Vibrational Spectroscopy and Photodissociation Properties of Ions As Determined by Two-Laser Photodissociation Techniques

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Iodobenzene, bromobenzene, and *m*-iodotoluene cations trapped in an ion cyclotron resonance (ICR) mass spectrometer undergo an enhanced visible photodissociation process in the presence of infrared irradiation. The infrared wavelength dependence in the 9.7–10.7-μm region for this effect exhibits features which relate to the infrared spectroscopy of these ions. The variation in extent of the infrared enhancement with visible wavelength is interpreted as reflecting two different mechanisms: at short wavelengths the enhancement is attributed to changes in visible-absorption cross section with increasing internal energy and gives a useful means of observing such effects, while at long wavelengths the enhancement is attributed to a perturbation of the two-photon dissociation kinetics. The photodissociation rates of several other ions were shown not to undergo an enhancement effect when irradiated with the infrared laser.

Introduction

The ability to do photodissociation spectroscopy in gas-phase ions trapped in an ion cyclotron resonance (ICR) mass spectrometer has allowed detailed studies of molecular photoprocesses. Photodissociation has been shown to be an effective method for obtaining otherwise difficult spectroscopic information for ions.[1,2] In addition, the discovery of a sequential multiphoton dissociation process[3] in gas-phase ions has allowed studies of excited-state intermediates. In this report we describe experiments involving use of two lasers, one visible and the other infrared, which are used to generate and spectroscopically probe excited-state ions. This information is of importance in obtaining an understanding of multiphoton absorption and has interesting potential as a route to studying the infrared spectroscopy of ions.

In an earlier report[4] we showed that the visible-wavelength photodissociation of iodobenzene ions is dramatically increased as a result of simultaneous irradiation by an infrared laser. The fact that the infrared laser was unable to cause any dissociation, or affect the ion signal in any way on its own, was of particular interest. Since then bromobenzene[5] and *m*-iodotoluene cations have been found to undergo this enhanced photodissociation process with infrared irradiation. Experiments involving separate infrared and visible irradiation periods have determined that the infrared laser first excites the ions which then undergo a faster visible-photon dissociation process.

In order to study this enhancement process further the wavelength dependences for both the infrared and visible lasers have been studied. The results can be interpreted to provide information about the vibrational spectroscopy of these ions and also the visible-wavelength photochemistry of vibrationally excited species.

Experimental Section

The technique of ICR-PDS involving two lasers have been previously described.[4,5] Briefly stated, the ICR spectrometer functions to produce ions by a short pulse ($\sim$100 ms) of ionizing electrons followed by a period where ions are trapped in the ICR cell for a typical period of $\sim$3 s. The ions are then detected according to their mass and finally the cell is quenched of ions to begin another cycle. During the trapping period of the ions are irradiated by the infrared and visible lasers and the photodissociation kinetics are determined by monitoring the ion signal in the presence and absence of irradiation during the trapping period. The visible and infrared lasers were individually shuttered and the beams were directed by mirrors into the ICR cell nearly collinearly.

The instrumentation consisted of a Varian ICR-9 spectrometer modified to operate in the pulsed mode using the trapped ion cell configuration. Visible lasers involved an argon ion laser and a dye laser utilizing R6G dye. Beams were expanded to $\sim$2 cm to ensure good overlap with the trapped ions. The infrared laser was a home-built CO_2 laser with a maximum output of $\sim$12 W. An NaCl window on the instrument was used to allow both IR and visible beams to irradiate the ions. Pressures in the ICR spectrometer were in the (5–10) $\times$ 10^{-8} torr range and were determined by use of a calibrated vacion pump. Samples were obtained commercially and used without further purification.

Results

Infrared. The procedure was used to investigate the infrared wavelength dependences was as follows. The visible laser was fixed at a constant wavelength and power to provide a moderate level of photodissociation ($\sim$30%) without the IR laser. The infrared laser wavelengths were varied keeping a constant power usually of several watts. The additional fractional dissociation caused by the infrared laser on the visible-only dissociation was found to vary with the infrared wavelength. Plots of this for iodobenzene, bromobenzene, and *m*-iodotoluene are shown in Figures 1–3, respectively. Shown also for comparison are the infrared spectra of the neutral species in this wavelength region.

