

Time-resolved two-color photoacoustic and multiphoton ionization spectroscopy of aniline^{a)}

D. J. Moll,^{b),c)} G. R. Parker, Jr.,^{d)} and A. Kuppermann

Arthur Amos Noyes Laboratory of Chemical Physics,^{e)} California Institute of Technology, Pasadena, California 91125

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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,^{1,2} I₂,^{1,3} H₂S,⁴ NH₃,⁵ benzene,^{1,3,6,7} acetaldehyde,⁸ aniline,⁹ azulene,¹⁰ naphthalene,¹⁰ and organometallics.¹¹ 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 $A^2\Sigma^+$ ($\nu = 3$) state of NO,² and in azulene.¹⁰ Mechanism (3) has been observed in weakly bound organometallic systems.¹¹

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.¹² 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,¹³⁻²⁰ emission,²¹⁻³⁰ and multiphoton techniques.^{9,31-34} 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 0.3.²⁴ 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.²⁴

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 .²⁸ The ratio of phosphorescence to fluorescence quantum yields was 3.1, and total luminescence quantum yields were estimated at close to unity.²⁸ An additional low-lying T_2 state (3B_2) was postulated to be isoenergetic with S_1 to explain early fluorescence lifetime data,²¹ 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 .²⁷

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^{c)} Current address: Dow Chemical Company, Midland, Michigan, 48640.

^{d)} NSF predoctoral fellow.

^{e)} Contribution No. 6914.

Extremely efficient two-photon ionization, observed for aniline using S_1 as an intermediate state, is made possible by its low I.P. ($62\ 100\ \text{cm}^{-1}$ ³⁵) and the fully allowed nature of the transitions between S_0 and S_1 .^{31,32} At intensities below $10\ \text{MW}/\text{cm}^2$ the parent ion accounted for 100% of the ion signal. When increased to $20\ \text{MW}/\text{cm}^2$ the parent ion still accounted for 85% of the ion signal.⁹

III. EXPERIMENTAL

A. Apparatus

The time-resolved two-color photoacoustic and MPI techniques used in this paper are similar to those reported previously.¹² 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 Δt at different TRANSFER wavelengths. In MPI experiments, the total ion current is also measured as a function of Δt 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.¹² The MPI cell is a simple biased parallel plate-type cell.³⁶ Briefly, it consists of a stainless steel cell having quartz windows con-

taining 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 $10\ \text{V}/\text{pC}$. Since the pulse output of this preamplifier has a decay time of $50\ \mu\text{s}$, 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 5×10^{-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 $34\ 032\ \text{cm}^{-1}$ with the PUMP pulse and measuring the photoacoustic and MPI signals as a function of Δt 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 $34\ 032\ \text{cm}^{-1}$ with the PUMP pulse, using the Nd:YAG second harmonic at 532 nm as the TRANSFER pulse, and varying Δt . For $|\Delta t| \geq 20\ \text{ns}$ 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 $0.5\ \mu\text{J}/\text{pulse}$ 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 $|\Delta t| < 5\ \text{ns}$, 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. 4.⁹ 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

