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Strong Field Effects in the Spectroscopy of the $\tilde{B}$ Rydberg State of CH_3I

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One- and two-color molecular beam resonance-enhanced multiphoton ionization (REMPI) excitation spectra of the Rydberg $\tilde{B}$ state of CH_3I revealed pronounced strong field effects manifested by apparent splittings in the molecular line shapes, appearance of new transitions, and large frequency shifts. The splittings or dip features occur in a saturation broadened regime due to a competition between rates of predissociation and photoionization from the $\tilde{B}$ state origin, the latter of which varies with the temporal intensity profile of the laser pulse. The dip can be made to disappear and the line width to narrow by the introduction of a second intense ionizing pulse. Appropriate rate equations were integrated to simulate the predissociation line shape and other observed trends.

Introduction

Few polyatomic molecules have attracted as much interest for spectroscopic and dynamic studies as CH_3I. The lowest lying nearly degenerate group of repulsive configurations, known as the $\tilde{A}$ states, has become a convenient model for experimental studies of direct dissociation in isolated molecules,[1-5] clusters,[6,7] and solution.[8] The next higher series of states are Rydberg in character due to (5p → 6s) configurations. These states have attracted considerable attention because of their predissociation to the $\tilde{A}$ states, their relatively low and accessible energy (6–7 eV), and their rich spectroscopic properties (i.e., strong spin–orbit coupling, near degenerate vibronic interactions, and a dynamic Jahn–Teller effect).[9-14] An excellent basis for understanding these spectroscopic effects can be found in early discussions of low-resolution ambient absorption spectra.[9,10]

More recently, the (5p → 6s) Rydberg states have been studied by two- and three-photon resonant absorption and MPI detection in ambient samples,[12] by dispersed broad-band single-photon absorption in a supersonic jet,[13] and by spontaneous resonance Raman scattering in a supersonic jet.[14] In some of these studies, unusual behavior was observed that could not be explained. For instance, the multiphoton absorption work reported large shifts in the line positions relative to earlier one-photon absorption spectra. It was suggested that the shifts might be due to different selection rules for one-, two-, and three-photon absorption in the ambient-temperature CH_3I. It is also known that the $\tilde{B}$ state undergoes predissociation to the $\tilde{A}$ state; however, an unusual dependence of the transition line shapes on laser intensity raises some uncertainties regarding the upper limit to the $\tilde{B}$ state lifetime.

In this report, we present single-photon spectra of the $\tilde{B}$ Rydberg state, recorded by molecular beam REMPI mass spectrometry. These higher resolution jet-cooled spectra make use of one- and two-color 1 + 1 REMPI to substantiate and explain a few intriguing laser field dependent effects, namely, (1) unusual *predissociation dips* in the line shapes that depend on the competition between ionization and predissociation from the $\tilde{B}$ state, (2) two-color narrow line-width studies that indicate that the Rydberg lifetime may be longer than previously thought, and (3) the appearance of new transitions and pronounced line frequency shifts at higher laser power densities. An understanding of these effects has strong bearing on the interpretation of recently published work and quite likely work currently in progress regarding the (5p → 6s) Rydberg states.

Experimental Section

The present work employed a pulsed molecular beam time-of-flight (TOF) mass spectrometer.[15] The CH_3I sample was contained in a bubbler cooled to dry ice/acetone or ice water temperature (about 5–50 Torr of CH_3I) and entrained in a flow of He or Ar at a pressure of about 15–25 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.

The lowest lying $\tilde{B}$ states were studied over the range 197–205 nm. These wavelengths were produced 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. The input beams entered the BBO crystal collinearly, and the polarizations were rotated into alignment by a custom-coated phase retarder that effected approximately half-wave rotation to ω and full-wave rotation to 2ω. The KDP crystal used to generate 2ω was angle tuned with a commercial autotracking device. The angle of the BBO crystal used to generate 3ω was tracked by a home-built device employing a dual photodiode detector sensitive in the far-ultraviolet region. Excitation spectra were recorded by 1 + 1 REMPI using one-color excitation by 3ω and two-color excitation by $3\omega + 2\omega$. Pulse energies were about 10 mJ for 2ω and 0.1–1.0 mJ for 3ω. 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 actual wavelength (ignoring vacuum corrections) for all observed spectra is obtained by adding 0.05 nm.

