precise structural relationships, and the skew angle of the four dienic carbons.

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Supplementary Material Available: The Cartesian coordinates for compounds IV-XI (1 page). Ordering information is given on any current masthead page.

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Acid-Base Properties of Molecules in Excited Electronic States Utilizing Ion Cyclotron Resonance Spectroscopy

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Abstract: A general method is described for obtaining excited state acid-base properties of molecules and ions in the gas phase which utilizes ion cyclotron resonance spectroscopy for studying photochemical processes involving ions. These processes, including photodissociation and photodetachment, yield in favorable instances electronic excitation energies of ions. A comparison of the excitation energies of a base B with the corresponding acid-base complex AB yields the excited state basicity of B. Similarly, a comparison of the excitation energies of a chromophoric acid A with the complex AB yields information about the excited state acidity of A. Studies of the first type are described using the reference acids H^+ and Li^+ with the bases C_6H_5X (X = H, CN, NH_2, CHO, $COCH_3$, NO_2, OCH_3, O^-, and S^-), pyridine, and ferrocene. In several instances photodissociation spectra of solvated acid-base complexes of the type B_2Li^+ have been obtained and analyzed to determine the effects of further solvation on the excitation spectra of these complexes. A comparison of the gas-phase excitation spectra of a number of ions to their solution absorption spectra is made. Studies of the second type (excited state acidities) are described using the reference base H^- with the acids $C_6H_5CO^+$ and $C_6H_5CHOH^+$. Calculated changes in acidity and basicity are used to infer changes in electron distributions and dipole moments for excited states, and yield insight into the types of transitions involved. In particular these studies are used to assess the controversial role played by intramolecular charge transfer in the lowest two singlet $\pi \rightarrow \pi^*$ transitions of monosubstituted benzenes. These results are compared with findings from related experiments and calculations when available.

One of the most important and useful concepts in chemistry is that of the acid-base properties of molecules. Several treatises have been written on the subject, including classic papers by Brønsted and Lewis among others.[2] Despite different points of view, a general description emerges: a base is a species which is electron donating and an acid is one which is electron accepting. This definition alone suggests an intimate relationship between the acid-base properties of a molecule and its charge distribution. Since charge densities are often modified by electronic excitation, it is expected that the acid-base properties of a molecule in an excited state will also vary from its properties in the ground state. Conversely, a determination of excited state acid–base properties can be used to infer associated changes in electron density and dipole moment. Determining these quantities has been a subject of considerable interest both theoretically and experimentally and, because of their interrelationship, determining any one property sheds light on the others.

The direct measure of acid–base properties of molecules in excited states in solution remains an active area of research.[3-5] These studies mainly utilize absorption data and fluorescence data in conjunction with the Förster cycle[3] to determine changes in pK in excited singlet and triplet states.[4] Most of this work is confined to Brønsted acids and bases, though some work on Lewis acid systems has been reported.[5] New and promising research areas involve utilization of excited state acid–base properties to promote ground state reactions[6] and the application of pulsed picosecond lasers to study the kinetics of excited-state proton-transfer reactions. Work having indirect significance to excited-state acid–base properties includes calculations on charge distributions of molecules in their ground and excited states,[7-9] from which dipole moments can be obtained. In addition, there are numerous experimental approaches which yield dipole moments of molecules in excited electronic states.[10-17] For molecules in metastable excited states having sufficiently long lifetimes, the usual methods for obtaining dipole moments in ground states may be successfully applied.[14,15] For short-lived systems, alternate methods have been devised utilizing the effects of electric fields on absorption spectra[10-13] (electrochromism) and the influence of solvent on the spectra[10a,16,17] (solvatochromism). These results aid in understanding the types of transitions involved, provide a test for the accuracy of theoretical calculations, and again suggest excited-state acid–base properties.