Visible. The method used to study the visible-wavelength variations is analogous to that used for the IR wavelength dependence. The IR laser was set at a constant wavelength and power. For each visible wavelength investigated the power of the visible laser was adjusted to cause approximately the same level of dissociation without the IR laser. The additional fractional dissociation caused by the IR laser was then plotted as a function of visible

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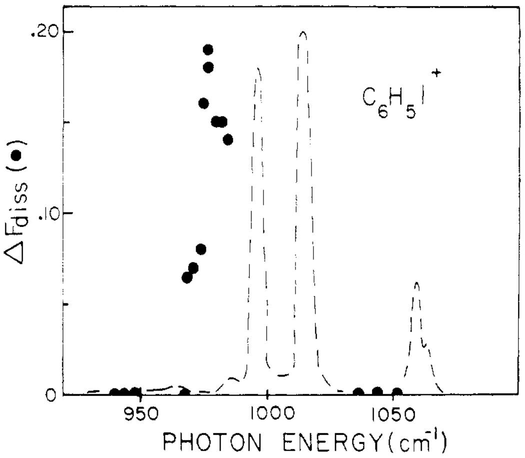

Figure 1. Enhancement (additional fractional dissociation caused by the infrared laser) as a function of infrared photon energy for iodobenzene. Visible-only dissociation (610 nm) was set to ~30% while the infrared intensity was 15 W/cm^2 at each wavelength. The dotted line is the infrared spectrum of neutral iodobenzene from ref 8 shown for comparison.

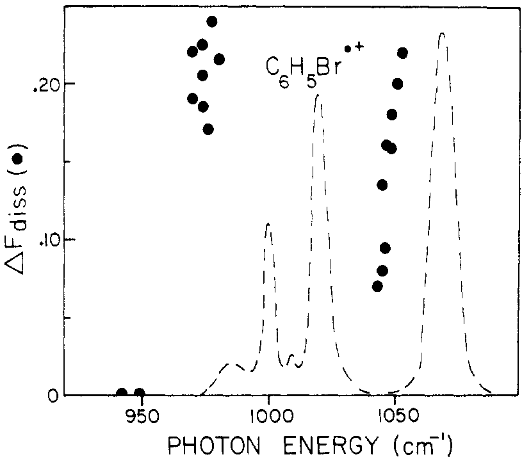

Figure 2. Enhancement (additional fractional dissociation caused by the infrared laser) as a function of infrared photon energy for bromobenzene. Visible-only dissociation (515 nm) was set to ~30% while the infrared intensity was 15 W/cm^2 at each wavelength. The dotted line is the infrared spectrum of neutral bromobenzene from ref 8 shown for comparison.

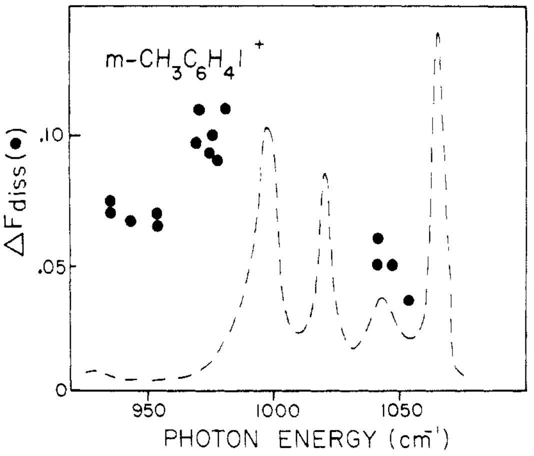

Figure 3. Enhancement (additional fractional dissociation caused by the infrared laser) as a function of infrared photon energy for m-iodotoluene. Visible-only dissociation (610 nm) was set to ~30% while the infrared intensity was 15 W/cm^2 at each wavelength. The dotted line is the infrared spectrum of neutral m-iodobenzene from ref 8.

wavelength. Figures 4–6 present the results for iodobenzene, bromobenzene, and m-iodotoluene, respectively.

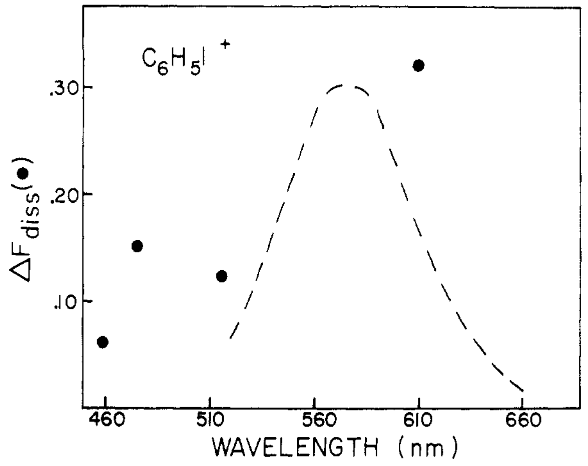

Figure 4. Iodobenzene: Additional fractional dissociation (ΔF_{diss}) caused by the infrared laser as a function of visible wavelength. The infrared laser was kept fixed (978 cm^{-1}, 15 W/cm^2) while the visible laser was adjusted to keep the visible-only dissociation at ~30% for each wavelength. The dotted line represents the low-resolution photodissociation spectrum from ref 6 and is included to show how the photodissociation band corresponds to the wavelength region studied here.

