Predissociation lifetimes of the $\tilde{B}$ and $\tilde{C}$ Rydberg states of CH_3I

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Single-photon direct absorption and resonance-enhanced multiphoton ionization excitation spectra were recorded for CH_3I in a jet-cooled molecular beam. The rovibrationally cold molecules yield lineshapes that are lifetime broadenend by predissociation. Lorentzian fits were used to extract lifetimes for specific vibronic excitation in the $\tilde{B}$ and $\tilde{C}$ Rydberg states. The measured lifetimes of the $\tilde{B}$ state are 0.87 ps (origin), 0.83 ps (ν_2), 0.92 ps (ν_3), and 0.67 ps (ν_6). The $\tilde{C}$ state origin has a lifetime of 0.25 ps. These results are compared to previous measurements and discussed in terms of possible mode-specific predissociation.

1. Introduction

There is considerable evidence that the Rydberg tates of CH_3I undergo very rapid rates of predissociation to the group of close-lying repulsive configurations known as the $\tilde{A}$ states. Femtosecond molecular beam measurements by Zewail and coworkers indicate that the $\tilde{A}$ states decay on the order of 100 fs [1]. The direct $\tilde{A}$ state dissociation of the C–I bond is also supported by measurements of fragment anisotropy [2–4] and emission [5]. Few measurements of Rydberg lifetimes have been made. The only direct measurement is from the Zewail group who measured a lifetime of 175 fs for the origin of the 5pπ–6p Rydberg state using two-photon absorption, one-photon ionization (i.e. 2+1 resonance-enhanced multiphoton ionization (REMPI)) [6].

Only indirect measurements of predissociation rates exist for the lower-lying 5pπ–6s Rydberg states usually referred to as the $\tilde{B}$ and $\tilde{C}$ states (see section 2). Vaida and co-workers have published a series of papers on jet-cooled CH_3I using direct absorption to study the $\widetilde{B2}$ state and 2+2 REMPI to study the $\widetilde{C2}$ state [7–9]. In the former work they reported that the ν_3 (C–I stretch) and ν_6 (methyl rock) vibronic bands are more diffuse than the 35 cm^{-1} instrument resolution indicating lifetimes of less than 150 fs [7]. Amirav and Penner measured jet-cooled absorption lineshapes of the $\widetilde{B2}$ state origin, however, this was done to examine cluster effects and not at a sufficient resolution to resolve the monomer lineshape [10]. Sapers and Donaldson recorded 1+1 and 2+2 REMPI excitation spectra of the $\widetilde{B2}$ state of ambient CH_3I and CD_3I in a flow system and also concluded that the ν_3 level is much shorter lived than the vibrationless level [11]. Ziegler and co-workers have applied spontaneous resonance Raman and hyper-Raman depolarization measurements to determine lifetimes for the $\widetilde{B2}$ and $\widetilde{C2}$ states [12–14]. They reported $\widetilde{B2}$ lifetimes of 0.5 ps for the origin, ν_2, and ν_6 levels, 1.5 ps for ν_3, and 60 fs for ν_1 [12,13]. These results, which indicate that ν_3 excitation suppresses the rate of predissociation, differ from the previous results, which reported a substantial rate acceleration by ν_3.

In a previous study we measured $\widetilde{B2}$ state lineshapes for jet-cooled CH_3I using 1+1 REMPI and obtained predissociation lifetimes for the origin, ν_3, and ν_6 levels that are in fair agreement with the resonance Raman depolarization measurements [12,13], but show only modest evidence of mode-specificity [15]. The origin transition is quite strong ($\epsilon = 50000\ \ell\ mol^{-1}\ cm^{-1}$ [16] or $\sigma \sim 10^{16}\ cm^2$) and is easily saturated. Because of the competition between ionization and predissociation, the origin lineshape exhibits an interesting hole-burning effect under saturation-broadened conditions. A dynamic model for the lineshape indicated an excited-state lifetime of about 1 ps. The vastly weaker ν_3 and ν_6 vibronic transitions did not saturate under our ex-

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citation conditions and gave Lorentzian lineshapes consistent with lifetimes of 0.6–1.0 ps [15].