The bond dissociation energy D(A–B) determined for the general reaction

$$\mathrm{AB} \rightarrow \mathrm{A} + \mathrm{B} \qquad \Delta H_{\mathrm{rxn}} \equiv D(\mathrm{A{-}B}) \tag{1}$$

defines acid–base strengths as considered throughout this paper. Thus, for a particular reference acid, A, B_2 is a stronger base than B_1 if $D(\mathrm{A{-}B_2}) > D(\mathrm{A{-}B_1})$. Similarly, for a particular reference base B, A_2 is a stronger acid than A_1 if $D(\mathrm{A_2{-}B}) > D(\mathrm{A_1{-}B})$.

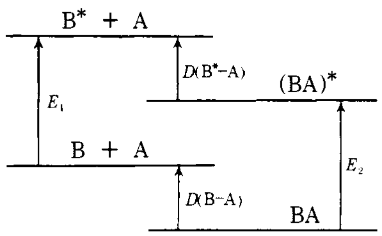
Gas-phase methods[18] such as flowing afterglows,[19,20] high-pressure mass spectrometry,[18,21,22] drift tubes,[23,24] and ion cyclotron resonance spectroscopy[25-31] (ICR) have been instrumental in determining intrinsic ground-state acid–base properties in the absence of complicating solvation effects. The reactions studied are generally the equilibria processes

$$\mathrm{AB_1} + \mathrm{B_2} \rightleftharpoons \mathrm{AB_2} + \mathrm{B_1} \tag{2}$$

$$\mathrm{A_1B} + \mathrm{A_2} \rightleftharpoons \mathrm{A_2B} + \mathrm{A_1} \tag{3}$$

For process 2, numerous studies have been reported using the reference acids H^+,[18,19-21,25,26] Li^+,[27] and more recently $CpNi^+$ [28] to determine the basicities of a wide variety of n- and π-donor neutral bases as well as of anionic bases in the case of H^+. For process 3, relative acidities have been tabulated for a great number of cationic and neutral acids using the reference bases H^-,[18,22,29] F^-,[18,29,30] Cl^-,[30] and Br^-.[31] In all of these cases, the criteria for study is that one of the species involved in the general processes 2 and 3 must be positively or negatively charged.

Scheme I



In this paper we report a straightforward method for determining the gas-phase acid–base properties of molecules in excited electronic states using the techniques of ion cyclotron resonance spectroscopy.[32,33] Methodology for determining excited-state basicities is general and follows directly from the thermochemical cycle in Scheme I, where A is a reference acid, B is a neutral or negatively charged base in the ground state, B* is the base in an excited state, E_1 is the excitation energy of the base, E_2 the excitation energy of the acid–base complex AB, and D(B–A) and D(B*–A) define the base strengths in the ground and excited states, respectively. The determination of binding energies in excited electronic states relative to the ground state is then determined from the equation

$$\Delta D(\mathrm{B{-}A}) = D(\mathrm{B^*{-}A}) - D(\mathrm{B{-}A}) = E_1 - E_2 \tag{4}$$

Since ΔD(B–A) is a thermodynamic quantity, E_1 and E_2 in eq 4 should correspond to adiabatic transition energies. Unfortunately, measurements of the 0–0 transition energies cannot be accurately determined due to the lack of vibrational structure in these spectra. However, if the band shapes of the base and conjugate acid are similar, using vertical energies does not introduce large errors. It is emphasized that cycles such as depicted in Scheme I and eq 4 are used to *formally define* excited-state acid–base properties.