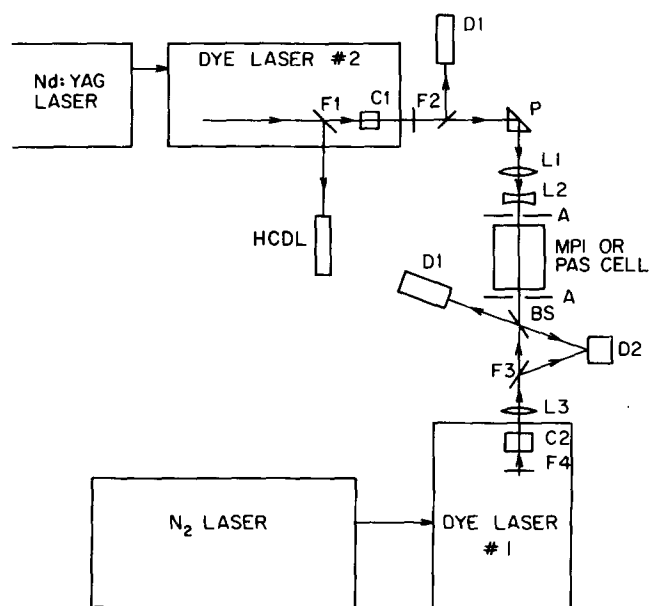


FIG. 1. Experimental arrangement for time-resolved two-color photoacoustic and multiphoton ionization experiments. The PUMP beam from dye laser #1 and the TRANSFER beam from dye laser #2 enter a photoacoustic spectroscopy (PAS) or multiphoton ionization (MPI) cell collinearly from opposite directions. The various labels are defined as follows: A—aperture, BS—beam splitter, C1 and C2—KDP doubling crystals, D1—pyroelectric energy probe, D2—high speed photodiode, F1 and F4—UV blocking filter, F2 and F3—UV pass filter, HCDL—uranium/neon hollow cathode lamp, L1 and L2—beam contracting telescope, L3—25 cm focal length lens, P—prism.

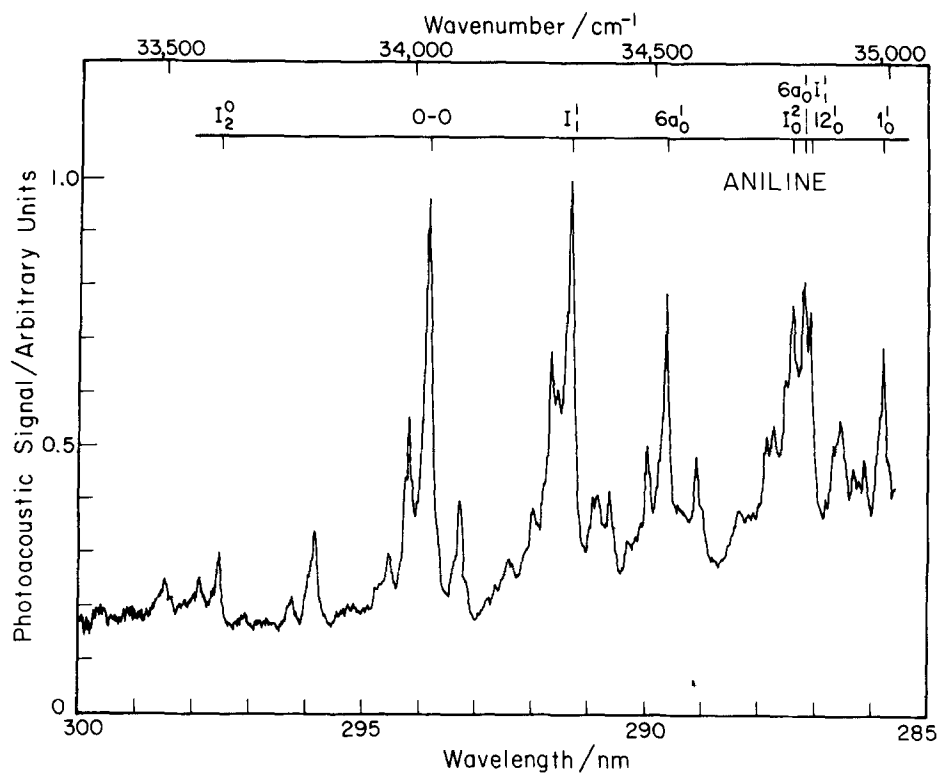


FIG. 2. Pulsed photoacoustic spectrum of a portion of the $\tilde{X}^1A_1 \rightarrow \tilde{A}^1B_2$ transition in aniline obtained using a 0.37 Torr sample pressure. The photoacoustic signal has been corrected for the variation in incident laser pulse energy with wavelength. Pulse energies ranged from 1 to 10 μJ . The vibronic bands are labeled by the symbol $k v''$, which implies a transition from v'' quanta in mode k in the ground electronic state to an excited electronic state with v' quanta in mode k . $k = I$ represents the NH_2 out-of-plane rocking mode. $k = 6a$ and 12 represent a_1 symmetry ring modes. $k = 1$ represents a ring-stretching mode. The assignment was taken from Ref. 14.