Direct time-resolved measurements of the $\tilde{B}$ and $\tilde{C}$ states would be desirable, however, these states lie in a difficult spectral region for one-photon laser excitation (175–205 nm), so other methods are warranted. In this Letter, we report absorption spectra of the $\widetilde{B2}$ and $\widetilde{C2}$ origins (201.17 and 182.96 nm, respectively) using a low-power dispersed light source at sufficient resolution (1–2 cm^{-1}) to measure lifetime broadened lineshapes. We also analyze two-color 1+1 REMPI lineshapes of the $\widetilde{B2}$ ν_3 and ν_6 modes (199.14 and 197.78 nm) using low-intensity absorption, high-intensity ionization. These unsaturated rotationally cold lineshapes should give accurate predissociation lifetimes; at the very least they set lower limits on lifetimes.

2. Background

Fig. 1 summarizes electronic-state symmetries, spin multiplicity, and correlations to ion-core states for the ground $\tilde{X}$, dissociative $\tilde{A}$, and Rydberg $\tilde{B}$ and $\tilde{C}$ states of CH_3I. The electronic states considered here are due to the following transitions

$\tilde{A}$: $(5p\pi)^3\sigma^* \leftarrow \tilde{X}$: $(5p\pi)^4$,

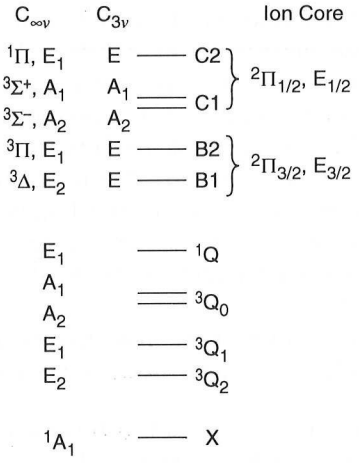

Fig. 1. Electronic sublevels for lower-lying electronic states of CH_3I. The relative energy spacing for the $\tilde{B}$ and $\tilde{C}$ states is approximate for the equilibrium C–I distance. Alternative symmetry designations for $C_{\infty v}$ are given and used for all states shown.

$\tilde{B}$, $\tilde{C}$: $(5p\pi)^3 6s \leftarrow \tilde{X}$: $(5p\pi)^4$.

The $(5p\pi)^3(\sigma^*)^1$ configurations give rise to five excited states referred to as the $\tilde{A}$ states. The $C_{\infty v}$ symmetries and the commonly used Q-state designations are given in fig. 1. The $(5p\pi)^3(6s)^1$ configurations give rise to five excited states that group into two sets of states, referred to as $\tilde{B}$ and $\tilde{C}$. These correspond, respectively, to a 6s Rydberg electron interacting with either the $^2\Pi_{3/2}$ or the $^2\Pi_{1/2}$ CH_3I^+ ion-core spin–orbit states [17,18]. $\tilde{B}$ is comprised of two states of symmetry Δ and Π in $C_{\infty v}$, which we designate as $\widetilde{B1}$ and $\widetilde{B2}$, respectively [#1]. The one-photon transition from the $\tilde{X}\,^1\Sigma$ ground state is orbitally forbidden for $\widetilde{B1}$ and allowed for $\widetilde{B2}$. The threefold C_{3v} potential, imposed by the hydrogen atoms, can mix the Δ and Π states (both become E states in C_{3v}) and gives some activity to the transition to $\widetilde{B1}$; however, this effect is very weak [15,18]. $\tilde{C}$ is comprised of two states of symmetry (Σ^+, Σ^-) and Π, which we designate as $\widetilde{C1}$ and $\widetilde{C2}$, respectively (see footnote 1). The $\widetilde{B2} \leftarrow \tilde{X}$ and $\widetilde{C2} \leftarrow \tilde{X}$ transitions are perpendicular-type transitions with large transition moments.

The vibrational modes of CH_3I are denoted ν_1–ν_6. The first three modes are a_1 symmetry type and the last three are doubly degenerate e type modes (in C_{3v}). In this work we consider the vibrationless level, ν_2 (umbrella), ν_3 (C–I stretch), and ν_6 (methyl rock).