Background

The excited-state configurations of $(5p\pi)^3$ $(6s)^1$ give rise to five excited states.[9,10] Because of the Rydberg character of these states

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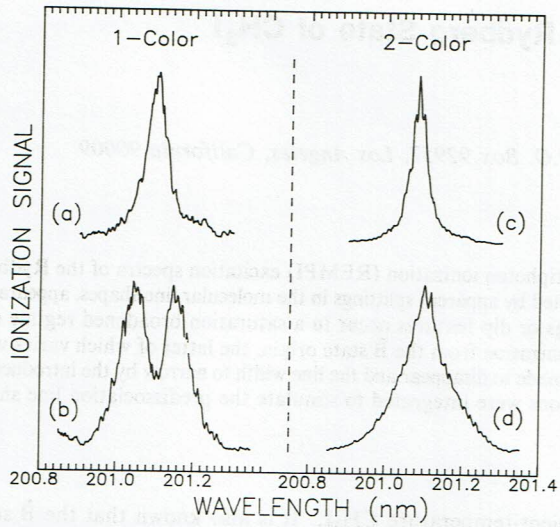

Figure 1. One- and two-color 1 + 1 REMPI $\tilde{B}2 \leftarrow \tilde{X}$ origin transition under different pulse intensities (photons cm^{-2}): (a) $I_1 = I_2 \sim 10^{17}$; (b) $I_1 = I_2 \sim 10^{18}$; (c) $I_1 \sim 10^{17}$, $I_2 > 10^{19}$; (d) $I_1 \leq 10^{18}$, $I_2 > 10^{19}$.

and the strong spin–orbit splitting between the unpaired valence (core) electron and the I atom nucleus, these configurations group into two sets of states, referred to as $\tilde{B}$ and $\tilde{C}$ and corresponding to the 6s Rydberg electron interacting with either the $^2\Pi_{3/2}$ or the $^2\Pi_{1/2}$ CH_3I^+ ion core spin-orbit states. $\tilde{B}$ is comprised of two states of symmetry Δ and Π in $C_{\infty v}$, which we designate as $\tilde{B}1$ and $\tilde{B}2$, respectively. The one-photon transition from the $\tilde{X}^1\Sigma$ ground state is orbitally forbidden for $\tilde{B}1$ and allowed for $\tilde{B}2$. 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 $\tilde{B}1$; however, this effect is observed to be very weak (see later section).[9,10] The $\tilde{B}2 \leftarrow \tilde{X}$ transition is a perpendicular type transition.

The vibrational modes of CH_3I are denoted $\nu_1 - \nu_6$. The first three modes are a_1 symmetry type, and the last three are doubly degenerate e type modes (in C_{3v}). This work focuses mainly on the $\tilde{B}2$ origin transition (designated $2:0_0^0$). The only vibrational modes that enter the present discussion are ν_3 (C–I stretch) and ν_6 (methyl rock), which were observed by the $2:3_0^1$, $2:6_0^1$, and $1:6_0^1$ transitions (the latter being a transition to $\tilde{B}1$).

Predissociation Dips in Line Shapes

The 1 + 1 REMPI line shape of certain $\tilde{B}2$ transitions exhibit striking intensity-dependent splittings. An example of this effect is presented for the origin transition in Figure 1. Under relatively moderate power, one-color excitation ($I_1 \sim 10^{17}$ photons cm^{-2}), a weak and rather broad line shape was observed (Figure 1a). Under more focused irradiation ($I_1 \sim 10^{18}$ photons cm^{-2}) the line shape broadened and developed a dip at line center (Figure 1b). Dips that reached the base line with apparent splittings as large as 80 cm^{-1} were observed under the most intense excitation. A dramatic change in the shape and intensity of the line shapes was obtained when a second laser pulse ($\sim$300 nm) was introduced to allow much greater ionization rates from the intermediate Rydberg state. For the same resonant excitation intensity I_1 used in Figure 1b, the addition of a strong ionizing pulse ($I_2 \geq 10^{19}$ photons cm^{-2}) caused the dip to disappear, the line shape to narrow, and the signal to increase significantly in strength (Figure 1d). This appears to be the result of a recovery of signal in the central part of the line shape when the intense I_2 field is present. By reducing I_1, the line width could be further reduced (Figure 1c) to values less than that which could be achieved with the weakest observable one-color excitation ionization.