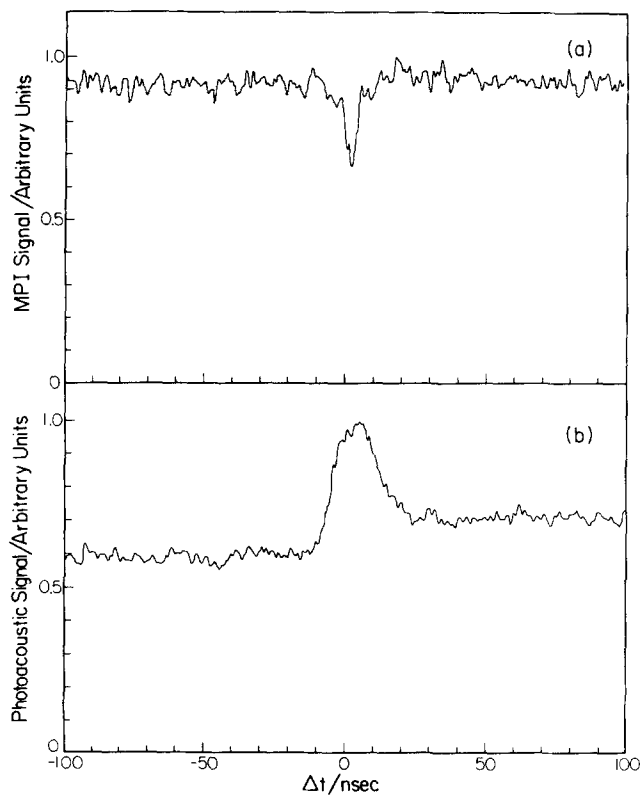


FIG. 3. Time-resolved two-color spectra of aniline. The PUMP pulse excites the $S_0 \rightarrow S_1$ 0-0 transition at $34\,032\text{ cm}^{-1}$. The TRANSFER pulse photon energy is $18\,797\text{ cm}^{-1}$ (532 nm). The abscissa gives the time delay between pulses, $t = t_{\text{TRANSFER}} - t_{\text{PUMP}}$. (a) Multiphoton ionization detection. The sample pressure was 0.010 Torr. The PUMP and TRANSFER pulse energies were 0.5 μJ and 2.0 mJ, 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 mJ, respectively. Neither spectra has been corrected for fluctuations in pulse energy.