3. Experimental

The different apparatus used to measure direct absorption spectra and REMPI excitation spectra have been discussed in detail elsewhere [15,19,20]. Only brief descriptions are given here. The CH_3I sample was contained in a bubbler cooled to dry ice/acetone, dry ice/chloroform, or ice water temperature (about 2–50 Torr CH_3I) and entrained in a flow of He or Ar at a pressure of about 10–25 psi. The CH_3I was purified by vacuum–freeze–thaw cycles. Low energy electron-impact (EI) ionization was used as a diagnostic for assessing and minimizing cluster formation in the REMPI apparatus.

[#1] Our designations of $\widetilde{B1}$, $\widetilde{B2}$, $\widetilde{C1}$, and $\widetilde{C2}$ are often referred to as [1], [2], [3], and [4], respectively.

The direct absorption spectra were recorded in a free-jet apparatus using a dispersed broadband D_2 lamp as the excitation source [20]. A resolution of 1.5 cm^{-1} at 200 nm was achieved using a 0.5 m vacuum monochromator, 3600 line/in grating, and 15 μm slit widths. The monochromator resolution and wavelength calibration were determined using atomic resonance lines from various reference lamps. Absorption strengths were measured by dual-gated photon counting. One gate was overlapped with the gas pulse to measure I and a second gate was placed before the gas pulse to measure I_0. The reported spectra correspond to plots of $\ln(I_0/I)=\sigma nl$.

The 1+1 REMPI spectra were recorded on a pulsed molecular beam time-of-flight (TOF) mass spectrometer [15,19]. A short-wavelength limit of 197 nm was achieved by sum frequency generation in a BBO crystal using as inputs the fundamental (ω) and frequency doubled (2ω) output of a Nd:YAG pumped dye laser operating at about 0.1 cm^{-1} resolution [15]. The 3ω output (0.5 mJ/pulse maximum) and 2ω output (5–10 mJ/pulse) were used for excitation and ionization, respectively. Pulse power densities were varied by using neutral density filters and by changing focusing conditions by translating a 35 cm focal length spherical lens. The BBO crystal used to generate 3ω was tracked using a home-built autotracker. The 2ω output of the dye laser was tracked using commercial hardware.

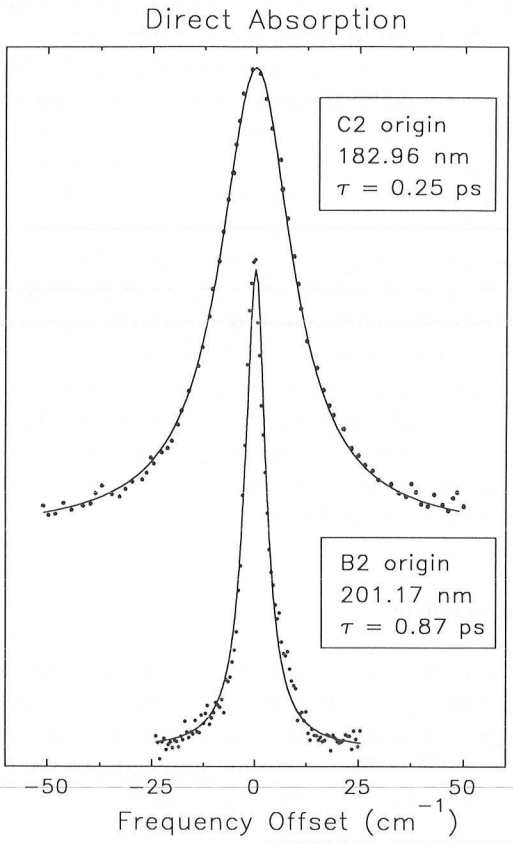

Fig. 2. Direct absorption spectra of the $\tilde{B}$ and $\tilde{C}$ origin transitions of jet-cooled CH_3I.