Using H^+ for A, Scheme I can be applied in determining proton affinities in excited states, and corresponds to the Förster cycle[3] utilized in solution work. The proton affinity PA(B) of a neutral or anionic base B is defined as the heterolytic bond dissociation energy for process 1 where A is H^+. The excited-state proton affinity PA(B*) is determined relative to the ground-state proton affinity PA(B) using the equation

$$\Delta \mathrm{PA(B)} = \mathrm{PA(B^*)} - \mathrm{PA(B)} = E_1 - E_2 \tag{5}$$

which follows directly from eq 4 and the definition of proton affinity. When B is a neutral species, E_1 is obtained from the gas-phase absorption spectrum of B and E_2 is obtained using ICR techniques developed for examining the photodissociation of gaseous ions,[32,35-37] the latter phenomenon being generalized in the equation

$$\mathrm{C^+} + h\nu \rightarrow \mathrm{D^+} + \mathrm{E} \tag{6}$$

The measured quantity in reaction 6 is the photodissociation cross section, $\sigma_d(\lambda)$, which is proportional to the product of the intrinsic transition probability or gas-phase extinction coefficient, $\epsilon_g(\lambda)$, and the photodissociation quantum yield, $\varphi_d(\lambda)$, as written in the equation

$$\sigma_d(\lambda) \propto \epsilon_g(\lambda)\varphi_d(\lambda) \tag{7}$$

If the quantum yield for photodissociation is relatively constant over an absorption band, then $\sigma_d(\lambda)$ will reflect the absorption spectrum and directly yield the vertical excitation energy.[36] If, on the other hand, φ_d varies significantly over an absorption band, then $\sigma_d(\lambda)$ will not yield exactly the vertical excitation energy. The latter situation would occur, for example, in the vicinity of the thermodynamic threshold for dissociation, below which $\varphi_d(\lambda) = 0$.

When B is an anion such as phenoxide ($C_6H_5O^-$), E_2 is obtained from the gas-phase absorption spectrum of the conjugate acid, and E_1 is obtained from the excitation spectrum of the anion. Excited states of anions are generally higher in energy than the electron affinity, EA(B), of the corresponding neutral; hence they lie in the photodetachment continuum.[38-40] Following absorption, excited states decay by autodetachment[38-40] or dissociation.[41-43] In the former case, peaks appear

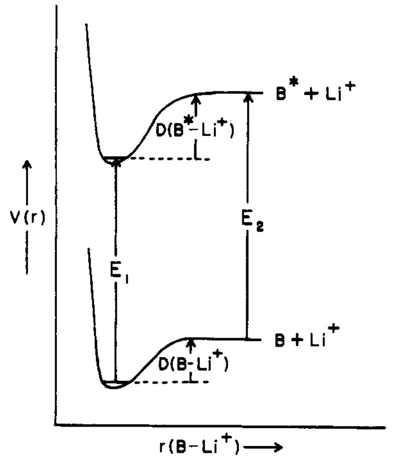


Figure 1. Potential energy diagram for the formation of BLi^+ in its ground state as well as in a selected excited state.

in the photodetachment spectrum; in the latter case, eq 7 is applicable with $\sigma_d(\lambda)$ being directly determined by monitoring the appearance of corresponding photofragment ions.

The alkali ions, especially Li^+, have received considerable attention both theoretically and experimentally as reference Lewis acids to measure base strengths of molecules.[27,44-46] Interesting differences in both the quantitative and qualitative ordering of base strengths using Li^+ compared to H^+ arise[27] due to the strictly electrostatic bonding of Li^+ compared to the covalent bonding available to the proton.[45] The core electrons on Li^+ interact repulsively with electrons on the base (Pauli principle), preventing the close contact necessary for covalent bonding.[45] Thus, while important information can be obtained about excited-state proton affinities using H^+, studies with Li^+ yield a more straightforward analysis of the changes in charge distribution of a neutral base accompanying excitation, since the purely electrostatic bonding in Li^+ does not perturb the nature of the chromophore.