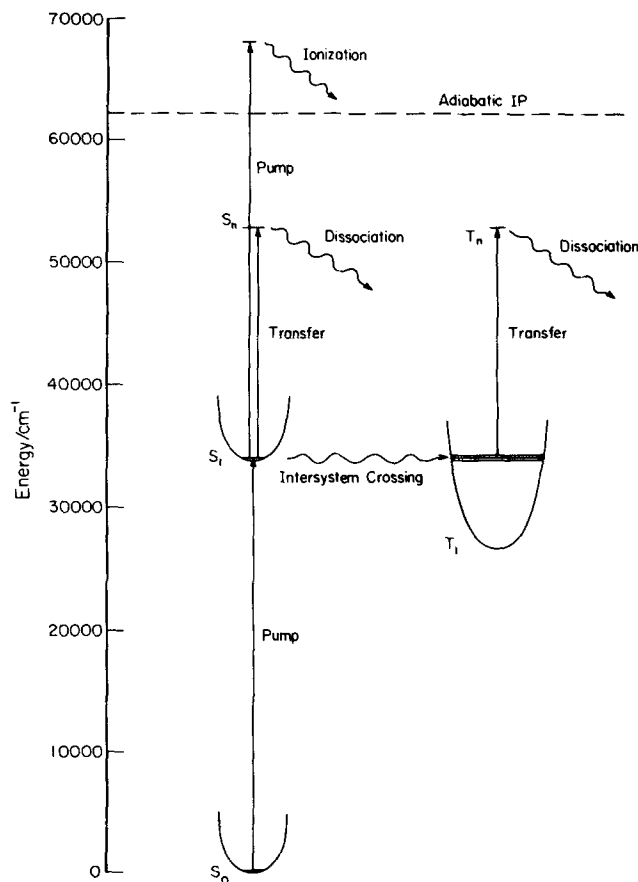


FIG. 4. Energy level diagram indicating the excitation processes corresponding to the spectra of Fig. 3. The PUMP and TRANSFER pulses have photon energies of $34\,032$ and $18\,797\text{ cm}^{-1}$, respectively. The potential curves, their relative horizontal displacement and the vibrational levels are schematic and do not correspond to known molecular parameters.

VUV studies^{16,17,19} which show strong absorptions near $52\,800\text{ cm}^{-1}$, 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 $30\,200\text{ cm}^{-1}$, making it the lowest energy dissociation pathway.³⁷

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 $\Delta t > 20\text{ ns}$ (TRANSFER pulse after PUMP pulse) is about 20% larger than for $\Delta t < -20\text{ ns}$ (TRANSFER pulse before PUMP pulse).

The pulsed photoacoustic technique is sensitive to energy deposited in the sample and transformed into translational energy on a μs time scale. As can be seen from Fig. 3, values of $\Delta t \sim 0$ 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_2 have been predicted theoretically³⁸ and observed experimentally.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 μs 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 Δt in Fig. 3(b) where an increase in photoacoustic signal is seen (i.e., $\Delta t \gtrsim 0$), the pressure wave appears at the microphone about 2 μs earlier than for $\Delta t < -10\text{ ns}$ in which case only S_1 is excited. (In aniline at 0.37 Torr we normally detect the pressure wave about 65 μs 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 $\Delta t \sim 0$ also supports the efficient release of kinetic energy through dissociation. If S_1 and S_n 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 $\Delta t \gtrsim 0$ the pressure wave is detected about 2 μs earlier

than when $\Delta t < -10\text{ ns}$, 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 3A_1 state, and fluorescence.^{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 $\Delta t > 20\text{ ns}$, the increase must be caused by triplet–triplet absorption from 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.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_n 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 $34\,032\text{ cm}^{-1}$ PUMP pulse, the molecule can be excited to about 4700 cm^{-1} above the adiabatic I.P. of $62\,100\text{ cm}^{-1}$.³⁵

In Fig. 5(a) the MPI signal shows a sharp eightfold increase in yield as Δt increases beyond zero, and decays exponentially after that with a time constant of $8.9 \pm 0.2\text{ ns}$ 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 Δt .) 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 constant²⁴ 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 $\Delta t \sim 0$ to $\Delta t \gtrsim 10\text{ ns}$, since complete collisional deactivation of the vibrationally excited triplet produced by intersystem crossing is unlikely at 0.004 Torr for time scales $< 50\text{ ns}$ and there is no inherent reason why ionization from triplet states should be difficult.³⁶