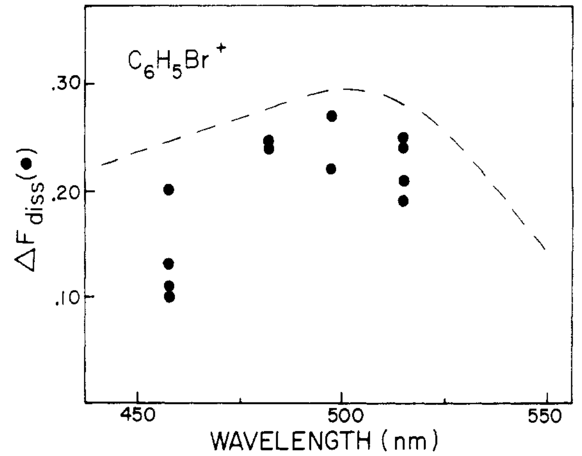

Figure 5. Bromobenzene: Additional fractional dissociation (ΔF_{diss}) caused by the infrared laser as a function of visible wavelength. The infrared laser was kept fixed (978 cm^{-1}, 15 W/cm^2) while the visible laser was adjusted to keep the visible-only dissociation at ~30% for each wavelength. The obtained line repesents the low resolution photodissociation spectrum from ref 6 and is included to show how the photodissociation band corresponds to the wavelength region studied here.

Also shown for reference in Figures 4–6 are the low-resolution photodissociation spectra obtained from ref 6 and 7. As discussed below, however, the apparent correspondence of photodissociation intensity and IR enhancement seems to be coincidental.

Discussion

In order to interpret these wavelength dependences, previous results must be discussed. In a set of experiments having considerable bearing on the interpretation of the present results, two-laser photodissociation observations were made in all three of these ions in which the visible and infrared irradiation periods were separated and not allowed to overlap. Enhancement was seen only when the infrared irradiation preceded the visible irradiation, while

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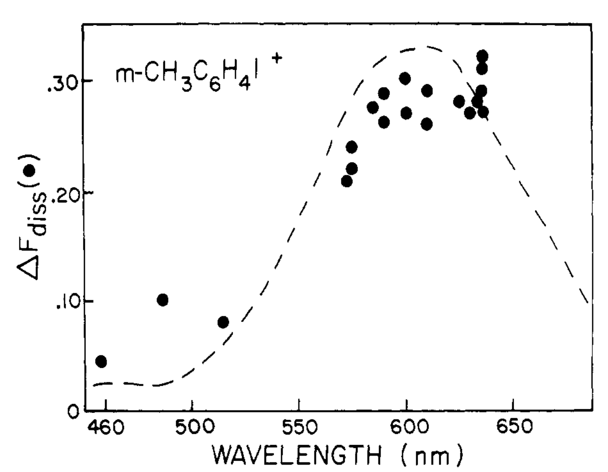

Figure 6. *m*-Iodotoluene: Additional fractional dissociation (ΔF_{diss}) caused by the infrared laser as a function of visible wavelength. The infrared laser was kept fixed (978 cm^{-1}, 15 W/cm^2) while the visible laser was adjusted to keep the visible-only dissociation at 30% for each wavelength. The dotted line represents the low-resolution photodissociation spectrum from ref 7 and is included to show how the photodissociation band corresponds to the wavelength region studied here. The apparent coincidence of photodissociation and IR enhancement wavelength dependences in Figures 4–6 appears to be accidental.

there was no effect if the order was reversed.[5] From these experiments it was concluded that thermal or near-thermal ions were first absorbing IR photons and then these excited ions were undergoing a faster photodissociation process when probed by a visible laser.

