Time-resolved two-color photoacoustic and multiphoton ionization spectroscopy of aniline

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The multiphoton ionization and photoacoustic signals from aniline have been detected as a function of time delay between two laser pulses of different wavelength. The first pulse excited the \( S_0 \rightarrow S_1 \) 0-0 transition. The second pulse either excited \( S_1 \) to a higher singlet state, or a triplet state produced by intersystem crossing to a higher triplet state, depending on the time delay between pulses. Both ionization and dissociation processes are observed. By varying the conditions of excitation it appears that a given amount of energy can be selectively channeled almost exclusively into either ionization or dissociation pathways. The results are explained using a simple Franck-Condon factor model.

I. INTRODUCTION

In typical resonance-enhanced multiphoton ionization (MPI) experiments, an intense UV or visible laser pulse is focused into a gaseous sample, producing an ionization current which is measured as a function of wavelength. When integral multiples of the photon energy are resonant with states in the sample an increase in ionization current occurs. Recent MPI experiments have detected the masses of fragments produced and/or the kinetic energy of released electrons in molecules such as NO, \( H_2 \), \( H_2 S \), \( NH_3 \), \( benzen e \), \( acetaldehyde \), \( aniline \), \( azulene \), \( naphthalene \), and organometallics. Three mechanisms have been proposed to explain the observed fragmentation: (1) multiple absorption of photons through neutral valence, Rydberg, and autoionizing states to produce superexcited states which eventually autoionize and dissociate into the observed fragments, (2) initial preparation of the parent ion by multiphoton absorption with subsequent absorption by that ion of more photons to dissociative or predissociative states, and (3) dissociation from the neutral manifold before reaching the ionization potential (I.P.), followed by ionization or further dissociation of the fragments. There is strong evidence, particularly from MPI photoelectron studies, that indicates that most molecules follow mechanism (2) where ionization to the parent ion occurs as soon as sufficient energy to reach the I.P. of the molecule has been absorbed. Mechanism (1) has only been reported in a few scattered cases, as a minor process in MPI through the \( A^2 \Sigma^+ \) (\( v = 3 \)) state of \( NO \), and in azulene. Mechanism (3) has been observed in weakly bound organometallic systems.

This paper presents time-resolved two-color photoacoustic and MPI results for aniline which strongly support the presence of mechanism (3) in that molecule for excitation from a state prepared by intersystem crossing. In this specific case, the molecule is excited above the adiabatic I.P., but dissociates almost exclusively into neutral fragments rather than ionizing. By varying the conditions of excitation in aniline, a given amount of energy can be channeled almost exclusively into either ionization or dissociation.

Aniline was initially selected for these experiments because of our interest in photoacoustic detection of stimulated emission pumping. After initial excitation to a vibronic level in the lowest excited singlet state \( 1B_2 (S_1) \) we observed only additional excitation to higher excited states, when a second laser pulse was introduced, instead of stimulating emission back down to a vibrational level of the ground electronic state. An investigation of the excited state absorption phenomena is reported in this paper.

II. BACKGROUND

The electronically excited states of aniline have been extensively studied by absorption, emission, and multiphoton techniques. The electronic absorption spectrum of this molecule displays a 0-0 transition at 34 032 cm\(^{-1}\) to the \( S_1 \) state, exhibiting sharp single vibronic levels superimposed on a broad underlying continuum. Fluorescence lifetime and quantum yield measurements of single vibronic levels indicate a fluorescence lifetime ranging from 5.8 to 9.8 ns and a quantum yield for fluorescence ranging from 0.1 to 0.3. The 0-0 level of \( S_1 \), which is used in this study, has a fluorescence lifetime and quantum yield of 8.57 ns and 0.30, respectively.

\( T_1 \) phosphorescence with a lifetime of 4.2 s has been observed from the low-lying \( 3A_1 \) state in aniline in solid solution at 77 K after exciting \( S_1 \). The ratio of phosphorescence to fluorescence quantum yields was 3.1, and total luminescence quantum yields were estimated at close to unity. An additional low-lying \( T_2 \) state was postulated to be isoenergetic with \( S_1 \) to explain early fluorescence lifetime data, but no direct evidence for the location of that state has been published. The energy of \( T_1 \) was determined from phosphorescence studies which place that state about 7200 cm\(^{-1}\) below \( S_1 \).