The results in Figure 1 can be explained by a mechanism involving a competition between the rates of predissociation and photoionization, the latter of which varies across the laser intensity temporal profile. The dip line shape occurs when the excitation rate and decay rate are fast relative to the excitation pulse duration. The origin of the effect can be understood qualitatively as follows. Under sufficiently strong laser intensity, an on-resonance excitation can produce an excited-state population distribution that peaks during the early part of the laser pulse where the intensity is weak. For a short-lived excited state, the ionization rate cannot compete effectively with the decay. For off-resonance excitation, saturation occurs later in the pulse where the intensity is stronger and ionization is more effective. The overall REMPI line shape represents a product of a saturated absorption profile that exhibits a maximum at line center and an ionization probability that exhibits a minimum at line center. The observation of dips in saturated line shapes has recently been reported for He (ionization versus emission from 2^1S),[16] H_2 (ionization versus predissociation from $4p\pi^1\ \Pi_u^+$),[17] and H_3 (ionization versus predissociation from three states).[18] We are not aware of any examples of decay dips for larger molecules.

Predissociation lineshapes for the $\tilde{B}2\ 0_0^0$ transition were calculated from the following set of rate equations for the population of the ground state, N_1, the excited $\tilde{B}2$ state, N_2, and the ion, N_3.

$$\dot{N}_1 = -\sigma_{12}(\nu)\ I_1(t)[N_1 - N_2] \quad (1)$$

$$\dot{N}_2 = \sigma_{12}(\nu)\ I_1(t)[N_1 - N_2] - \{\sigma_{23}I_2(t) + k\}N_2 \quad (2)$$

$$\dot{N}_3 = \sigma_{23}I_2(t)N_2 \quad (3)$$

The terms $I_1(t)$ and $I_2(t)$ are the instantaneous photon flux (photons/cm^2 s) for the resonant absorption and the ionization steps, respectively, during the temporal evolution of the laser pulse. The pulse shapes are assumed to be Gaussian of width τ_L (fwhm). Quoted values of laser intensity are for the time-integrated photon flux (i.e., photon areal density) given by $I = \int I(t)\ dt$ (photons/cm^2). The terms σ_{12} and σ_{23} are the excitation cross sections for resonant absorption and ionization, respectively. The former is fitted to a Lorentzian function with a fwhm of $k/2\pi$, where k is the predissociation rate constant and is assumed to be the dominant decay process for the $\tilde{B}2$ origin. We estimate a value of $\sigma_{12} \sim 5 \times 10^{-17}$ cm^2/molecule at line center based on the reported absorption strengths in ambient spectra,[9,10] although this value will only be approximate for a jet-cooled sample. The ionization cross section σ_{23} unfortunately is not known; we assume a value of $\sim 2 \times 10^{-17}$ cm^2, independent of frequency, based on what we guess to be a reasonable upper limit. The predissociation from $\tilde{B}2$ represents an irreversible decay. We treat the stimulated emission term $\sigma_{12}I_1N_2$ as reversible even though the rotational selection rules $\Delta K = \pm 1$ for the $\tilde{B}$–$\tilde{X}$ transition allow ground-state repopulation to rotational levels different from the originating level. Removal of the $\sigma_{12}I_1N_2$ production term from eq 1 had very little effect on the calculations for $k \gg \sigma_{12}I_1$, a condition that applies to our experimental results.

Calculated REMPI line shapes for conditions consistent with the experimental results in Figure 1 are presented in Figure 2. The above model explains the general trends observed in Figure 1, namely, the occurrence of line broadening and dip formation under one-color excitation (Figure 2a,b) and the dip suppression and line narrowing in the presence of an intense ionizing pulse (Figure 2c,d). The dip line shape is predicted to occur for a wide range of reasonable conditions as long as k^{-1} is much smaller than the pulse duration. In fact, the dip line shape should be a rather common observation in REMPI excitation through short-lived states under strong excitation. Our model, however, predicts that the dip removal and line narrowing in the presence of an intense I_2 pulse become increasingly difficult to achieve as the intermediate lifetime becomes smaller. This is because the condition for suppressing the dip is $\sigma_{23}I_2(t) > k$.

