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Theory of continuum mediated two-photon ionization, with applications to CH₃I

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Theory of two-photon ionization via intermediate dissociative states is developed. The theory is applied to the one-color two-photon ionization of CH₃I for which the 3Q_0 and 1Q_1 dissociative states serve as intermediate resonances. Both CW and transient ionization spectra are calculated. The computed methyl iodide CW ionization line intensities are in profound disagreement with line intensities derived from two-photon zero kinetic energy electrons (ZEKE) experiments. The discrepancy may be viewed as evidence that ZEKE line-intensities are not simply proportional to the population of the ionic-core states. This extra dependence on the ionic-core states, most likely due to the existence of external ions, can be accounted for by comparing our calculations to the observed ZEKE line intensities. The dynamics revealed by ultrashort pulsed two-photon ionization is also studied. In methyl iodide, we find that pulses capable of revealing "real-time" dissociative dynamics must be considerably shorter than 50 fs. © 1996 American Institute of Physics. [S0021-9606(96)01445-6]

I. INTRODUCTION

The dissociation of CH₃I has been the focus of exciting experimental and theoretical research for many years. Recently, this molecule has been probed by a new way of studying dissociation dynamics, in which one combines ZEKE spectroscopy with two-photon ionization.¹⁻⁵ If we can properly interpret the ZEKE line intensities, the coupling of a resonantly enhanced two-photon excitation with ZEKE detection would allow one to obtain detailed information about the intermediate resonant state involved. When, as in CH₃I, the intermediate resonant state is dissociative, such measurement will yield important information about the dissociation dynamics.

That the intermediate state affects the ZEKE spectra in CH₃I is known from the experiments of Strobel *et al.*^{1,2} who showed that there are significant differences between the one-photon and the two-photon ZEKE spectra. In contrast to the one-photon spectra, an intense progression in the totally symmetric C-I stretching mode (ν_3^+) was observed in the two-photon spectra.

In the ZEKE PFI (pulse field ionization) experiments,⁶ highly excited long-lived Rydberg states are ionized by a pulsed electric field after a field-free delay period. In this way ZEKE spectroscopy attains high resolution of vibrational and rotational ionic core-states. The evolution of the system during the field free phase is, however, more complicated⁷⁻¹¹ than initially thought. In particular, Chupka,⁷ Merkt and Zare,⁸ and Vrakking *et al.*¹² have pointed out that the lifetimes of the states probed in the ZEKE experiments are strongly affected by the influence of external fields and neighboring ions. It is not clear whether these effects are a function of the ionic-core states. If they are, then the observed line strengths do not reflect the relative populations of the various core levels.

An experiment related to the two-photon ZEKE spectroscopy is that of continuum Raman scattering.¹³⁻²² In fact, the only difference between the two types of experiments is

that in the continuum Raman process the second photon is (spontaneously) emitted (rather than absorbed) to the ground state. In the CH₃I case,^{4,15,17,20,21} the continuum Raman scattering of 266 nm photons involves exactly the same 3Q_0 1Q_1 intermediate pair of dissociative states as in the two-photon ionization case, and since the vibrational frequencies and geometries of the final potential surfaces (the ground state of CH₃I and CH₃I⁺, respectively) are quite similar, one would expect similar line intensities in the two types of experiments.

Experiments do not support these expectations: The ZEKE line intensities actually observed by Strobel *et al.*^{1,2} differ drastically from the continuum Raman line intensities.^{14,15,17} For example, in the continuum Raman case, the ν_3 progression peaks at excitation wavelengths of 266 nm at $v=2$, whereas in the two-photon ionization case the distribution peaks at $v=4$.

The aim of the present paper is to compute the actual populations obtained as a result of a two-photon ionization of CH₃I and compare the results to the two-photon ZEKE line-strengths. In this way we are able to directly answer the questions raised above, namely whether the ZEKE derived line-strengths are proportional to the population of the core states.

The response of the system to two laser pulses is calculated by applying time dependent second order perturbation theory to the case of a continuum of intermediate states.²³ The input to this theory are dipole matrix elements between the ground and the mixed 3Q_0 and 1Q_1 continuum states and between these states and the bound states of the ground CH₃I⁺ potential. These bound-free matrix elements are conveniently obtained using the artificial channel method.^{24,25}

The molecular dipole matrix elements are obtained by treating CH₃I as a pseudo-triatomic molecule.^{20,26} While not perfect,²⁷⁻²⁹ this model leads to quite good agreement with continuum Raman experiments^{21,26} and photodissociation-data. In particular, the model correctly predicted the wave-

