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Ion dip spectroscopy of higher excited vibronic states of aniline

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Double resonant ion dip spectroscopy (IDS)[1-4] via single vibronic level (SVL) excitation in a supersonic molecular beam[3] provides a powerful means for detecting higher excited electronic states and their underlying vibrational structure.[2] These excited states are often too short-lived to be detected by conventional ionization or fluorescence detection methods. Direct detection by multiphoton absorption is likewise difficult to implement due to the low optical densities for such transitions in molecular beams.

Using two-color tunable excitation in a supersonic molecular beam, time-of-flight (TOF) mass spectrometer, we have recorded SVL absorption spectra corresponding to absorption from the first excited single state (S_1) origin to a higher excited electronic state (S_n) of aniline and aniline-d_5. The aniline S_n spectrum in Fig. 1 was recorded by generating an ion signal by resonance two-photon ionization (R2PI) via the $S_1(\tilde{A}\ ^1B_2) \leftarrow S_0(\tilde{X}\ ^1A_1)0_0^0$ transition (ω_1) while a second dye laser (ω_2), overlapped and synchronous in time, was tuned through the $S_n(v) \leftarrow S_1(0)$ resonances. These absorptions compete with ionization, thereby creating the ion dip signals. The experimental apparatus will be described in detail elsewhere.[5] Briefly, two tunable dye lasers are used to generate ω_1 and ω_2. The differentially pumped molecular beam apparatus employed a pulsed supersonic nozzle[6] which was operated at 10 Hz, 50 °C, 50 psi He, with a 500 μm aperture. Excitation spectra were mass selected by gating the appropriate TOF ion signal (in the present case, the parent ion, M^+).

The identification of the ion dip spectra as belonging to an $S_n \leftarrow S_1$ absorption was made by ruling out other possible mechanisms, namely down-pumping to vibrational levels in S_0 or absorption by parent ion, M^+, to give fragments $[M-m]^+ + m$. The first possibility (also referred to as stimulated emission pumping) can be ruled out by knowledge of the S_0 vibrational levels and transition moments. The possibility that M^+ absorbs light to give fragment ions, thereby depleting the M^+ ion signal, has also been ruled out by recording ion dip spectra for total ion signal. Furthermore, by delaying the ω_2 pulse by 8 ns, the ion dip spectrum disappeared. Since M^+ ion depletion by dissociative absorption should not be very sensitive to delay in the absorbing light, our result is consistent only with an ω_2 absorption that *competes* with ionization from the S_1 electronic state.

The 0_0^0 transition wavelengths for $S_n \leftarrow S_1$ occur at 770.9 nm (aniline) and 779.2 nm (aniline-d_5) which correspond to absolute energies above the S_0 vibrationless level of 47 012 cm^{-1} (5.829 eV) and 47045 cm^{-1} (5.833 eV), respectively. The S_n vibrational intervals identified in Fig. 1 compare reasonably well with previously observed S_0 and S_1 vibrations,[7] indicating that the S_n state is characterized by geometry and force constants similar to the lower energy electronic states.

Recent studies on the MPI of aniline[8-10] have revealed a strong visible region absorption that occurs from the S_1 level and which competes effectively with ionization. These studies involved 532 nm absorption in a supersonic molecular beam,[8] 532 nm absorption in a thermal vapor cell,[9] and fixed wavelength visible absorption in a thermal vapor cell,[9] and fixed wavelength visible absorption in an effusive molecular beam.[10] The excitation energies in these studies were as much as 6000 cm^{-1} greater than those used in the present work and hence one cannot assume that the same excited state is being monitored. Moreover, since these results did not involve SVL excitation using tunable light, no determination of the electronic state energy or vibrational frequencies was made. We therefore refer to this higher energy state as $S_{n'}$. Since, the apparent $S_{n'}$ state did not appear to undergo