The predissociation lifetime for the $\tilde{B}2$ origin has been reported to be about 0.5 ps from resonance Raman depolarization measurements.[14] Our observed spectral line widths for excitation to the $\tilde{B}2$ state origin ($\leq$10 cm^{-1}, Figure 1c) and to the ν_3 and ν_6 modes (6 cm^{-1}, Figure 3) are not inconsistent with this value, except to suggest that the lifetimes may be as long as 1 ps. These

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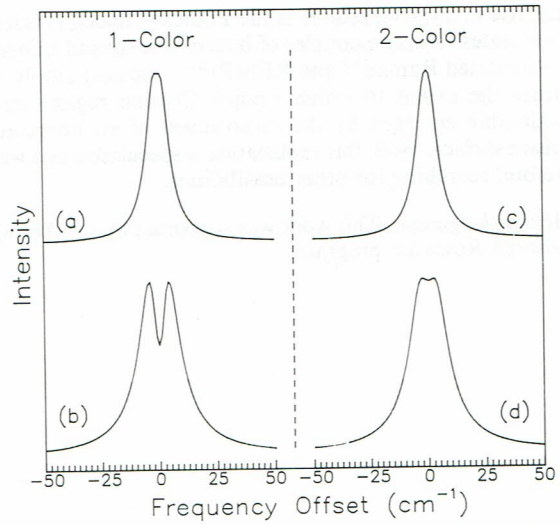

Figure 2. Calculated 1 + 1 REMPI $2:0_0^0$ line shapes for the following photon densities (photons cm^{-2}): (a) $I_1 = I_2 = 10^{16.8}$; (b) $I_1 = I_2 = 10^{17.3}$; (c) $I_1 = 10^{16.8}$, $I_2 = 10^{21.9}$; (d) $I_1 = 10^{17.3}$, $I_2 = 10^{21.9}$. The calculations assume the following parameters: $\sigma_{12} = 5 \times 10^{-17}$ cm^2 (at line center), $\sigma_{23} = 2 \times 10^{-17}$ cm^2, $k^{-1} = 1$ ps, $\tau_{L1} = 4$ ns, $\tau_{L2} = 5$ ns. All plots are normalized to the same intensity. Relative peak intensities, where 1.0 corresponds to ionization of the entire excitation volume, are 0.177×10^{-3}, 0.570×10^{-3}, 0.903, and 0.928, respectively.

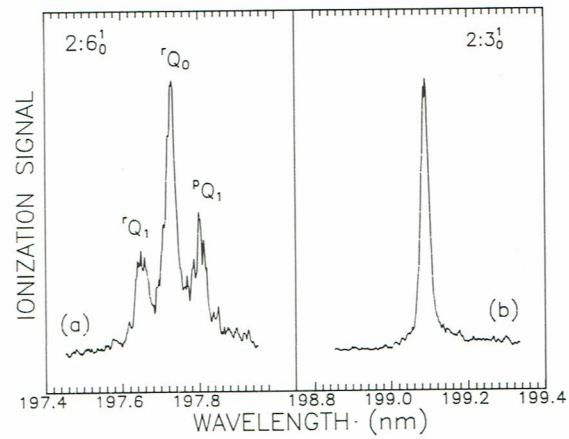

Figure 3. Two-color 1 + 1 REMPI spectra of the $2:6_0^1$ and $2:3_0^1$ transitions. The bands have fwhm values of 6 cm^{-1}. The expected wide Q-branch spacing for a perpendicular transition to a degenerate e type mode[9] is observed in (a). The rotational cooling in the supersonic expansion is evident by the near absence of subbands originating from levels $K > 1$.

results, however, are in conflict with the predissociation model of Vaida and co-workers,[6] who assert that the ν_6 and ν_3 vibrations undergo very rapid (~1 ps) mode-specific rates of decay. The spectrally resolved line widths observed here, though, cannot support a lifetime much less than 1 ps. This conclusion is made more secure by considering that rotational structure and possible saturation broadening probably obscures an even narrower homogeneous line width. The calculated two-color line shapes in Figure 2 assumed values of $k^{-1} = 1$ ps and $\tau_{L2} = 5$ ns which, in order to adequately agree with the observed two-color results, required a photon density of $I_2 = 8 \times 10^{21}$ photons cm^{-2}. This value exceeds the experimental conditions used to record Figure 1d and may indicate that the actual value of σ_{23} is much larger than anticipated. The lack of quantitative precision may also be attributed to the simplicity of the rate equation model. We are working on a density matrix approach that will retain the off-diagonal coherence terms, allow for the overlap of Q branches in the $\tilde{B}2 \leftarrow \tilde{X}$ transition,[9] and include better pulse shape functions. We have noticed, for example, that the observed line shapes can be better described if the intense I_2 ionizing pulse is advanced in time so that its peak intensity occurs early in the I_1 excitation pulse