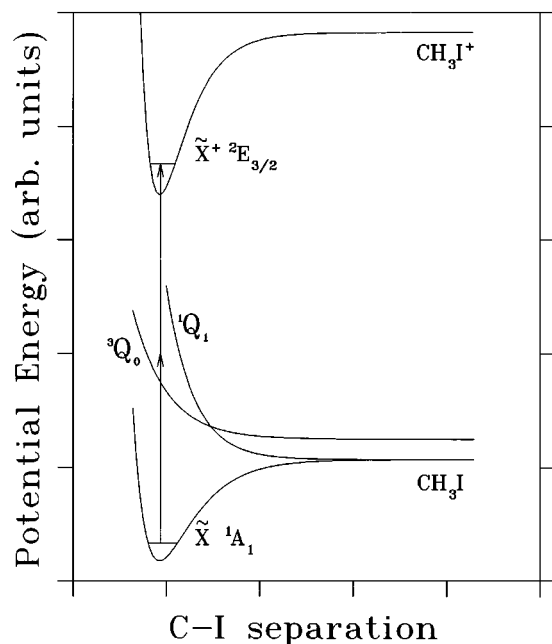


FIG. 1. Schematic description of the one-color two-photon photoionization experiments.

length dependence of the $I(^2P_{1/2})$ to $I(^2P_{3/2})$ branching ratio²⁰, as recently confirmed experimentally.³⁰

This paper is organized as follows: In Section II we outline the theoretical model used for describing the continuum mediated two-photon ionization. In Section III, we present calculations on CH_3I and compare them with the ZEKE experimental data. The implications of the discrepancy between the calculated and measured results are discussed in Section IV.

II. THEORY OF CONTINUUM MEDIATED TWO-PHOTON IONIZATION

We view the continuum mediated two-photon ionization process as comprised of two virtual steps: In the first step the neutral molecule is excited to a dissociative continuum, creating an evolving wave packet. In the second step, while evolving, the molecule absorbs another photon and becomes ionized. A schematic description of the one-color two-photon ionization of CH_3I is shown in Fig. 1.

In the weak-field CW regime, the probability of ionization as a result of two photon absorption is given in second-order perturbation theory as:³¹

$$P \sim \left| \int dE \frac{\sum_n \langle E_\nu | \mu_2 | E, n^- \rangle \langle E, n^- | \mu_1 | E_g \rangle}{\omega_{E,g} - \omega_L} \right|^2. \quad (1)$$

In the above, ω_L is the laser frequency, $\omega_{E,g} = (E - E_g)/\hbar$ is the transition frequency between a continuum energy level and the initial state, $|E_g\rangle$ is the initial state of the neutral molecule with energy E_g , and $|E_\nu\rangle$ is a final state of the ion, corresponding to the set of quantum numbers ν . $|E, n^- \rangle$ are the intermediate scattering states

which evolve, in the distant future, to a product of $|n\rangle$, the internal state of the fragments, and a free translational state $|E_n\rangle$,

$$\lim_{t \rightarrow \infty} |E, n^- \rangle = |E_n\rangle |n\rangle. \quad (2)$$

μ_1 and μ_2 are the electronic transition moments for the two consecutive transitions. To obtain the dipole transition matrix elements of Eq. (1) we use the Artificial Channel Method.²⁴ The method has been described in detail a number of times in the past (see, e.g., Refs. 24 and 25).

In the pulsed case, we have to address the effect of *delaying* one pulse relative to the other. We therefore assume two pulses of the form,

$$\mathcal{E}_i(t) = \frac{\varepsilon_i}{2} \exp(-i\omega_i t - 4 \ln 2 (t - t_i)^2 / \Delta_{it}^2), \quad i=1,2, \quad (3)$$

where ω_1 and ω_2 are the “carrier frequencies,” and t_1 and t_2 are the pulse peak times. (The $4 \ln 2$ factor is introduced to ensure that Δ_{1t} , Δ_{2t} are exactly the FWHM of the pulses.)

With the above Gaussian form, the Fourier transform of each pulse assumes the form,

$$\begin{aligned} \bar{\varepsilon}_i(\omega, t_i) &\equiv \int dt \mathcal{E}_i(t) \exp(i\omega t) \\ &= \varepsilon_i(\omega) \exp[-i(\omega_i - \omega)t_i], \end{aligned} \quad (4)$$

where

$$\begin{aligned} \varepsilon_i(\omega) &= \frac{(2 \ln 2)^{1/2} \varepsilon_i}{\hbar \Delta_{i\omega}} \exp[-4 \ln 2 (\omega_i - \omega)^2 / \Delta_{i\omega}^2], \quad (5) \\ \Delta_{i\omega} &= 8 \ln 2 / \Delta_{it}, \quad i=1,2. \end{aligned}$$

Assuming that the carrier frequencies of the two pulses are sufficiently different, such that one pulse (the “pump” pulse) is in exclusive resonance with the ground-to-continuum transitions, and the other pulse (the “probe” pulse) is in resonance between the continuum and the ionic ground state, it is possible to distinguish between the action of the two pulses. The wave function resulting from the action of the pump pulse is given, in first order perturbation theory, as³²,

$$\begin{aligned} \psi_I(t) &= 2\pi i \sum_n \int dE e^{-iEt/\hbar} |E, n^- \rangle \\ &\quad \times \langle E, n^- | \mu_1 | E_g \rangle \bar{\varepsilon}_1(\omega_{E,g}, t_1) c_E(t - t_1), \end{aligned} \quad (6)$$

where each $\bar{\varepsilon}_1(\omega_{E,g}) c_E(t)$ coefficient describes the build-up of all the degenerate continuum states of energy E during and after the pump pulse. In first order perturbation theory, the c_E coefficients are proportional to the finite-time Fourier transform of the pulse,^{33,34} or alternatively,

$$c_E(t) = \frac{1}{\varepsilon(\omega_{E,g})} \int d\omega \varepsilon(\omega) \frac{\exp[i(\omega_{E,g} - \omega)t]}{i(\omega_{E,g} - \omega)}. \quad (7)$$