IR Wavelength Dependences. Since the enhancement undoubtedly results from ion infrared absorption, it should correlate with the infrared spectrum of the ion, which is of particular interest because infrared spectra for these ions are otherwise unavailable. Since the photodissociation spectra of these ions in ref 6 and 7 agree with values predicted from the photoelectron spectra of the neutrals it has been assumed that these ions retain the neutral structure, so that direct comparison of the ion enhancement spectra with the IR spectra of the corresponding neutral compounds,[8] as shown in Figures 1–3, should be relevant. The wavelength coverage of the IR enhancement spectra is too sparse for comprehensive comparison. We may conclude however that there are IR peaks, as well as regions of no IR enhancement, for the ions in this wavelength region (which is a region of ring vibrational modes) and that the IR features are shifted relative to the peaks in the neutral spectra. There are ion IR features appearing at longer wavelengths than any neutral peak; such a red shift in ring vibrations is reasonable, since ionization involves removal of a π-bonding electron largely localized on the ring.

Visible-Wavelength Dependences and Mechanism of Enhancement. To rationalize the visible-wavelength results the visible-laser-only photodissociation process must be discussed. Thermochemistry for the lowest energy dissociation pathways for the three ions of interest are as follows:

$$C_6H_5I^+ \rightarrow C_6H_5^+ + I \qquad \Delta H = 2.4 \text{ eV (517 nm, ref 9)}$$

$$C_6H_5Br^+ \rightarrow C_6H_5^+ + Br \qquad \Delta H = 2.76 \text{ eV (450 nm, ref 10)}$$

$$m\text{-}CH_3C_6H_42^+ \rightarrow C_7H_7^+ + I \qquad \Delta H = 0.7 \text{ eV (1770 nm, ref 11)}$$

For iodobenzene and bromobenzene, dissociation is observed with photons of energy less than the threshold and is believed to proceed by a sequential two-photon process.[3,12] Energy from the first photon is stored as vibrational energy in a long-lived intermediate which absorbs a second photon to place it above the dissociation threshold. For *m*-iodotoluene the absorption of a visible photon provides sufficient energy for dissociation, but, as discussed in the following, this ion in fact behaves like a two-photon ion and can be considered from the same point of view as the others.

Although the IR enhancement of visible-wavelength photodissociation of ions has by now received a substantial amount of study, the mechanism of the effect is still not certain. Two general types of mechanisms seem most reasonable: One, a perturbed visible-absorption mechanism, postulates that IR-laser excitation of the ion changes its cross section for absorption of visible light. The other, a perturbed two-photon mechanism, postulates that the visible photodissociation of ground-state ions is a two-photon process but that IR excitation can raise some of the ions into the one-photon region where photodissociation is much faster. Equation 1 illustrates this visible two-photon mechanism, which is quite well established as the photodissociation mechanism for a number of ions below the one-photon dissociation threshold wavelength:

$$C_6H_6X^+ \xrightarrow{\sigma_1 I} [C_6H_5X^+]^* \xrightarrow{\sigma_2 I} \text{dissociation products} \qquad (1)$$

where σ_1 and σ_2 are visible-wavelength photon absorption cross sections, I is the light intensity, and $[C_6H_5X^+]^*$ represents a vibrationally hot ground-state ion (arising from fast internal conversion of the initially formed excited electronic state of the ion). The perturbed two-photon mechanism of IR enhancement operates in effect by replacing the σ_1 photoexcitation step with vibrational up-pumping by the IR laser.

For iodobenzene ion at wavelengths longer than 515 nm,[13] and for bromobenzene ion at wavelengths longer than 440 nm,[13,14] two-photon dissociation is the predominant process for visible-only dissociation, and the perturbed two-photon mechanism accounts in a very satisfactory way for the very large enhancements observed in these cases.

If this is in fact the mechanism, it might be expected that IR radiation alone could induce dissociation. IR photodissociation has indeed been observed in a number of ions[15] with lasers comparable to that used here, and it seems probable that, if high enough IR intensities has been reached in the present experiments, it would have been seen. However, the dissociation thresholds of the ions studied here are relatively high, and fast infrared radiative relaxation at high internal energies is likely to make IR up-pumping to dissociation difficult. Extensive kinetic modeling of the iodobenzene ion case[16] gives quantitative

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support to this qualitative expectation.