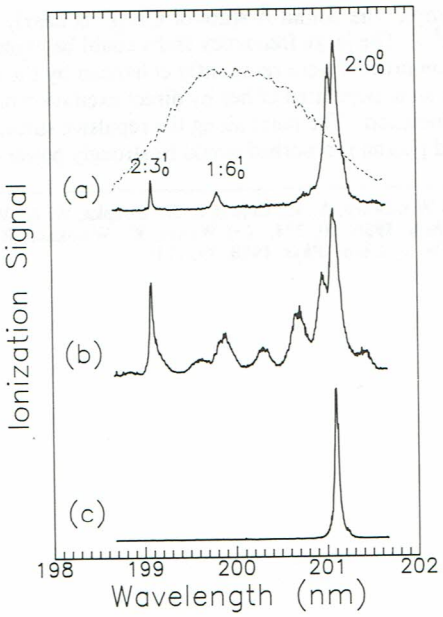

Figure 4. 1 + 1 REMPI $\tilde{B}2$ state spectra: (a) one-color, moderate field strength, ($I_1 = 10^{17}$–10^{18} photons cm^{-2}); (b) one-color, strong field strength ($I_1 > 10^{18}$); (c) two-color excitation ($I_1 \sim 10^{17.5}$, $I_2 \geq 10^{19}$). The plotted spectra were normalized linearly to the wavelength tuning intensity curve given by the dotted curve.

temporal profile. These and other calculated results underscore the sensitivity of the line shape dips to the properties of the laser pulses.

Strong Field Bands and Frequency Shifts

The REMPI spectra in Figure 4 reveal significant variations under different excitation conditions. In Figure 4a, the moderate-to-strong field dip feature in the saturated line shape is evident in the $2:0_0^0$ band, but not in $2:3_0^1$ because the much weaker absorption cross section causes the latter transition to be in the weak field limit. The formally forbidden (in $C_{\infty v}$) $1:6_0^1$ transition is clearly observable in Figure 4a,b at high laser power; however, a search for the $1:0_0^0$ origin transition failed to yield a signal. The weak $2:3_0^1$ and $1:6_0^1$ bands are visible in Figure 4a only because the $2:0_0^0$ transition is strongly saturated and depleted in intensity due to the aforementioned competition between ionization and dissociation. The spectrum of Figure 4c, recorded under two-color strongly ionizing conditions, is taken to be a better representation of relative absorption strengths in agreement with ambient one-color absorption spectra.[10a]

As the one-color excitation power increases, new bands begin to appear as seen in Figure 4b. These bands were observed to shift by as much as 50 cm^{-1} under different strong field conditions. The cause of these bands is unknown; however, we can rule out a few possibilities. The bands are not believed to be due to van der Waals complexes or long-range collisional interactions with the carrier gas because they persisted for neat CH_3I expansions and when either He or Ar was used as a carrier gas. We argue against clusters being the origin because the bands also occurred in spectra recorded when the CH_3I bubbler was operated at dry ice/acetone temperatures (i.e., low partial pressure conditions). Recently, similar features were observed under ambient vapor-phase conditions[19] for which cluster formation is not expected to occur.

The signal strengths for the new bands in Figure 4b are very nonlinear with laser power, which suggests that they may be due to a two-photon absorption to highly energetic levels, such as doubly excited autoionizing neutral states or excited ion states.

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(For example, the bound $\tilde{A}$ state of CH_3I^+ is nearly coincident with $2h\nu$.[21]) The large frequency shifts could be explained if the two-photon process were resonantly enhanced by the neutral repulsive $\tilde{A}$ state populated either by direct excitation or by a $\tilde{B} \rightarrow \tilde{A}$ predissociation. The point along the repulsive surface at which the second photon is absorbed would be strongly power dependent, giving rise to large variations in the Franck–Condon overlaps to the ion states. Many examples of bound–free–bound transitions (by stimulated Raman[5,8] and REMPI[20] processes) amply demonstrate the extent to which Franck–Condon regions can be considerably enlarged by the involvement of an intermediate repulsive surface. Still, this explanation is speculative and we are, therefore, searching for other possibilities.

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