For a Gaussian pulse, Eq. (7) gives for $c_E(t)$ coefficients.^{23,35,36}

$$c_E(t) = \text{sgn}(t) 2\pi \{ \Theta(t) - \frac{1}{2} \exp[\beta(E, t)^2] W[\text{sgn}(t) \beta(E, t)] \}, \quad (8)$$

where $\text{sgn}(t) = 1$ for $t \geq 0$, $\text{sgn}(t) = -1$ for $t < 0$,

$$\beta(E, t) = \alpha(\omega_1 - \omega_{E,g}) + it/2\alpha,$$

$$\alpha = \Delta_{1f}/4(\ln 2)^{1/2} = 2(\ln 2)^{1/2}/\Delta_{1\omega},$$

and $W[z]$ is the complex error function.³⁷

After a time delay $\tau (= t_2 - t_1)$, the probe pulse, whose carrier frequency is ω_2 , excites the dissociating molecule to the ionic ground electronic state. At the end of the pulse, the ionization amplitude from an intermediate continuum state is given as,

$$a(E_\nu, E, n, t_2) = 2\pi i \langle E_\nu | \mu_2 | E, n^- \rangle \bar{\varepsilon}_2(\omega_{\nu,E}, t_2), \quad (9)$$

where $\omega_{\nu,E} = (E_\nu - E)/\hbar$.

Combining Eq. (9) and Eq. (6) we obtain that the overall amplitude for producing a single $|E_\nu\rangle$ state in the two photon process, is

$$a(E_\nu, \tau) = -4\pi^2 \int dE c_E(\tau) \sum_n \langle E_\nu | \mu_2 | E, n^- \rangle \times \langle E, n^- | \mu_1 | E_g \rangle \bar{\varepsilon}_2(\omega_{\nu,E}, t_2) \bar{\varepsilon}_1(\omega_{E,g}, t_1), \quad (10)$$

where we have summed over all events leading from $\psi_I(t)$ of Eq. (6) to a single $|E_\nu\rangle$ state.

Assuming that the population of ions created by the two pulses is proportional to the number of photons absorbed, the photoionization probability, $P(\tau)$, can be therefore written as

$$P(\tau) = \sum_\nu |a(E_\nu, \tau)|^2, \quad (11)$$

where the ν summation includes the final states whose energies are within the $[\omega_2 - \Delta_{2,\omega}, \omega_2 + \Delta_{2,\omega}]$ interval.

Substituting Eq. (10) into Eq. (11) we finally obtain that,

$$P(\tau) = 16\pi^4 \sum_\nu \left| \int dE c_E(\tau) \sum_n \langle E_\nu | \mu_2 | E, n^- \rangle \times \langle E, n^- | \mu_1 | E_g \rangle \exp(-iE\tau/\hbar) \varepsilon_1(\omega_{E,g}) \varepsilon_2(\omega_{\nu,E}) \right|^2. \quad (12)$$

It can be shown, using the asymptotic form of Eq. (8),²¹ that this formula reduces to the CW limit when the pulse durations are made infinitely long.

III. APPLICATIONS TO CH₃I

In the one-color two-photon ionization experiment of methyl iodide, (a schematic illustration of which is shown in Fig. 1), the molecule is excited from the \tilde{X}^1A_1 electronic ground state to the $\tilde{X}^{+2}E_{3/2}$ ionic ground state via the intermediate 3Q_0 and 1Q_1 dissociative states.

According to the pseudo-triatomic model^{20,26} CH₃I is viewed as a collinear molecule composed of the I, C, and H₃ groups. Thus, in this model the C–I stretch, the C–H₃ “umbrella” motion, and the overall rotation are taken ex-

plicitly into account, while the other modes, which are assumed to be “inactive,” are neglected. This assumption is supported by CH₃I photodissociation experiments in which only moderate excitations of the rotation and the C–H stretch of the CH₃ fragment were observed.

The dissociative potential surfaces²⁰ consist of two diagonal diabatic potential energy surfaces, representing the 3Q_0 and 1Q_1 states, and an off-diagonal term, due to the deviation from collinearity, which couples the two states. The bound ground CH₃I surface and CH₃I⁺ surface are modelled as sums of a C–I Morse oscillator and a C–H₃ harmonic oscillator of variable equilibrium distance, reflecting the shape changes of the C–H₃ group from pyramidal (when the I atom is close by), to planar (when the I atom departs).