Consideration of vibrational effects offers an explana-

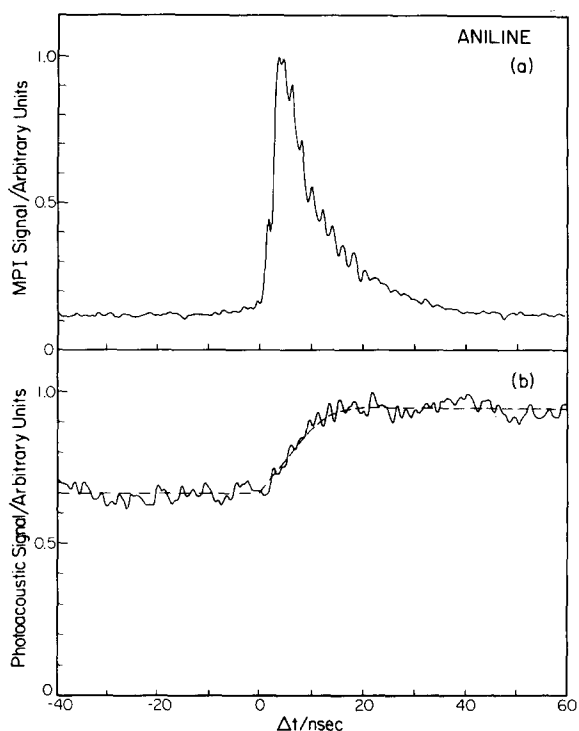


FIG. 5. Time-resolved two-color spectra of aniline. The PUMP pulse excites the $S_0 \rightarrow S_1$ 0-0 transition at $34\,032\text{ cm}^{-1}$. The TRANSFER pulse photon energy is $32\,787\text{ cm}^{-1}$ (305 nm). The abscissa gives the time delay between pulses, $\Delta t = t_{\text{TRANSFER}} - t_{\text{PUMP}}$. (a) Multiphoton ionization detection. The sample pressure was 0.004 Torr. The PUMP and TRANSFER pulse energies were 0.4 and $13\ \mu\text{J}$, respectively. (b) Photoacoustic detection. The sample pressure was 0.37 Torr. The PUMP and TRANSFER pulse energies were 5.2 and $300\ \mu\text{J}$, respectively. The dashed line gives the expected noise-averaged signal. Neither spectra has been corrected for fluctuations in pulse energy.

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_1 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_1 , 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_1 state. From the known small changes in geometries between S_1 and S_0 , it is expected that ionization through S_1 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_1 and T_1 may change the 7200 cm^{-1} difference, but nevertheless, the 305 nm TRANSFER pulse can apparently only ionize the S_1 state, and not the vibrationally excited triplet state, by a direct ionization process.

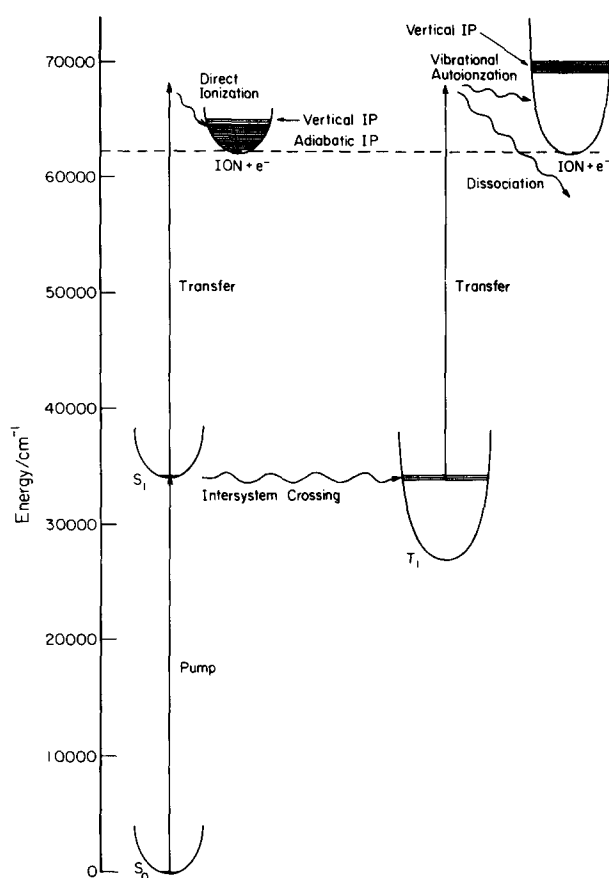


FIG. 6. Energy level diagram indicating the excitation processes corresponding to the spectra of Figs. 5(a), 5(b), and 7. The PUMP and TRANSFER pulses have photon energies of $34\,032$ and $32\,787\text{ cm}^{-1}$, respectively. The potential curves, their relative horizontal displacement, and the vibrational levels are schematic and do not correspond to known molecular parameters. The position of the vertical I.P.'s is discussed in Sec. IV B of the text.