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Extremely efficient two-photon ionization, observed for aniline using $S_1$ as an intermediate state, is made possible by its low I.P. (62 100 cm$^{-1}$) and the fully allowed nature of the transitions between $S_0$ and $S_1$. At intensities below 10 MW/cm$^2$ the parent ion accounted for 100% of the ion signal. When increased to 20 MW/cm$^2$ the parent ion still accounted for 85% of the ion signal.\

III. EXPERIMENTAL

A. Apparatus

The time-resolved two-color photoacoustic and MPI techniques used in this paper are similar to those reported previously. In summary, a gas phase sample of aniline is subjected to two counter-propagating collinear laser pulses (PUMP and TRANSFER) having different wavelengths. The delay time between them, $\Delta t = t_{\text{TRANSFER}} - t_{\text{PUMP}}$, is continuously adjustable with nanosecond precision. In photoacoustic experiments, the energy deposited into the sample is detected as a pressure wave by a microphone. The amplitude of this pressure wave is measured as a function of $\Delta t$ at different TRANSFER wavelengths. In MPI experiments, the total ion current is also measured as a function of $\Delta t$ and TRANSFER wavelength.

The experimental apparatus is shown schematically in Fig. 1. The details of the laser systems and optics, time delay generation, photoacoustic cell, and electronic data handling procedures have all been described previously. The MPI cell is a simple biased parallel plate-type cell. Briefly, it consists of a stainless steel cell having quartz windows containing two square parallel plates 0.75 in. on the side, separated by 0.75 in. The plates are biased with 22.5 V. The charge pulse produced by the MPI process is detected by a Canberra 2001A charge-sensitive preamplifier having a sensitivity of 10V/pC. Since the pulse output of this preamplifier has a decay time of 30 $\mu$s, the signals produced by two laser pulses separated in time less than a few microseconds are automatically added together.

B. Sample preparation

Aniline was obtained from Mallinckrodt, Inc. (Analytical Reagent Grade) and subjected to a minimum of four liquid $N_2$ freeze-pump-thaw cycles and a vacuum distillation in a vacuum line operated at $5 \times 10^{-7}$ Torr before use. Samples were stored in darkness. When filling the MPI or photoacoustic cells, the final pressure was allowed to stabilize for several minutes before closing the cell valve to minimize wall absorption effects.

IV. RESULTS

The photoacoustic spectrum of a 0.37 Torr sample of aniline in the region of the $S_1$ 0-0 transition is shown in Fig. 2. Several of the prominent bands, including the 0-0 transition, are labeled according to the assignment of Ref. 14. This spectrum was obtained by scanning the wavelength of dye laser #1 (see Fig. 1).

The results presented in the following sections were obtained by pumping the 0-0 transition at 34 032 cm$^{-1}$ with the PUMP pulse and measuring the photoacoustic and MPI signals as a function of $\Delta t$ for TRANSFER pulse wavelengths of 532, 305, and 266 nm. The 0-0 transition wavelength was chosen for the PUMP pulse to avoid the effects of vibrational energy redistribution within $S_1$. Preliminary studies where higher vibrational levels of $S_1$ were pumped gave similar results to those described below.

A. 532 nm TRANSFER Pulse

Figure 3(a) shows the MPI time-domain spectrum of aniline obtained by exciting the $S_1$ 0-0 transition at 34 032 cm$^{-1}$ with the PUMP pulse, using the Nd:YAG second harmonic at 532 nm as the TRANSFER pulse, and varying $\Delta t$. For $|\Delta t| > 20$ ns the MPI signal is due almost entirely to a two-photon ionization occurring through a one-photon resonance in $S_1$, induced by the PUMP pulse. The efficiency of this process required a reduction of the PUMP pulse energy to 0.5 $\mu$J/pulse to avoid saturation of the charge sensitive preamplifier, which occurs at ion yields greater than $10^7$ ions/pulse. The 2 mJ transfer pulse produced no detectable ions at these sensitivities.