We first present simulations of the two photon ZEKE experiments with ns pulses. The small bandwidth of such pulses relative to the continuum absorption bandwidth suggests that the use of single continuum energy (the CW formula of Eq. (1)) is perfectly justifiable. In addition, coherent effects are expected to be minimal due to the fact that the ns lasers used are not transform limited. The calculations, according to Eq. (1), are shown in Fig. 2(a), and the ZEKE experimental spectra² are presented in Fig. 2(b).

We see that while the calculated peak positions are in good agreement with the experimental ones, the relative intensities of the vibrational overtones differ substantially. Thus, in contrast to the experimental ZEKE results, the most intense calculated transition is to the 3_0 state, with the mixed $2_n 3_m$ states being also prominent. Whereas in the ZEKE experiment the most intense transition is to 3_4 state, the calculated line intensities of all the high 3_n states is very low.

In order to check whether this discrepancy is due to the treatment of the process in the CW limit (which implicitly assumes that the absorption of two photons occurs simultaneously), we have repeated the calculation using the time dependent formulation of Eq. (11) and Eq. (12).

The one-color two-photon ionization spectra of CH₃I for 1 ps pulses delayed 0.3 ps with respect to each other are shown in Fig. 3(a). Also shown are the experimental results of Ref. 2 (Fig. 3(b)). Both the experimental and theoretical results have been normalized according to the most intense member of the ν_3^+ progression (3_4 in the experimental spectrum and 3_0 in the calculated spectrum).

As expected, when the pulses are delayed there are differences with respect to the CW case, due to the fact that the probe pulse excites a wave packet that has moved and spread considerably relative to its value at $t=0$. Nevertheless, the discrepancy with the two photon ZEKE experiment still remains. In particular, in contrast to the experiment, the line strengths of the high members of the 3_n series are still very weak.

In anticipation of “real time” pump-probe experiments on dissociating molecules with ZEKE detection, we have systematically studied the dissociation dynamics as probed by varying τ - the delay time between the pump and the probe pulse. In Figs. 4–6 we present the photoionization probability as a function of τ and the probe carrier frequency