4. Results and discussion

Direct absorption lineshapes for the strong $\widetilde{B2}$ and $\widetilde{C2}$ origin transitions are given in fig. 2 and the 1+1 REMPI excitation lineshapes for the weak $\widetilde{B2}$ ν_3 and ν_6 transitions are shown in figs. 3 and 4. These spectra were fitted to a Lorentzian function of the form $I(\Delta\nu)=[1+(4\pi\tau\Delta\nu)^2]^{-1}$ where τ is the predissociation lifetime and $\Delta\nu$ is the detuning frequency from line center. The best-fit values of τ are listed in the figures and compared to previous work in table 1. We assume that the measured linewidths are a rigorous measure of the lower lifetime limits. The upper limits are less certain due to other possible linewidth contributions besides lifetime broadening. The $\widetilde{C2}$ origin absorption lineshape is significantly broader than the other measured lines and fits well to a Lorentzian function. We, therefore, assign a relatively small uncertainty of +20%, −10% to the measured lifetime of 0.25 ps. For the narrower recorded lineshapes in figs. 2–4, a rotational contour may contribute to the lineshape. However, this component should be asymmetric [#2] and is not noticeably evident in the symmetric and Lorentzian lineshapes observed here. We assume an uncertainty of +50%, −10% for the lifetimes of the $\widetilde{B2}$ origin, ν_2, ν_3, and ν_6 levels.

Other laboratories have reported evidence for mode-specific rates of predissociation. Vaida and co-

[#2] A rough indication of the jet-cooled CH_3I rotational distribution was obtained in a previous work, in which we directly ionized CH_3I ($\tilde{X}$) to CH_3I^+ by electron impact and recorded the vibronically well-resolved $\tilde{A}\leftarrow\tilde{X}$ ion spectrum by resonance ion dissociation [21]. The lineshapes showed a sharp rise and a distinct red shading with a width of about 5 cm^{-1}.

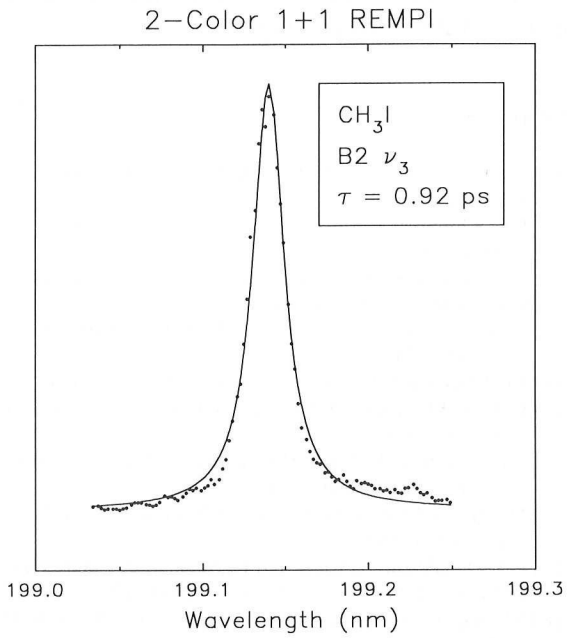

Fig. 3. Two-color 1+1 REMPI spectrum for excitation of the $\tilde{B}$ state ν_3 vibration.

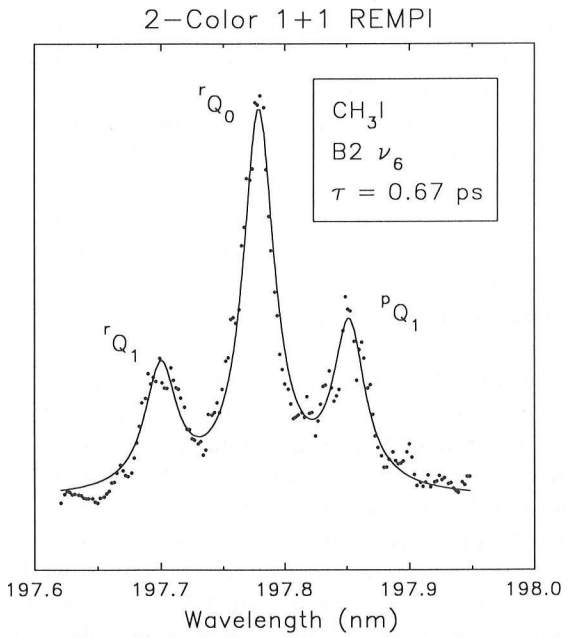

Fig. 4. Two-color 1+1 REMPI spectrum for excitation of the $\tilde{B}$ state ν_6 vibration. Note the wide Q-branch spacing characteristic of a perpendicular transition to a degenerate e-type mode. The rotational cooling in the supersonic expansion is evident by the near absence of sub-bands originating from levels $K>1$.