For $|\Delta t| < 5$ ns, i.e., both pulses overlapped in time, a sharp decrease in ion yield, greater than 25% is observed. This effect has been previously detected for molecular beam targets and attributed to competition between ionization from $S_1$ induced by a second PUMP photon, and excitation from $S_1$ to a rapidly predissociating state induced by the 532 nm TRANSFER pulse, as shown in Fig. 4. The predissociation process is apparently fast enough for the molecule to dissociate before another TRANSFER or PUMP photon can ionize the molecule. This mechanism is supported by

![Diagram of experimental setup](image-url)
FIG. 2. Pulsed photoacoustic spectrum of aniline excited by a portion of the 2A1 → 1B1 transition in aniline obtained using a 0.37 Torr sample pressure. The photoacoustic signal has been corrected for the variation in incident laser pulse energy with wavelength. Pulse energies ranged from 1 to 10 μJ. The vibronic bands are labeled by the symbol \( k \), which implies a transition from \( \nu \) quanta in mode \( k \) in the ground electronic state to an excited electronic state with \( \nu' \) quanta in mode \( k' \). \( k = 1 \) represents the NH out-of-plane rocking mode. \( k = 6\) and 12 represent \( a_i \) symmetry ring modes. \( k = 1 \) represents a ring-stretching mode. The assignment was taken from Ref. 14.

FIG. 3. Time-resolved two-color spectra of aniline. The PUMP pulse excites the \( S_0 \rightarrow S_1 \), 0-0 transition at 34,032 cm\(^{-1}\). The TRANSFER pulse photon energy is 18,797 cm\(^{-1}\) (532 nm). The abscissa gives the time delay between pulses, \( t = t_{\text{TRANSFER}} - t_{\text{PUMP}} \). (a) Multiphoton ionization detection. The sample pressure was 0.010 Torr. The PUMP and TRANSFER pulse energies were 0.3 μJ and 2.0 μJ, respectively. (b) Photoacoustic detection. The sample pressure was 0.38 Torr. The PUMP and TRANSFER pulse energies were approximately 5.4 μJ and 6.5 μJ, respectively. Neither spectra has been corrected for fluctuations in pulse energy.

FIG. 4. Energy level diagram indicating the excitation processes corresponding to the spectra of Fig. 3. The PUMP and TRANSFER pulses have photon energies of 34,032 and 18,797 cm\(^{-1}\), respectively. The potential curves, their relative horizontal displacement and the vibrational levels are schematic and do not correspond to known molecular parameters.
VUV studies\textsuperscript{16,17,19} which show strong absorptions near 52 800 cm\textsuperscript{-1}, the presence of a photodecomposition film on the windows after extended data collection, and the photoacoustic measurements presented next. The N–H bond energy is only 30 200 cm\textsuperscript{-1}, making it the lowest energy dissociation pathway.\textsuperscript{27}

Figure 3(b) shows the corresponding photoacoustic time-resolved spectrum. An increase of almost 70% in photoacoustic signal is observed near $\Delta t = 0$. In addition, the signal for $\Delta t > 20$ ns (TRANSFER pulse after PUMP pulse) is about 20% larger than for $\Delta t < -20$ ns (TRANSFER pulse before PUMP pulse).

The pulsed photoacoustic technique is sensitive to energy deposited in the sample and transformed into translational energy on a mesoscopic time scale. As can be seen from Fig. 3, values of $\Delta t \approx 0$ to 5 ns result in a substantial decrease of the MPI signal, whereas the corresponding photoacoustic signal shows a substantial increase. In this case it appears that the photoacoustic technique is more sensitive to the dissociation than to the ionization process. It is possible that the dissociation process directs a detectable amount of energy into translational energy of the fragments. For example, pressure waves from the vacuum UV photodissociation of O\textsubscript{2} have been predicted theoretically\textsuperscript{38} and observed experimentally.\textsuperscript{39}