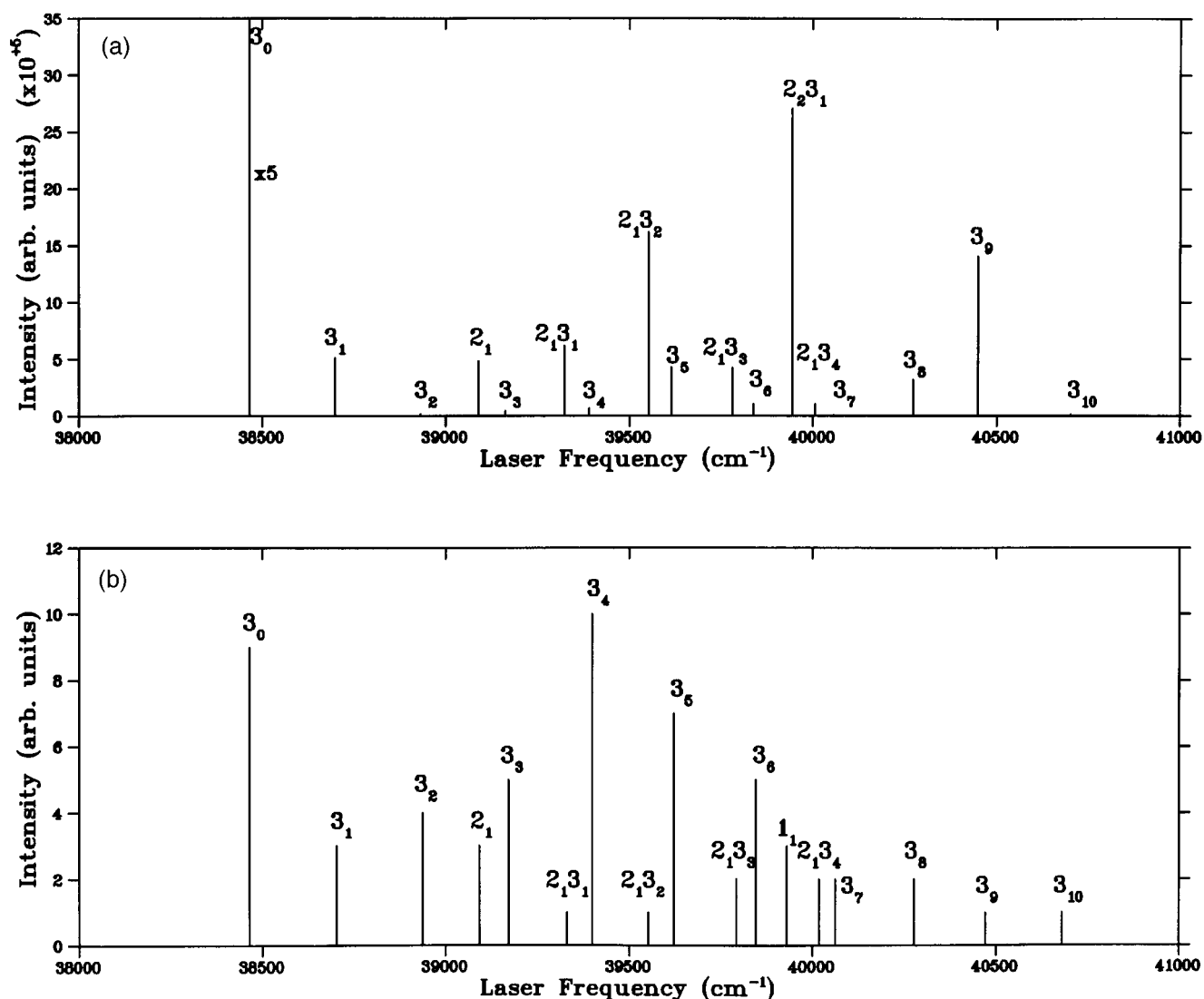


FIG. 2. Comparison of the calculated CW one color two-photon ionization spectra of CH₃I and the ZEKE experiment. (a) The calculated CW spectra using the artificial channel method and Eq. (1). (b) The ZEKE experimental results of Ref. 2.

ω_1 . Calculations are presented for Δ_t pulse durations (see Eq. (3)) varying between 200 and 50 fs and time delays varying between -400 and 1000 fs, depending on the pulse durations, for various carrier frequencies. In Figs. 4(a), 5(a) and 6(a) we show the ionization probabilities (given by Eq. (11)) as a function of the probe carrier frequency at three discrete values of the delay time, and in Figs. 4(b), 5(b), 6(b) the ionization probabilities as a continuous function of the delay time.

What is most striking about the transient results is that, contrary to the transient Raman spectra,²¹ the CH₃I⁺ vibrational distributions change very little with the pump-probe delay time. Only towards the end of the pump pulse, when the ionization probabilities are anyhow low, do the relative populations deviate significantly relative to their values at earlier times. This aspect of the two-photon ionization occurs for all pulse durations studied: 1 ps, 200 fs, 100 fs and 50 fs. It is clear that in the fast dissociation process of

CH₃I, pulses much shorter than 50 fs are needed in order to detect any motion of the intermediate $^1Q_1 / ^3Q_0$ state dissociative wave packet. In other words, at pulses of 50 fs or longer the intermediate state wave packet is already spread out to such an extent that the ionization probability hardly changes.

IV. THE DEPENDENCE OF THE ZEKE SIGNAL ON EXTERNAL IONS

The disagreement between the calculated two-photon ionization and the two photon ZEKE intensities can be understood if we allow for an extra dependence of the ZEKE signal on the ionic-core vibrational states. Differences in ZEKE signals which are not a result of population differ-