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.⁴¹⁻⁴⁴ This assumption was justified by Dietz *et al.*⁴² 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 quasidecrete 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 quasidecrete levels.⁵ A triplet quasidecrete level must exist in aniline near $66\,800\text{ cm}^{-1}$ 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

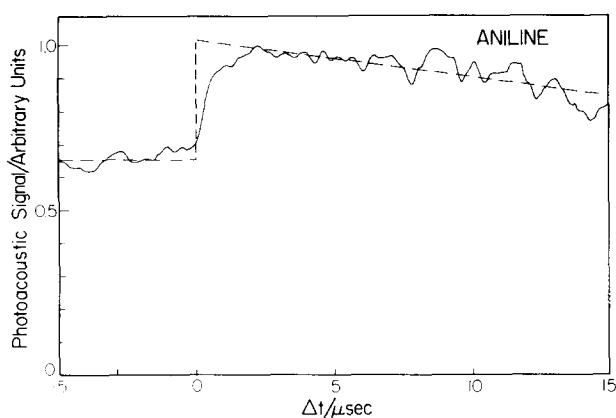


FIG. 7. Time-resolved two-color photoacoustic spectrum of aniline. The conditions are similar to those of Fig. 5(b) except that a wider range of Δt is shown. The dashed line indicates the expected signal if detection time constant and noise effects are removed. The downward drift for $\Delta t > 5 \mu\text{s}$ is discussed in Sec. IV B.

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 $1 - e^{-\alpha\Delta t}$ 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 Δt . 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 $15 \mu\text{s}$ 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 ($> 10 \mu\text{s}$) 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 lifetimes⁴⁵ 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 $2 \mu\text{s}$ earlier for $\Delta t > 10 \text{ ns}$, 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 Δt . Exciting the molecule through the singlet manifold channels the energy into ionization. Introducing a delay of $> 10 \text{ ns}$ 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 $\Delta t = 2-4 \text{ ns}$, 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 Δt 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 adiabatic

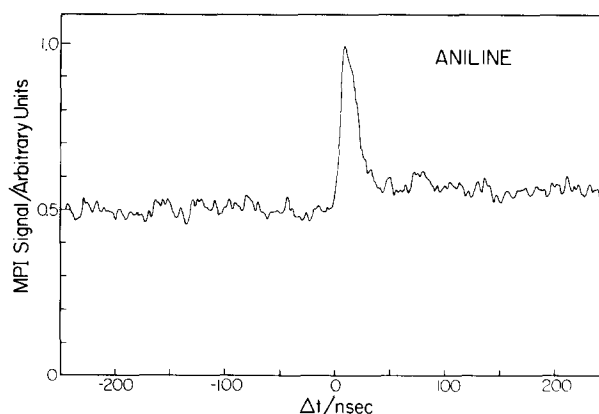


FIG. 8. Time-resolved two-color MPI spectrum of a 0.004 Torr sample of aniline. The $1.2 \mu\text{J}$ PUMP pulses excite the $S_0 \rightarrow S_1$ 0-0 transition at $34\,032 \text{ cm}^{-1}$. The $6.2 \mu\text{J}$ TRANSFER pulses have photon energies of $37\,590 \text{ cm}^{-1}$ (266 nm). The abscissa displays the time delay between pulses, $\Delta t = t_{\text{TRANSFER}} - t_{\text{PUMP}}$. The spectrum has not been corrected for fluctuations in pulse energies.

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 Δt near 0 a doubling of the MPI signal is observed, corresponding to excitation 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 was 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 TRANSFER pulse was 5.2 times as intense as the PUMP pulse. Photoacoustic signals produced by the 266 nm pulse alone arrive at the microphone 2–3 μ 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.²⁴ Therefore we feel that the state excited 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 $\sim 1\%$ 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 energy considerations and the MPI spectrum of Fig. 8, we conclude 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 technique is not highly sensitive to ionization processes in aniline, 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 additional information on the dissociation pathway, two more studies were undertaken.

