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ION DIP SPECTROSCOPY AND MULTIRESONANT PROCESSES IN AROMATIC MOLECULES BY SUPERSONIC MOLECULAR BEAM MASS SPECTROSCOPY

Jack A. Syage and John E. Wessel

The Aerospace Corporation
P. O. Box 92957
Los Angeles, CA 90009

Two-color, mass-resolved ion dip spectroscopy involving multiresonant single vibronic level excitation is described as a selective detection technique as well as a novel spectroscopic tool.

Multiresonant single vibronic level excitation and mass-resolved ion dip detection is employed to study highly excited electronic state properties of aromatic molecules and ions. In this technique, two-photon resonance ionization (R2PI) through an intermediate state, $|1\rangle$ generates an ion mass signal; this signal in turn experiences a decrease when a third photon competes with ionization by resonance excitation from the intermediate state, $|1\rangle$, to another state, $|n\rangle$. In another scheme, threshold R2PI is used to create rovibrationally cold ions. The excited electronic states of the cold ions are then detected by resonance ion dissociation (RID) spectroscopy.

Double resonant ion dip spectroscopy[1-3] is a powerful technique for recording vibrationally resolved spectra of higher excited electronic states that are too short-lived to be detected by conventional ionization or fluorescence detection methods. Using two-color tunable excitaton, we have recorded the absorption spectra[3] from the S_1 origin to a higher excited electronic states, S_n, of aniline and aniline-d_5. The aniline S_n spectrum in Fig. 1 was recorded by generating an ion signal by R2PI via the $S_1(\tilde{A}^1B_2) \leftarrow S_o(\tilde{X}^1A_1)$ 0_o^o 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 molecular beam apparatus[4] employed a pulsed nozzle, a time-of-flight (TOF) mass spectrometer and three stages of differential pumping. Excitation spectra were mass-selected by gating the aniline parent ion signal, M^+).

The 0_o^o transition wavelength 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_o vibrationless level of 47012 cm^{-1} (5.829 eV) and 47045 cm^{-1} (5.833 eV), respectively. The S_n vibrational intervals compare well with those for the S_o and S_1, states indicating geometry and force constants similar to the lower energy electronic state. The absorption linewidths exhibit a pronounced isotope effect, in accord with theories of radiationless decay.

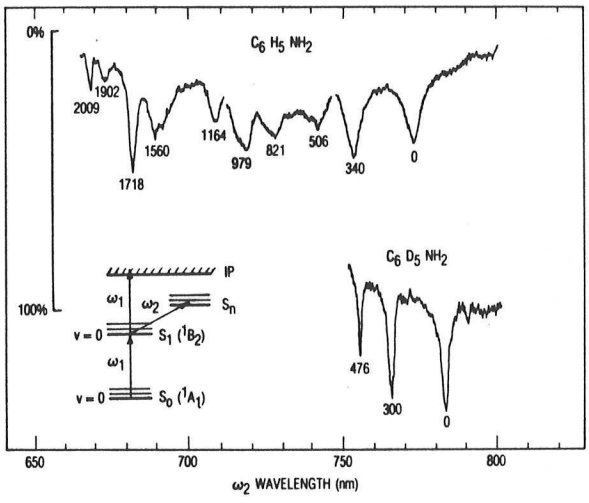

Fig. 1. In dip spectrum for the $S_n(v) \leftarrow S_1(v = 0)$ absorption of aniline. Ion dip strengths are plotted with respect to ω_2 off (0%) and ω_1 off (100%) ion signal levels. The low energy portion of the aniline-d_5 ion dip spectrum is illustrated along with the excitation scheme employed in this work. Vibrational intervals are reported in cm^{-1}.

Multiresonant excitation and mass-resolved detection in a supersonic molecular beam is also employed in our laboratory to study properties of ion excited states and dissociative pathways. SVL spectroscopy of the ions is achieved by forming cold ions by two-color threshold ionization followed by a third tunable dye laser to probe excited vibronic structure through resonance ion dissociation (RID). The dissociation process is evident by observing an ion dip signal for the parent ion, M^+, as well as the production of a fragment ion, $[M-m]^+$.

Vibrationally resolved absorption spectra have been recorded for napthalene and substituted naphthalene cations in cold matrices[5]. However previous attempts to monitor electronic state absorptions in the vapor phase have failed to reveal any vibrational structure[6], presumably due to the thermal energy content of the precursor neutral molecules. We have observed vibrationally resolved absorption in napthalene and 2-methylnapthalene (2-MeN) by recording RID spectra following state-selective preparation of the molecular cation. These studies focused on the low energy photodissociation channel yielding H atom in the naphthalene and 2-MeN cations as a probe of resonant intermediate states of the molecular ion. For 2-MeN cation, vibrational structure is evident in Fig. 2 for a low energy state at 662 nm. In addition, a featureless absorption appears to wavelengths as long as 860 nm which is believed to be about 3000-4000 cm^{-1} above the origin of a very low energy electronic state. Resolved UV absorptions have also been recorded for the cations of napthalene and 2-MeN. 0_o^o transition wavelengths occur at 304.7 nm 308.9 nm, respectively.

The linewidths in the RID spectra of the cations are rather broad for both the visible absorptions ($\sim$ 200 cm^{-1}, Fig. 2) and the UV absorptions ($\sim$ 150 cm^{-1}) although comparable to the matrix absorption spectra[5]. A pronounced power broadening is evident which is not unusual for the higher valence electronic states due to the dense manifold of interacting bath states. These effects are in good agreement with calculations based on a realistic model for the coupling of optically prepared states with a dense manifold of dissociating and/or nondissociating states.[4].

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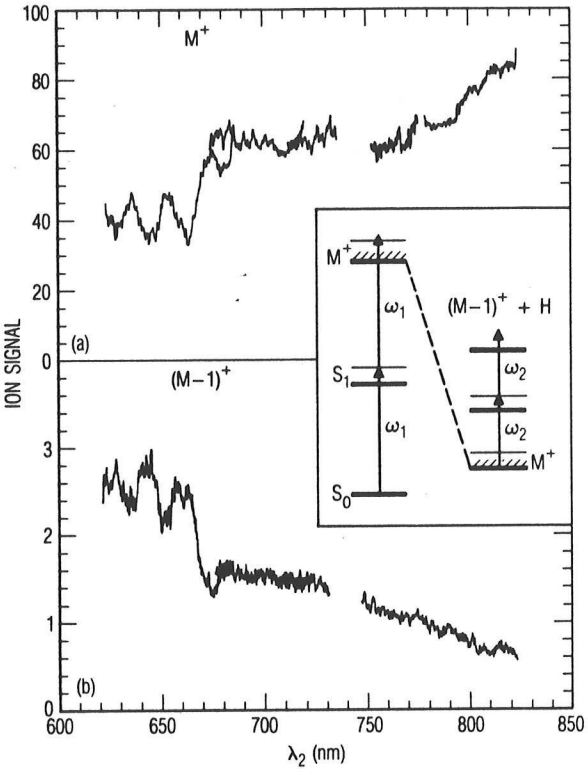

Fig. 2. Resonance ion dissociation (RID) spectra of 2-methylnapthalene (2-MeN) cation via low energy electronic states. (a) M^+ molecular ion dip spectrum, and (b) $[M\text{-}1]^+$ fragment ion formation spectrum. R2PI excitation by ω_1 at 308.3 nm populates the $^+\bar{8}_1$ state of the molecular cation (insert): Delayed excitation by ω_2 reveals a diffuse ion absorption at very low energy and a structured absorption at higher energy.

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