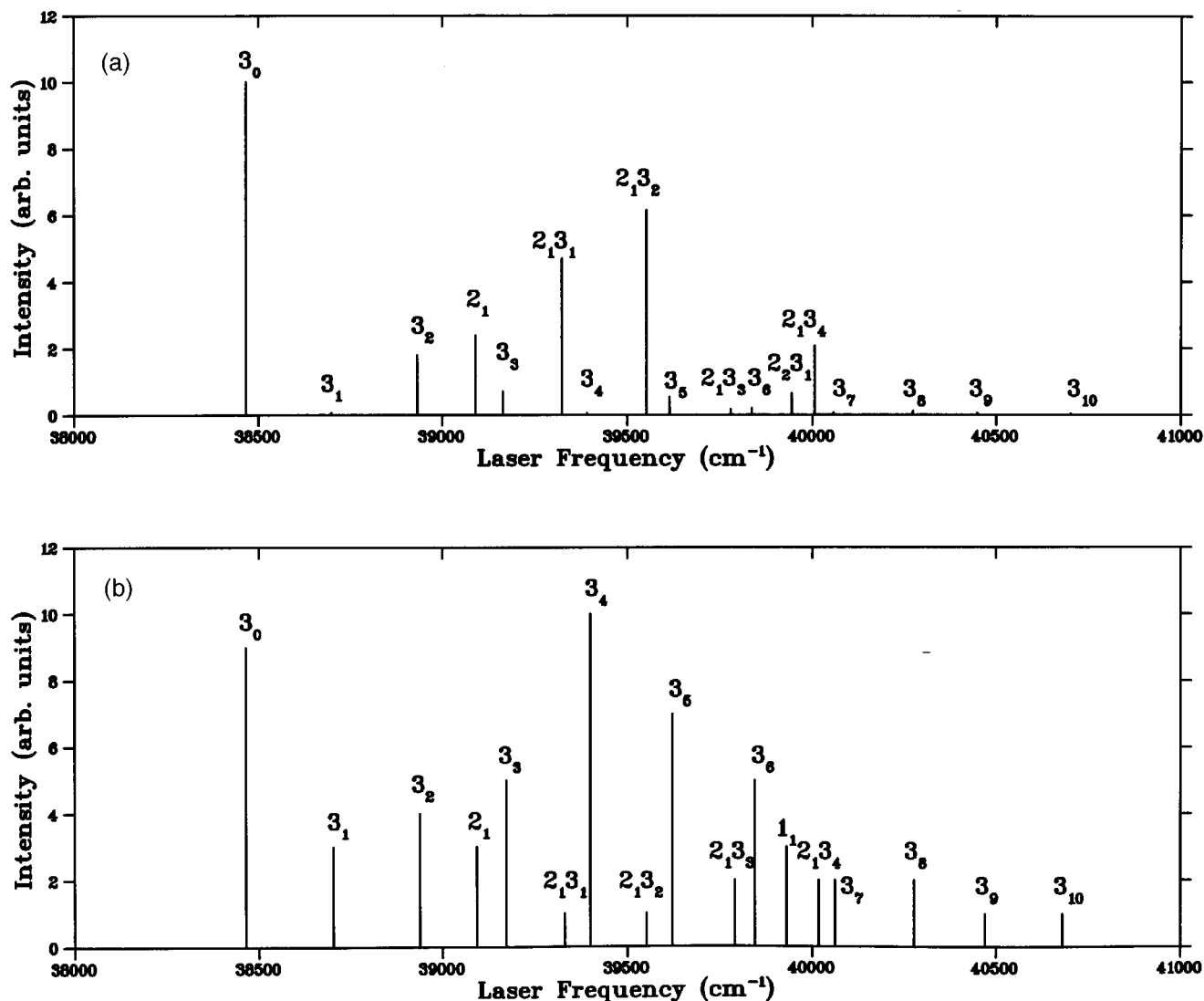


FIG. 3. One color two-photon ionization spectra of CH_3I with 1 ps pulses. (a) The calculated results, using Eq. (11) at pump-probe delay time τ of 0.3 ps. (b) The ZEKE experimental results of Ref.2. Both the experimental and calculated intensities are in arbitrary units.

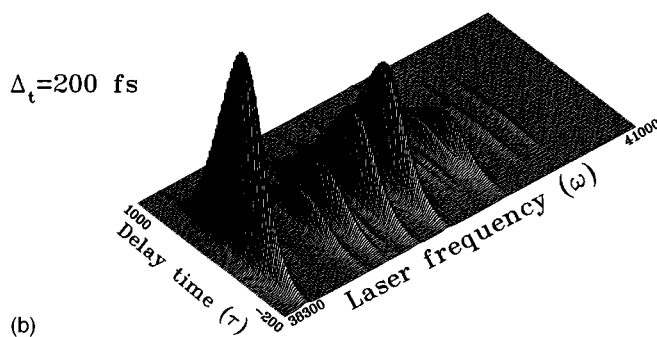
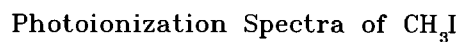
ences, are probably due to differences in the concentration of external ions. As shown by Vrakking *et al.*,¹² the external ions concentration affects in a dramatic way the ZEKE signal. Contrary to the high Rydberg states ("ZEKE states") which are the source of the ZEKE electrons, whose lifetime is not directly affected by the core vibrational states, the states giving rise to majority of the external ions, which are short lived and hence mostly low angular-momentum states, do couple to the vibrational core states. Since the concentration of ions dramatically affects the ZEKE signal, it is clear that an extra dependence on the core vibrations, not accounted by the optical transition probabilities to the high Rydberg states, is introduced in this manner.

If the ZEKE signal has such an extra dependence on the core vib-rotational states we cannot use the ZEKE line intensities to measure populations. We can remedy this situation by introducing *correction factors*, which empirically account for the extra core-dependence due to the ions, by using both

our calculated line intensities and the measured ZEKE signal. Denoting such correction factors for a given core state v as P^v , the observed line intensities may be written as,

$$I_{\text{exp}}^v = I_0^v P^v, \quad (13)$$

where I_0^v is the population of the ZEKE states at the end of the second excitation pulse. Assuming that our calculation line strengths are proportional to I_0^v we can use the Eq. (13) and the experimental line intensities to extract P^v . The values of P^v , thus extracted for various core states, relative to that of the 3_4 state, are presented in Fig. 7 where experimental results are being compared with the CW results as calculated with Eq. (1).