Nondissociative excited states such as $S_1$ require collisional deactivation before the internal vibronic energy is transferred into translational degrees of freedom, a process which may be less efficient than dissociation on the mesoscopic time scale for pressures less than 0.5 Torr. Photoacoustic detection of ionized states may also be inefficient depending on ion recombination and electron thermalization rates. The time dependence of the actual photoacoustic signal observed on an oscilloscope is also consistent with the interpretation that the electronic excitation energy is channeled into kinetic energy of the fragments. Indeed, for the values of $\Delta t$ in Fig. 3(b) where an increase in photoacoustic signal is seen (i.e., $\Delta t \approx 0$), the pressure wave appears at the microphone about 2 ns earlier than for $\Delta t < -10$ ns in which case only $S_1$ is excited. (In aniline at 0.37 Torr we normally detect the pressure wave about 65 ns after the laser pulse. This delay results from both collisional deactivation times and the transit time of the pressure wave from the laser beam to the microphone.) The 70% increase in photoacoustic signal for $\Delta t \approx 0$ also supports the efficient release of kinetic energy through dissociation. If $S_1$ and $S_2$ transfer electronic into translational energy with equal efficiencies, the maximum possible increase in the photoacoustic signal due to the TRANSFER pulse (i.e., every molecule excited by the PUMP pulse is also excited by the TRANSFER pulse), based on photon energies, is 55%. To produce instead a 70% increase, a mechanism like dissociation must be occurring which releases translational energy more efficiently than the collisional deactivation of $S_n$.

In summary, the experimental evidence that the PUMP and TRANSFER (532 nm) pulses result in a significant amount of dissociation is: (1) an increase in photoacoustic signal occurs when a decrease in MPI signal is observed, (2) for $\Delta t \approx 0$ the pressure wave is detected about 2 ns earlier than when $\Delta t < -10$ ns, and (3) the signal increase caused by the TRANSFER pulse is larger than predicted by photon energy considerations alone.

From fluorescence and phosphorescence quantum yields and lifetimes it is known that the initially excited 0–0 level of $S_1$ disappears with a lifetime of 8.57 ns due to intersystem crossing to a nearby triplet state, which is probably the $T_4$ state, and fluorescence.\textsuperscript{24,28} The increase in photoacoustic signal near $\Delta t = 0$ in Fig. 3(b) is therefore due to excitation to a dissociative state from the 0–0 level of $S_1$ prepared by the PUMP pulse. For $\Delta t > 20$ ns, the increase must be caused by triplet–triplet absorption form the state resulting from intersystem crossing of $S_1$. Triplet–triplet absorption in aniline has been observed from 320 to 600 nm in rigid solution at 77 K.\textsuperscript{40} Our gas phase photoacoustic results indicate an absorption at 532 nm from a vibrationally excited triplet state to a dissociative triplet state. Figure 4 is a diagram showing the processes occurring with the 532 nm TRANSFER pulse.

The differences in widths of the features near $\Delta t = 0$ in Figs. 3(a) and 3(b) result from two different processes. In Fig. 3(a), the MPI time domain spectrum, there is competition between the dissociation process from $S_0$ and the MPI caused by the PUMP pulse. However, since the $S_1$ and $T_1$ states last longer than the PUMP pulse, the sample can absorb photons from the TRANSFER pulse at later times. This results in the much slower decay in the photoacoustic time-domain spectrum of Fig. 3(b).

**B. 305 nm TRANSFER pulse**

Figure 5(a) shows the MPI time-domain spectrum of aniline obtained under conditions similar to the spectrum of Fig. 3(a), except that now the TRANSFER pulse wavelength is about 305 nm. At this wavelength the TRANSFER pulse’s photon energy falls just below that corresponding to the $S_0 \rightarrow S_1$ hot bands, but in combination with the 34 032 cm\textsuperscript{-1} PUMP pulse, the molecule can be excited to about 4700 cm\textsuperscript{-1} above the adiabatic I.P. of 62 100 cm\textsuperscript{-1}.\textsuperscript{35}

In Fig. 5(a) the MPI signal shows a sharp eightfold increase in yield as $\Delta t$ increases beyond zero, and decays exponentially after that with a time constant of 8.9 ± 0.2 ns back to the $\Delta t < 0$ signal level. This eightfold increase is in strong contrast to the decrease observed using the 532 nm TRANSFER pulse. (The periodic oscillations in the decay curve are not reproducible and result from jitter in $\Delta t$.) The spectrum in Fig. 5(a) is insensitive to pressure over a range of 0.004 to 0.37 Torr, and this decay time constant does not differ significantly from the 8.57 ns fluorescence decay constant\textsuperscript{24} of $S_1$ once the laser pulsewidths (~3 to 5 ns) are taken into account. This implies that after intersystem crossing from the $S_1$ 0–0 level, the TRANSFER pulse is no longer capable of efficiently ionizing the molecule.