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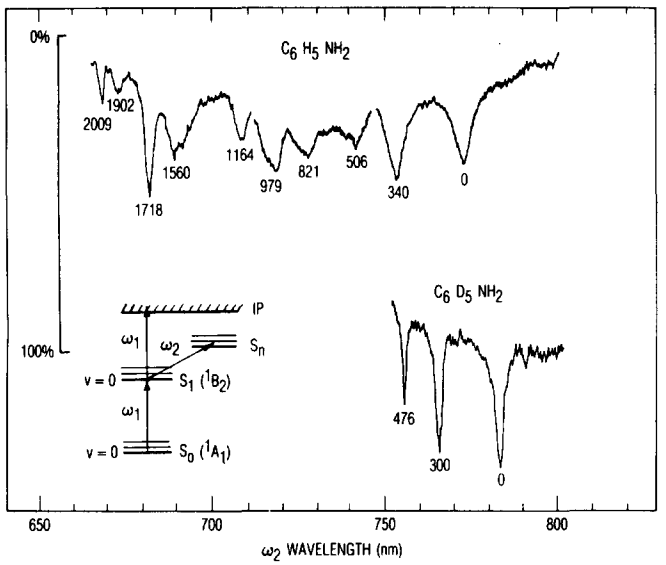

FIG. 1. Ion dip spectrum for the $S_n(v) \leftarrow S_1(v=0)$ absorption of aniline. Ion dip strengths are plotted with respect to ω_2 off (0%) and ω_1 off (100%) ion signal levels. The spectra were pieced together for three laser dye regions and are not normalized to ω_2 pulse energies. The low energy portion of the aniline-d_5 ion dips spectrum is illustrated along with the excitation scheme employed in this work. Vibrational intervals are reported to $\pm$ cm^{-1}. Calibrated wavelengths are given in the text.

subsequent ionization,[8-10] it was concluded that $S_{n'}$ is strongly predissociative. This view is consistent with the strong photoacoustic signal that is observed for the $S_n \leftarrow S_1$ absorption which can be explained by dissociation to fragments with high translational energy.[9]

The coherent nature of the ω_2 excitation process in ion dips can be exploited to obtained information on short-lived states. Saturation of a long-lived upper state would give a maximum ion dip signal of 50%. However, if the upper state decays at a rate greater than the ω_2 pumping rate, then the lower state can be quantitatively depleted leading to ion dip signals greater than 50%. The behavior of coherent pumping to a dissociative state was recently demonstrated by Xie *et al.*[4] for a stimulated emission pumping IDS scheme. We have been able to exceed 50% ion dips for nearly all $S_n(v) \leftarrow S_1(0)$ transitions in aniline and aniline-d_5. (This value is also dependent on the ω_1 ionization rate from S_1.) The set of states responsible for S_n broadening and ion dip amplitudes in excess of 50% must not themselves be subject to ionization. This limits their assignment to a dissociative state or a low energy state such as S_0 or T_1, which because of Franck–Condon restrictions are not ionizable by ω_1.

A few additional features regarding the S_n ion dips spectra deserve mention: (1) The absorption linewidths were considerably broader for aniline than for aniline-d_5 (95 vs 45 cm^{-1}, respectively, for the 0_0^0 at FWHM), (2) aniline exhibited a continuous background absorption that extended to significantly lower energies than the S_n origin. This background was less evident for aniline-d_5; (3) a strong and sharp feature was observed for both molecules [60 and 35 cm^{-1} ($-d_5$) FWHM] at about 1700 cm^{-1}. The first observation is consistent with the decrease predicted for nonradiative decay upon deuteration.[11] The reduction of vibrational frequencies due to deuteration leads to a weaker coupling between initial and final states as a result of a larger difference in quantum number. This Franck–Condon effect outweighs the effects of an increased density of states. Observations (2) and (3) are suggestive of other electronic state interactions. The strong, but featureless absorption that occurs to the red of the S_n origin in aniline is indicative of a strong coupling of an electronic state with the high density of bath states.[11] Again, the weak presence of this absorption in aniline-d_5 can be explained by the reduction in the coupling strengths due to deuteration. Finally, strong and sharp features that occur at about 1700 cm^{-1} for both compounds do not correlate well with known symmetric vibrations of aniline.[7] This fact, in addition to the perceptibly narrowed lineshape, may indicate the origin of another electronic state.

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