for the accelerated dissociation of the ν_6 level agrees with the linewidth studies. Contrary to the findings of either of the indirect studies, we also find the ν_2 level dissociation rate is faster, although slower than the ν_6. The lifetimes we obtain are either in agreement with or are longer than the lower limits from the linewidth studies.

It is interesting to compare the results for the $\tilde{B}$ state with other states for CH_3I. The $\tilde{A}$ state is comprised of numerous repulsive states. One (or several of these) is probably the predissociating state for the $\tilde{B}$ state as well as for higher lying Rydberg levels. Obvious differences between the Rydberg states and the $\tilde{A}$ state are readily seen in the absorption and resonance Raman/emission spectra. In the latter case, the

well known long ν_3 progression was observed for the $\widetilde{A}$ state,[8,9] whereas short progressions in primarily ν_2 were observed for the $\widetilde{B}$ state. Lao et al.[35] did not detect any emission they could ascribe to CH_3I after the curve crossing. Isotope effects for the I*/I ratios in the $\widetilde{A}$ state indicate the dissociation cannot be described within a simple Landau–Zener model.[9] The isotope dependence measured here for the $\widetilde{B}$ state does not conform to a pseudodiatomic (1D) dissociation for which the rates would be dictated by the mass-weighted kinetic energy partitioning (to be $CD_3I/CH_3I=1.18$, rather than the observed value of 1.41 for the origin bands).

Lifetime measurements have also been reported for higher lying Rydberg states of CH_3I. In studies similar to those for the $\widetilde{B}$ state, indirect methods were used to obtain lifetimes for the $\widetilde{C}$ $6s$ [4] state. For the origin band, Campbell and Ziegler[37] used resonance hyper Raman excitation profiles and depolarization dispersions to find a lifetime of 180 ± 30 fs, which is close to that reported by Syage based on linewidths, 250 fs ($+50,-25$ fs).[29] Better agreement between these studies for this case than for the $\widetilde{B}$ state may be expected since the dissociation is faster. A broader homogeneous linewidth renders the measurements less susceptible to competing broadening mechanisms, such as rotational structure. Campbell and Ziegler[37] found the $\widetilde{C}$ state ν_3 level lifetime of 440 ± 140 fs to be longer than for the vibrationless level. Sapers et al.[3] also measured narrower linewidths for the 3_0^1 band of the $\widetilde{C}$ state than for the origin band.

Predissociation rates were measured in the time domain by Janssen et al.[30,31] for the higher lying $6p$ and $7s$ Rydberg levels using two photon excitation (310–315 nm) and mass-resolved detection. They found the $6p$ [4] 3^1 lifetime (141 fs) to be slightly shorter than that for the vibrationless level (178 fs). Based on decays for excitation of the origin bands, the lifetime for CD_3I (333 fs) was close to twice as long as for CH_3I. The results for this Rydberg state are quite different from the $\widetilde{B}$ (and $\widetilde{C}$) state(s), in which substantially longer times are measured when the ν_3 is excited and, generally, the isotope effect is less than vibronic effects. Simply based on the magnitude and direction of the vibronic and isotopic variations, it appears that different mechanisms may be responsible for dissociation from the $6s$ and $6p/7s$ Rydberg states.

Without high level calculations for potential energy surfaces for the $\widetilde{B}$ state and the predissociation state(s), where the latter may be one of the surfaces that comprise the $\widetilde{A}$ state, it is difficult to clearly identify the predissociation mechanism. The importance of bending has been discussed in connection with the $\widetilde{A}$ state dissociation,[44] so it is tempting to consider the importance of bending or symmetry breaking for the $\widetilde{B}$ state. It is possible that the E symmetry $\widetilde{B}$ electronic state could be subject to Jahn–Teller distortion which would lower the symmetry (and reduce the opportunity for symmetry breaking effects), but there is evidence against this since intensity alternation consistent with C_{3v} structure was spectroscopically observed for the 6_0^1 subbands by Dagata

et al.[15,45] There is no indication, however, that antisymmetric, degenerate vibrations (E: ν_4, ν_5, and ν_6) alter the dissociation rates more than symmetric, nondegenerate modes (A: ν_1, ν_2, and ν_3). In fact, the symmetric modes exhibit the strongest effects. Based on the result of Wang and Zeigler[28] for CH_3I and also ours for CD_3I, excitation of the ν_1 C–H stretching mode results in the largest dissociation rate increase. This is for levels that have only one vibrational quantum of excitation, i.e., the ν_1 exhibits the highest dissociation rate acceleration per quantum; the $2\nu_6$ level exhibits the fastest dissociation rate of those studied. The ν_3 mode is unique since it is the only one measured that increases the lifetime. The ν_1 rate enhancement is greater for CH_3I than for CD_3I. If the acceleration and deceleration depend on the C–H and C–I internal coordinates, respectively, then the isotope effect may arise from the smaller contribution of the C–I internal coordinate to the ν_1 normal mode in CH_3I compared to in CD_3I. Coefficients for transforming between internal and normal coordinates for both isotopes can be found in Amatatsu et al.[7]

Compared to the extensive number of theoretical and computational studies for the $\widetilde{A}$ state,[7] there have been few similar investigations of Rydberg state predissociation dynamics. Calculations based on the FC overlap by Wang and Zeigler[28] have been described above. We have recently attempted a similar approach to account for the ν_3 and isotope variations using a pseudo-FC approach. This approach was based on the Walker method[46] for coupling the harmonic oscillator wave functions of the $\widetilde{B}$ state with the repulsive state wave functions. We found this approach did not yield useful results. Also, Donaldson et al.[19] presented two dimensional (2D) calculations (including the C–I and C–H_3 stretches) to account for their experimental results, where the latter have not been confirmed by others,[28,29] including this work. Guo and Zewail[32,47] have also used molecular dynamics calculations to reproduce the isotopic and vibronic lifetime variation measured in the experiments by Janssen et al.[31] on the $6p$ and $7s$ Rydberg states. Initially, the calculation was one dimensional in the C–I stretching mode with $\widetilde{B}$ state parameters for the quasibound state and an exponentially varying coupling.[47] The results qualitatively reproduced the mass effect by yielding a slower predissociation for CD_3I than CH_3I. The effect was smaller than that observed for the higher ($6p$, $7s$) states, but interestingly, is closer to what we have found for the $\widetilde{B}$ state. Subsequent 2D calculations including the H_3-C coordinate yielded better agreement for the isotope dependence and provided qualitative agreement for the ν_3 mode dependence. A successful description of the $\widetilde{B}$ state dissociation will require high level ab initio $\widetilde{A}$ and $\widetilde{B}$ state surfaces, where the former must extend to the region of interest for the $\widetilde{B}$ state, near 6.3 eV. The results reported here cannot be explained without detailed multidimensional potential energy surfaces for the bound and predissociating states involved.

V. SUMMARY

Tunable deep UV femtosecond photoionization spectroscopy has been used to measure excited state lifetimes for

many vibronic levels in the $\widetilde{B}$ state for CH_3I and CD_3I. The results are similar in various respects to the indirect studies. All the vibrationally excited levels studied exhibit lifetimes that are different than those for the origin levels. This study further demonstrates the multidimensional nature of the predissociation of the $\widetilde{B}$ state. These measurements provide an extensive study of the dissociation dynamics for the lowest Rydberg state of methyl iodide and are suitable for a detailed comparison with a high level calculation, and we hope that these measurements will encourage such a calculation for the $\widetilde{B}$ state.

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