From energy considerations alone there is no reason to expect the large decrease in ion yield in going from $\Delta t \approx 0$ to $\Delta t \approx 10$ ns, since complete collisional deactivation of the vibrationally excited triplet produced by intersystem crossing is unlikely at 0.004 Torr for time scales < 50 ns and there is no inherent reason why ionization from triplet states should be efficient.\textsuperscript{36} Consideration of vibrational effects offers an explana-
tion of the inability to ionize the state produced by intersystem crossing. Absorption by an aniline molecule of a first PUMP photon excites it to the ground vibrational state of the $S_0$ electronically excited state. During intersystem crossing to the $3a_1$ state, the total energy remains the same, but 7200 cm$^{-1}$ is transferred from electronic to vibrational degrees of freedom. The new wave function corresponds to a highly excited vibrational level with a vibrational energy of 7200 cm$^{-1}$. However, this vibrational energy is not available for direct ionization. The probability of direct ionization involves the Franck–Condon overlap integral between the vibrational wave function of the ion and the level of the neutral molecule from which ionization occurs. Therefore, for small changes in geometry between $S_0$ and $T_1$, and the ions, the vertical I.P. (i.e., the I.P. corresponding to maximum ionization signal) from the state produced by intersystem crossing $T_1$ is expected to be about 7200 cm$^{-1}$ higher than the vertical I.P. of the initial $S_0$ state. From the known small changes in geometries between $S_0$ and $S_{10}$, it is expected that ionization through $S_{10}$ occurs at approximately the same vertical I.P. as direct ionization from $S_0$. These relationships are shown in Fig. 6. Larger changes in geometry between $S_0$ and $T_1$ may change the 7200 cm$^{-1}$ difference, but nevertheless, the 305 nm TRANSFER pulse can apparently only ionize the $S_0$ state, and not the vibrationally excited triplet state, by a direct ionization process.

In recent studies on the time evolution of benzene and toluene triplet states using a two-color photoionization technique, it was assumed that both singlet and triplet states were detected with equal efficiencies. This assumption was justified by Dietz et al. using a Franck–Condon factor argument analogous to ours. If the two photon energy exceeds this effective triplet I.P. by an appreciable amount (as in all the previous experiments) then the direct ionization efficiency from both the singlet and triplet states should be approximately the same. We provide experimental evidence for this Franck–Condon factor explanation by showing that for two photon energies between the adiabatic I.P. and the effective triplet I.P., only the singlet state is directly ionized.

Even if Franck–Condon factors make the direct ionization process highly unlikely, there is still the possibility of a triplet–triplet absorption to a quasidiscrete level above the adiabatic I.P. that rapidly undergoes an autoionization process. Photoelectron energy analysis following MPI through the $\tilde{B}$ state in ammonia provides an example of vibrational autoionization occurring from quasidiscrete levels. A triplet quasidiscrete level must exist in aniline near 66 800 cm$^{-1}$ if such an absorption from $T_1$ is to occur.