On the other hand, for all three of these ions at shorter wavelengths, visible photodissociation is definitely a one-photon process. Thus, for iodobenzene and *m*-iodotoluene ions at short wavelengths, it is reasonable to suppose that the modest degree of enhancement observed arises through the perturbed absorption cross section mechanism; a maximum increase in cross section of the order of 50% is suggested by the amount of enhancement observed. (Other possible mechanisms are discussed below.) There is some precedent for a substantial increase in visible cross section for vibrationally excited ions: two-photon kinetic analysis of cyanobenzene[14,17] ion photodissociation suggests a 10-fold or more difference between σ_1 and σ_2, and similar analyses of bromobenzene[14] ion have been interpreted as showing a difference of about a factor of 2. These analyses do not indicate which of σ_1 and σ_2 is larger, but the present results would be consistent with an increase in σ of 50% upon absorption of several tenths of an electronvolt of energy from the IR laser. Wight and Beauchamp[18] have recently observed an IR-enhanced photodissociation in cyanobenzene ion which also may reflect such a perturbation, although the mechanism is not certain in this system.

The large IR enhancement observed in *m*-iodotoluene at red wavelengths was initially unexpected, since one-photon dissociation is energetically possible at all visible wavelengths, and it had always been assumed that one-photon kinetics were indeed followed in the iodotoluene ion dissociation. However, it has recently been established by pressure-dependence measurements[19] that this ion dissociates by two-photon kinetics in the red, apparently reflecting a highly nonadiabatic dissociation mechanism, and that the threshold for one-photon kinetic behavior is actually very similar to that in iodobenzene at about 540 nm. This being the case, it is not at all surprising that the behavior of the IR enhancement effect in *m*-iodotoluene ion is very similar to that in iodobenzene ion, and in this case also we interpret the results as indicating an IR-perturbed two-photon mechanism in the red, switching to an IR-perturbed visible-absorption mechanism in the green.

Just why the absorption cross section should change with few IR quanta of internal energy is not obvious. Evidence against irreversible isomerization comes from experiments in which the infrared and visible irradiation periods were separated and the excited iodobenzene,[5] bromobenzene,[5] and iodotoluene ions were observed to relax back to unexcited ions. More likely is an actual change in the visible-absorption cross section upon internal excitation, either by increased hot-band intensity or by changed Franck–Condon factors. Since there are several (at least three) electronic transitions which may contribute to the rather weak optical absorption around 440 (bromobenzene ion) or 500 (iodotoluene and iodobenzene ions[6]) nm, there are many possible ways to account for the IR perturbation of absorption in these wavelength regions. Other alternative classes of explanation, such as IR-perturbed quantum yields for dissociation, or IR perturbation of intersystem crossing processes, can of course not be ruled out.

A glance at Figures 4 and 5, and particularly Figure 6, showing the extent of enhancement rising parallel to the visible photodissociation cross section, may give the impression that a true correlation exists. This is apparently purely coincidental. The shape of the visible photodissociation spectrum is determined by the visible-wavelength spectroscopy of the ion, while, following the discussion above, the shape of the IR enhancement curve as a function of visible wavelength is determined by the differing photophysics of the enhancement process in different wavelength regions. There is no reason to expect a connection between these two phenomena.

Other Molecules. Several other ions were examined and showed no significant enhancement effect when irradiated with the infrared laser. All three available IR wavelength regions (10.5–10.7, 10.15–10.3, 9.5–9.7 μm) were examined for the following ions at the visible wavelengths indicated: (1) styrene (595 nm), (2) 1-methylnaphthalene (600 nm), (3) 2-methylnaphthalene (610 nm), (4) pentafluorobromobenzene (515 nm), (5) pentafluoroiodobenzene (595 nm). These candidates were chosen either because the neutrals have IR absorption in the CO_2 laser region or, in the case of the fluorinated compounds, because the C–F stretches often fall in the range of CO_2 laser frequencies. With these negative results we are unable to state whether these ions did not absorb the IR photons or whether instead the excited ions did not undergo a speeded-up dissociation process.

Conclusion

The results discussed in this work provide insights into both thermal (or near-thermal) and excited ions. A moderate-power CW infrared laser has been shown to be optically pumping ions to produce excited species with markedly changed photodissociation properties. The infrared wavelength dependences for the enhancement effect suggest that this may be an effective technique for obtaining IR spectroscopy information for gas-phase ions. The IR laser is only required to excite the ions and not to cause dissociation, thereby eliminating the need for high-powered and/or pulsed lasers. The variation in extent of the infrared enhancement with visible wavelengths is interpreted as reflecting two different mechanisms: at short wavelengths the enhancement is attributed to changes in visible-absorption cross section with increasing internal energy and gives a useful means of observing such effects, while at long wavelengths the enhancement is attributed to a perturbation of the two-photon dissociation kinetics.

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Registry No. $C_6H_5I^+$, 38406-85-8; $C_6H_5Br^+$, 55450-33-4; *m*-$CH_3C_6H_4I^+$, 58436-64-9.

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