First, an attempt was made to detect any possible photoproducts 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 predominant 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 reference gas. Irradiation times were 45 min at a 10 Hz repetition rate with pulse energies of about 3 and 500 μ J for the PUMP and TRANSFER pulses, respectively. Subsequent to irradiation, the He/H₂ ratio was first measured after liquid nitrogen 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 more H₂ 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). H₂ 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 C₆H₁₄N₂ are known to give strong mass 114 peaks,^{48,49} but producing these molecules from aniline requires breaking the aromatic ring and adding more H atoms. The results presented here are only preliminary, and we are investigating other more direct ways of monitoring the fragmentation 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 electronic state, and an RRKM calculation was performed.⁵⁰ This indicated that the largest rate constants are for dissociation out of highly vibrationally excited levels of S_0 which are isoenergetic with the initially prepared levels of S_n or T_n . If a TRANSFER pulse wavelength of 532 nm is used, the maximum dissociation rate is only $7 \times 10^5 \text{ s}^{-1}$, 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 recombination (followed by vibrational relaxation) is probably too slow a process for efficient photoacoustic detection.

We therefore conclude that dissociation occurs nonstatistically through repulsive states. These states could be reached either by direct absorption to such a state or by absorption to a bound state followed by curve crossing to the repulsive state (predissociation). Both of these processes are known to have rate constants as large as 10^{13} s^{-1} .⁴⁶ In addition, dissociation through a repulsive state is expected to release up to 60.6 kcal/mol into translational degrees of freedom if the N–H bond breaks for a TRANSFER pulse wavelength of 532 nm. The implications of these experimental results and calculations is that detection of photodissociation products by the photoacoustic technique is significantly enhanced when the dissociation fragments have substantial translational energy, as is frequently the case in predissociation processes. Though it appears that the dissociation processes in aniline observed in this paper do occur nonstatistically 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.

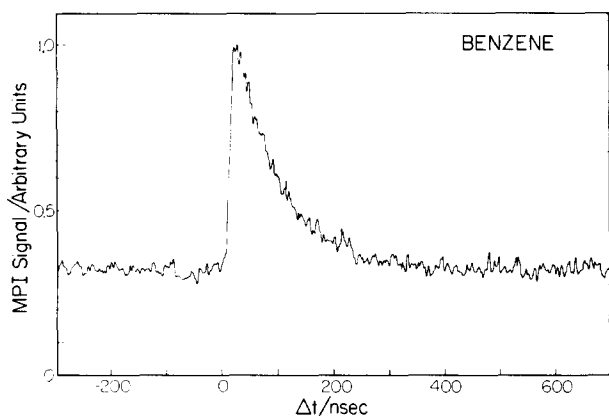


FIG. 9. Time-resolved two-color MPI spectrum of a 0.021 Torr sample of benzene. The $0.6 \mu\text{J}$ PUMP pulses excite the $\tilde{X}^1A_{1g} \rightarrow \tilde{A}^1B_{2u} \nu'_{18}-0$ transition at $38\,607 \text{ cm}^{-1}$. The $1.4 \mu\text{J}$ TRANSFER pulses have photon energies of $37\,590 \text{ cm}^{-1}$ (266 nm). The abscissa displays the time delay between pulses, $\Delta t = t_{\text{TRANSFER}} - t_{\text{PUMP}}$. The spectrum has not been corrected for fluctuations in pulse energies.

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 Δt between the PUMP and TRANSFER pulses (when the respective wavelengths are 294 and 305 nm) the energy can be selectively channeled 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 $\tilde{X}^1A_{1g} \rightarrow \tilde{A}^1B_{2u} \nu'_{18}-0$ transition,⁵¹ at 259.0 nm, and using a 266 nm TRANSFER pulse. The ionization signal decays exponentially with a time constant of 82 ± 2 ns, in close agreement to the observed fluorescence lifetime of 79 ns.⁵² 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^{41,43,44} and toluene⁴² 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

energy analysis and mass analysis of fragments are logical next steps of increase our understanding.

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