Figure 5(b) shows the time-domain photoacoustic spectrum corresponding to the conditions of Fig. 5(a). Two features are immediately obvious. First, the sharp increase in
MPI signal observed in Fig. 5(a) does not appear. This agrees with the result of the previous section where it was shown that the photoacoustic technique has a low sensitivity to ionization. It also implies that substantial amount of dissociation (to which the photoacoustic technique is sensitive) are unlikely, in agreement with previous aniline MPI fragmentation studies.\(^8,^{31}\) Second, the increase in the photoacoustic signal with respect to its value for \(\Delta t < 0\) is proportional to \(1 - e^{-\text{ad}}\) and results in a 40% increase over a time scale similar to the decay time observed in Fig. 5(a). Figure 7 shows a spectrum similar to that of Fig. 5(b), but covers a larger range of \(\Delta t\). The apparent rise time of Fig. 7 was limited by the effective time constant and is therefore an experimental artifact. The rise time of Fig. 5 was limited only by the laser pulsewidth. The photoacoustic signal increase over its \(\Delta t < 0\) value decays slowly with time, taking about 15 \(\mu\)s to decrease to half of its maximum increase. This decay may be due in part to vibrational relaxation of the \(T_1\) state. Alternatively, it may be an artifact of the photoacoustic detection technique caused by the pressure waves created by the PUMP and TRANSFER pulses no longer arriving at the microphone when the integration gate is open, or by diffusion of the initially excited molecules out of the laser beam region. The decay rate did not change when an electric field of 80 V/cm was applied, indicating that the increase in photoacoustic signal is not caused by absorption of the TRANSFER pulse by ions resulting from the PUMP pulse.

The photoacoustic results imply that the triplet state produced by intersystem crossing from \(S_1\) is long-lived (>10 \(\mu\)s) in the gas phase, and that it does absorb the 305 nm TRANSFER pulse. This absorption must populate a quasi-discrete level above the adiabatic I.P. which, according to the MPI results, does not ionize. Autoionizing molecular states are expected to have lifetimes\(^{46}\) shorter than \(10^{-13}\) s. The only process that could compete effectively with the formation of ions on that time scale would be a fast dissociation process. Photodissociation quantum yields of 10% have been measured in the excitation of \(H_2^+\) both for single photon absorption above the I.P.,\(^{46}\) and MPI processes above the I.P.\(^{47}\) The photoacoustic pressure wave reaches the micro-

phone about 2 \(\mu\)s earlier for \(\Delta t > 10\) ns, as compared to \(\Delta t < 0\), which is expected for a dissociation process, as discussed in Sec. IV A. Further support for the dissociation mechanism comes from the photoproduct analysis discussed in Sec. V.

Figure 6 depicts the processes involved in the 305 nm TRANSFER pulse experiments. It is interesting that a given amount of energy can be deposited into aniline and selectively channeled either into ionization or dissociation channels almost exclusively, depending on the way in which the energy is put into the molecule, i.e., the TRANSFER pulse wavelength used and the value of \(\Delta t\). Exciting the molecule through the singlet manifold channels the energy into ionization. Introducing a delay of >10 ns between the PUMP and TRANSFER pulses allows intersystem crossing to occur which results in a new electronic manifold of states and converts some electronic energy into vibrational energy. The subsequent excitation of the triplet state is then directed into a dissociative channel.

Attempts were made to detect stimulated emission in aniline using the photoacoustic detection technique as described elsewhere.\(^{12}\) By using the PUMP laser to excite the 0–0 level of \(S_1\) and then scanning the TRANSFER laser wavelength from 305.5 to 300.5 nm with \(\Delta t = 2–4\) ns, we attempted to stimulate emission from the state responsible for the fluorescence lines observed near 302.5 nm.\(^{26}\) No decreases in the photoacoustic signal were observed. Instead, we detected weak hot band absorption to \(S_1\) and a small wavelength independent increase in photoacoustic signal caused by the excited state absorption from the small triplet population produced at the values of \(\Delta t\) we used.

C. 266 nm TRANSFER pulse

Figure 8 shows a time-domain MPI spectrum obtained again by pumping the 0–0 transition of \(S_1\) but using a TRANSFER pulse at 266 nm, the fourth harmonic of the Nd:YAG laser. Excitation by both the PUMP and TRANSFER pulses brings aniline about 9500 cm\(^{-1}\) above its adiab-

![Figure 8](image-url)
tic I.P., enough excess energy to ionize either $S_1$ or $T_1$ by a
direct ionization process. As expected, for all values of $\Delta t > 0$
an increase in MPI signal is observed. For $\Delta t$ near 0 a dou-
bbling of the MPI signal is observed, corresponding to excita-
tion from $S_1$ by the TRANSFER pulse. For $\Delta t > 25$ ns, the
increase in MPI signal with respect to its $\Delta t < 0$ value is 15%,
implying that the triplet produced by intersystem crossing
from $S_1$ is now being ionized. The signal to noise ratio in the
spectrum of Fig. 8 is low, but the increase in signal for
$\Delta t > 25$ ns is reproducible.