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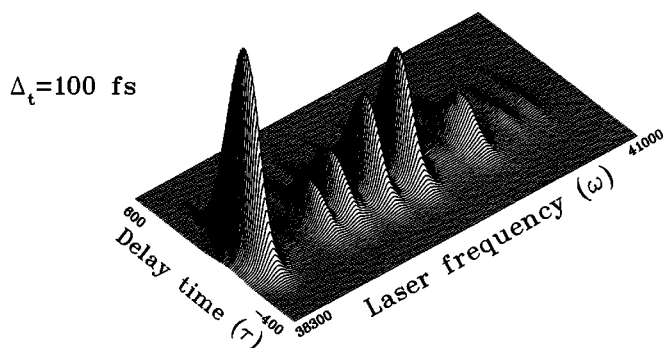
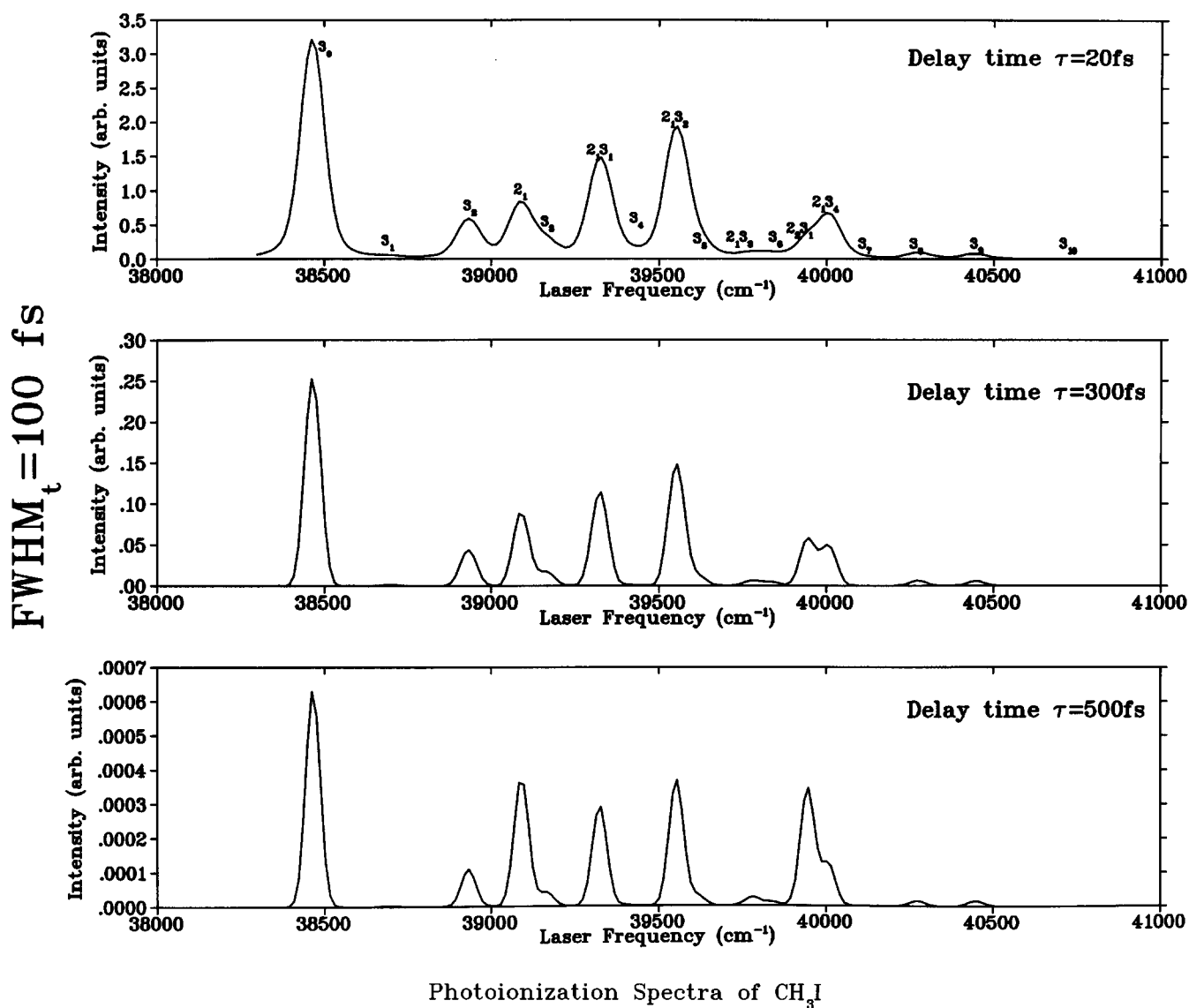


FIG. 5. The same as in Fig. 4 for a 100 fs pump pulse.

core vibrational states, the states giving rise to majority of the ions are short lived and hence mostly low angular-momentum states. Such states do couple to the vibrational core states. Since it was shown¹² that the concentration of

ions dramatically affects the ZEKE signal it is clear that an extra dependence on the core vibrations, not accounted by the optical transition probabilities to the high Rydberg states, is introduced via the dependence of the ion concentration on