workers [7,8] and Sapers and Donaldson [11] report an enhanced rate of predissociation for the ν_3 mode relative to the vibrationless level (the former group also reports acceleration for ν_6). Ziegler and co-workers in contrast report that ν_3 actually suppresses the rate of predissociation [12–14]. Our results indicate that the lifetimes for the vibrationless, ν_2 (not shown), and ν_3 levels are very similar (0.89, 0.83 and 0.92 ps, respectively) and, therefore, do not support mode-specificity for ν_3 (table 1). We can rule out the possibility for a rate enhancement as reported by Vaida and co-workers and Sapers and Donaldson since our observed linewidths establish lower limits on lifetime. Vaida and co-workers reported that the ν_3 transition appears in direct absorption spectra of clusters, but not of monomers. They attributed the latter observation to spectral diffusiveness caused by rapid predissociation. Sapers and Donaldson could not observe the ν_3 transition in the $2+2$ $\widetilde{B2}$ state REMPI spectrum of CD_3I. They attribute this result to a predissociation rate that is much faster for ν_3 than for other modes. However, ν_3 and ν_6 are very weak Franck–Condon transitions whose intensities may be significantly affected by small changes in equilibrium geometry exerted by clustering or deuteration. Hence, the relative weakness or absence of these bands may simply be a Franck–Condon intensity effect.

Table 1
Predissociation lifetimes for the $\widetilde{B2}$ and $\widetilde{C2}$ states of CH_3I

Excited state		Lifetime (ps)		
		this work	refs. [12–14]	refs. [7,8]
$\widetilde{B2}$	origin	0.87	0.5	>0.6 [a]
	ν_2	0.83	0.5	
	ν_3	0.92	1.5	<0.15
	ν_6	0.67	0.5	<0.15
$\widetilde{C2}$	origin	0.25	0.18	
	ν_2			
	ν_3		0.44	
	ν_6			

[a] Estimated from linewidth.

It is a little more difficult to comment on the ν_3 rate suppression reported by Ziegler and co-workers [12–14] because of the uncertainty in the upper limit

of our lifetimes. They attribute the slow rate to an $\tilde{A}$ state that crosses with the Rydberg states in such a way that the continuum wavefunction experiences poor Franck–Condon overlap with the one quantum wavefunction of ν_3. A difficulty of this explanation is that the ν_3 suppression is observed in both $\widetilde{B2}$ and $\widetilde{C2}$, indicating that the repulsive part of the $\tilde{A}$ state potential is essentially vertical in this region. Finally, we note that the origin lifetimes for the $\widetilde{B2}$ and $\widetilde{C2}$ state reported by Ziegler and co-workers are somewhat smaller than the lower limits established here (table 1).

Calculated potential energy curves for the dissociative $\tilde{A}$ states indicate that the A_2 component of the $^3Q_0$ state undergoes a crossing through the low-energy regions of $\widetilde{B2}$ and $\widetilde{C2}$ and, therefore, is the most likely state to induce predissociation [9,22,23]. Based on this assumption, it is possible to explain by electronic symmetry and spin selection rules the different lifetimes for the $\widetilde{B2}$ and $\widetilde{C2}$ origins and the apparent mode-specificity of the ν_6 mode relative to ν_2, ν_3 and the origin of $\widetilde{B2}$ (table 1). The $^3Q_0$ state corresponds to a $\Pi_{1/2}$ ion core (by nature of its correlation to the $I(^2P_{1/2})$ product channel) and, therefore, should couple more strongly to $\widetilde{C2}$ ($\Pi_{1/2}$ ion core) than to $\widetilde{B2}$ ($\Pi_{3/2}$ ion core). This interpretation is consistent with the faster rate of predissociation from $\widetilde{C2}$ than from $\widetilde{B2}$. The issue of mode-specificity for $\widetilde{B2}(E)$ state predissociation, in which ν_6 decays faster than ν_3 and the origin, may be explained by vibronic symmetry. The ν_6 mode is an e-type vibration; hence, the vibronic symmetry product $E\otimes E=E+A_1+A_2$, may account for a relatively strong surface crossing interaction with the A_2 component of $^3Q_0$. The vibrationless, ν_2, and ν_3 states of a_1 symmetry, on the other hand, have a vibronic symmetry product of $E\otimes A_1=E$ and may possibly interact more weakly with $^3Q_0(A_2)$.

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