One could ask why the 266 nm pulse TRANSFER does
not excite molecules which can be ionized by the PUMP
pulse for $\Delta t < 0$, especially when it is noted that the TRANS-
FER pulse was 5.2 times as intense as the PUMP pulse. Pho-
toacoustic signals produced by the 266 nm pulse alone arrive
at the microphone 2–3 $\mu$s earlier than for excitation of the
$S_0 \rightarrow S_1$ 0–0 transition by the 294 nm PUMP pulse. The
TRANSFER pulse excites aniline to a state which has an
energy about 7400 cm$^{-1}$ above the N–H bond dissociation
energy, and the absorption has become broad and diffuse at
that energy. Therefore we feel that the excited state by this
TRANSFER pulse alone predissociates with a reasonable
quantum yield, decreasing the ion yield from subsequent
ionization by the PUMP pulse for $\Delta t < 0$.

The photoacoustic time-domain spectrum using the
266 nm TRANSFER pulse is almost flat for $-100 < \Delta t < 100$ ns for conditions similar to those in Fig. 3(b) or
Fig. 5(b). A slight increase of ~1% may occur across $\Delta t > 0$,
but this effect is almost obscured by noise. The 266 nm pulse
alone, as mentioned earlier, leads to dissociation. From en-
ergy considerations and the MPI spectrum of Fig. 8, we con-
clude that the molecules excited first by the 294 nm PUMP
pulse and then further excited by the 266 nm TRANSFER
pulse predominantly ionize. Since the photoacoustic tech-
nique is not highly sensitive to ionization processes in ani-
line, the increase in signal due to this excited state absorption
process is expected to be very small compared with the large
signal due to the background dissociation caused by the 266
nm pulse alone.

V. DISSOCIATION PROCESS

The experimental evidence presented in Sec. IV B has
shown that excited states of aniline can follow one of two
alternative pathways, ionization or dissociation, depending
on the excitation scheme employed. In order to obtain addi-
tional information on the dissociation pathway, two more
studies were undertaken.

First, an attempt was made to detect any possible pho-
toproductions by a mass spectrometric analysis. This was done
for two sets of irradiation conditions: (a) $\Delta t = 0$–5 ns, (b)
$\Delta t = 100$ ns. In both cases the PUMP pulse was tuned to the
$S_0 \rightarrow S_1$ 0–0 transition at 293.8 nm and the TRANSFER
pulse wavelength was 305 nm. For case (a) ions should be
produced predominately, whereas for case (b) the predomi-
nant products should be neutral dissociation fragments.
Two new matched quartz absorption cells (1 in. diameter $\times 4$
in. long) with Teflon stopcocks were filled simultaneously
with typically 0.37 Torr aniline and 0.10 Torr He as a refer-
ence gas. Irradiation times were 45 min at a 10 Hz repetition
rate with pulse energies of about 3 and 500 $\mu$J for the PUMP
and TRANSFER pulses, respectively. Subsequent to irra-
diation, the He/H$_2$ ratio was first measured after liquid ni-
trogen trapping of other volatiles; the liquid nitrogen was
then removed, the trap warmed up to room temperature, and
the mass spectrum of the volatile products was also obtained.
Preliminary results indicate that there is a H$_2$ is produced for
case (b) conditions than for case (a). Case (b) conditions also
produce a small amount of product with a $m/e$ peak at 114,
which is not produced for case (a). H$_2$ could be produced by
the breaking of a N–H or C–H bond, followed by the H atom
abstracting another H atom in a reactive collision. The mass
114 peak is more difficult to explain. Several molecules with
the formula $C_9$H$_{14}$N$_2$ are known to give strong mass 114
peaks; putting these molecules from aniline requires breaking
the aromatic ring and adding more H atoms. The results presen-
ted here are only preliminary, and we are investigating other
more direct ways of monitoring the frag-
mentation process in aniline.