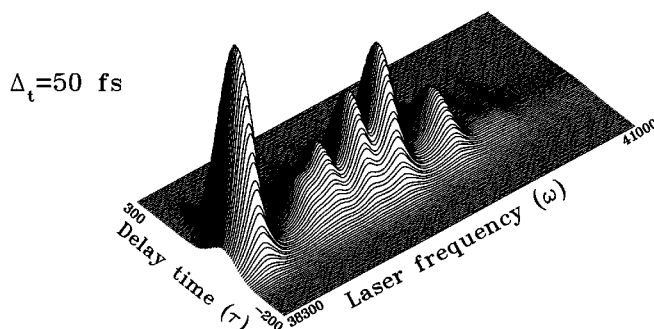
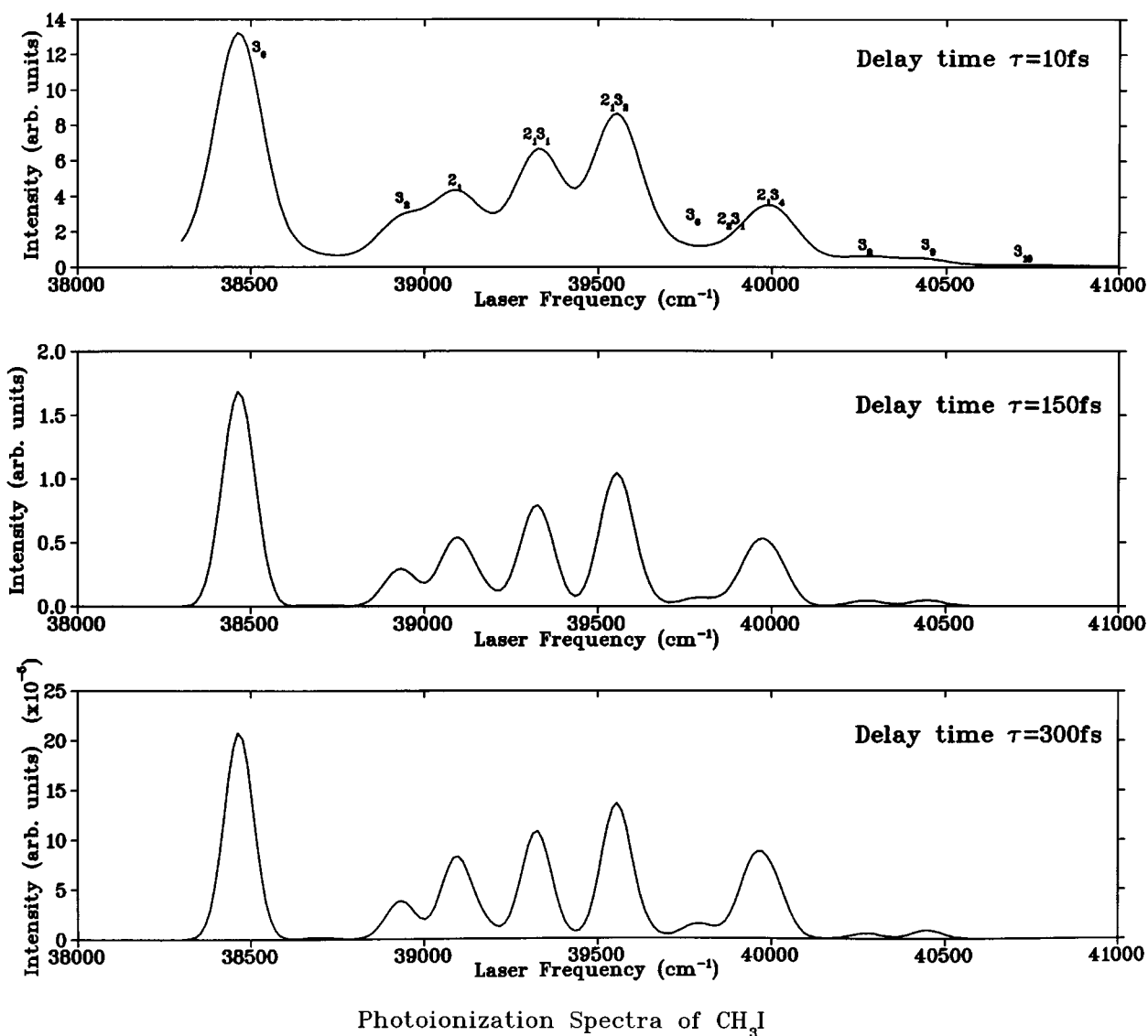
FWHM_t = 50 fs

FIG. 6. The same as in Fig. 4 for a 50 fs pump pulse.

the core states.

Transient two-photon ionization spectra have also been calculated. The relative yields to various core states has been found to change very little with the pump-probe delay time.

These observations hold for laser pulse of 50 fs or longer. We conclude therefore, that in CH_3I , pulses shorter than 50 fs are needed in order to follow the dynamics of populating different ionic vibrational states.

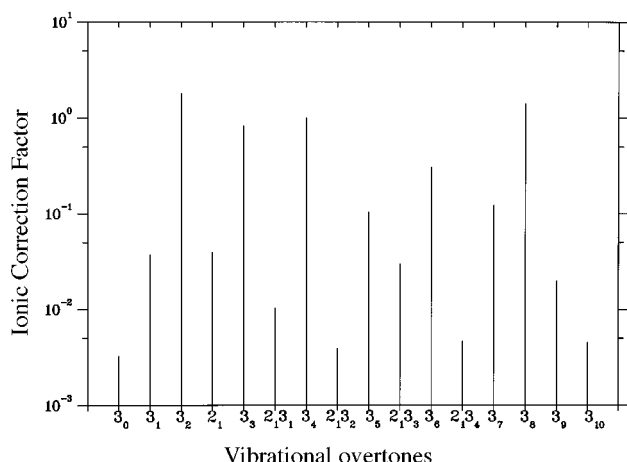


FIG. 7. P_v — ionic correction factors — as a function of the vibrational ionic-core states, relative to that of the 3_4 ionic-core state. The CW theoretical calculations have been used for comparison with the experiment.

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