Second, a theoretical examination of several possible
dissociation pathways was undertaken. It was first assumed
that dissociation occurred statistically from a bound elec-
tronic state, and an RRKM calculation was performed.
This indicated that the largest rate constants are for dissocia-
tion out of highly vibrationally excited levels of $S_0$ which are
isotopically mixed with the initially prepared levels of $S_1$ or $T_1$.
If a TRANSFER pulse wavelength of 532 nm is used, the max-
imum dissociation rate is only $7 \times 10^7$ s$^{-1}$, a result which is
2.5 orders of magnitude lower than the rate constant needed
to explain the experimental observations. In addition, the
calculations predicted that on the average only 4 kcal/mol
out of a total of 147 kcal/mol internal excitation energy is
released into translational degrees of freedom. This small
translational energy release could not directly produce the
large effects we observed. Subsequent radical–radical re-
combination (followed by vibrational relaxation) is probably
too slow a process for efficient photoacoustic detection.

We therefore conclude that dissociation occurs nonstatisti-
cally through repulsive states. These states could be
reached either by direct absorption to such a state or by ab-
sorption to a bound state followed by curve crossing to the
repulsive state (predisociation). Both of these processes are
known to have rate constants as large as $10^{13}$ s$^{-1}$. In addi-
tion, dissociation through a repulsive state is expected to
release up to 60.6 kcal/mol into translational degrees of free-
dom if the N–H bond breaks for a TRANSFER pulse wave-
length of 532 nm. The implications of these experimental
results and calculations is that detection of photodissoci-
ation products by the photoacoustic technique is significant
enhanced when the dissociation fragments have substantial
translational energy, as is frequently the case in predisocia-
tion processes. Though it appears that the dissociation pro-
cesses in aniline observed in this paper do occur nonstatisti-
cally through repulsive states, much further work needs to be
done on the excited electronic states of aniline to establish
more directly the existence, positions, and potential energy
surface characteristics of such repulsive states.
energy analysis and mass analysis of fragments are logical next steps of increase our understanding.

VI. CONCLUSIONS

The time-resolved two-color photoacoustic and MPI results presented in this paper give indirect but strong evidence for both ionization and dissociation occurring in aniline for energies slightly above the adiabatic I.P. By simply varying the delay time $\Delta t$ between the PUMP and TRANSFER pulses (when the respective wavelengths are 294 and 305 nm) the energy can be selectively channelled almost exclusively into either ionization or dissociation. This selectivity is believed to occur because conversion of a large amount of electronic energy into vibrational energy takes place during intersystem crossing, and thereby alters the Franck-Condon factors for direct ionization and increases the energy of the vertical I.P. The intersystem crossing also transfers the electronic energy into a different manifold of electronic states. The ability to channel a given amount of energy selectively into either ionization or dissociation channels is an exciting possibility for the field of laser selective chemistry.

The decay of the ionization signal during intersystem crossing does not seem to be an artifact of aniline alone. Figure 9 shows preliminary results on benzene obtained by pumping the $\tilde{X}^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+ V_{1s}$ transition, at 259.0 nm, and using a 266 nm TRANSFER pulse. The ionization signal decays exponentially with a time constant of $82 \pm 2$ ns, in close agreement to the observed fluorescence lifetime of 79 ns.\(^{32}\) Previous two-color MPI experiments on azulene and benzophenone did not detect exponential decays in ionization signal,\(^{10}\) whereas two-color MPI experiments on benzene\(^{43,44}\) and toluene\(^{42}\) detected biexponential decays corresponding to both singlet and triplet decay. Since the Franck-Condon factor explanation of the observed MPI signal decays holds for internal conversion as well as intersystem crossing, the time-resolved two-color MPI technique may be a powerful tool for investigating ultrafast internal conversion processes using picosecond lasers.

Additional experiments are needed to completely understand the excited state dynamics in aniline near its I.P. Time-resolved two-color MPI studies with photoelectron


G. Parker (unpublished calculations).