A potential energy diagram for the formation of BLi^+ in its ground state as well as in a selected excited state is shown in Figure 1. The determination of Li^+ binding energies of molecules in excited states relative to the ground state follows directly using eq 4 with $A = Li^+$ to yield the equation

$$\Delta D(\text{B-Li}^+) = D(\text{B}^*\text{-Li}^+) - D(\text{B-Li}^+) = E_1 - E_2 \quad (8)$$

where E_1 is determined from the gas-phase absorption spectrum of B and E_2 is obtained readily by monitoring the photodissociation reaction.

$$BLi^+ + h\nu \rightarrow B + Li^+ \quad (9)$$

During the course of the above studies on weakly bound Li^+ complexes, it was found that at long times or at high pressures these complexes are further solvated as indicated by reaction 10. The dimer species are observed to photodissociate via reaction 11, allowing a comparison of their spectra to those of the corresponding neutral and monomer complex. These results yield information relating to the effects of further solvation on the electronic excitation energies of the acid–base complex.

$$BLi^+ + B \rightarrow B_2Li^+ \quad (10)$$

$$B_2Li^+ + h\nu \rightarrow BLi^+ + B \quad (11)$$

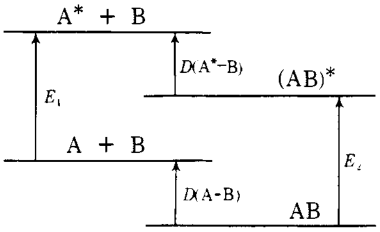
Scheme II can be used to detail the change in acidity of a molecule or ion in a manner analogous to Scheme I. This scheme yields the equation

$$\Delta D(\text{A-B}) = D(\text{A}^*\text{-B}) - D(\text{A-B}) = E_1 - E_2 \quad (12)$$

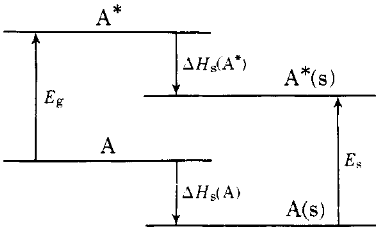
where $\Delta D(\text{A-B})$ is the change in the acidity of A between its excited-state acidity, defined by $D(\text{A}^*\text{-B})$, and its ground-state acidity, defined by $D(\text{A-B})$, and where E_1 and E_2 are obtained from the excitation spectrum of the acid A and the complex AB, respectively. As noted above, for this analysis to be straightforward, the reference base B must not greatly change the nature of the chromophore. For cationic acids ($A = R^+$) and using H^- as the reference base, eq 12 becomes

$$\Delta D(\text{R}^+\text{-H}^-) = D(\text{R}^{+*}\text{-H}^-) - D(\text{R}^+\text{-H}^-) = E_1 - E_2 \quad (13)$$

Scheme II



Scheme III



This equation is used below to deduce information about the excited-state acidities of several carbonium ions.

Scheme III is used to determine solvent effects on absorption spectra of ions, where A is the gaseous ground-state species, A* is the gaseous excited-state species, A(s) is the solvated ground-state species, A*(s) is the solvated excited-state species, E_g is the excitation energy in the gas phase, E_s is the excitation energy in solution, and $\Delta H_s(\text{A})$ and $\Delta H_s(\text{A}^*)$ are the heats of solvation for the ground and excited states, respectively. Solvent shift is an effective spectroscopic tool both for determining the character of absorption bands and for yielding insight into the intermolecular forces between solute and solvent.[47] From Scheme III, for example, it is clear that the solvent shift $E_g - E_s$ yields information about the changes in solvation energy between the ground and excited states, $\Delta H_s(\text{A}) - \Delta H_s(\text{A}^*)$. Several ions whose spectra have been obtained in both gas and solution phase will be discussed.

Since in the present experiments excited states are detected only by monitoring photodissociation processes, it follows that the state is not bound and acid–base properties cannot be defined thermodynamically. Derived quantities are thus only formally defined for the initially formed state of the system. Internal conversion is expected to be rapid and the system may evolve into other states with markedly different acid–base properties than the state initially accessed in the photoexcitation process (e.g., a vibrationally excited ground state).

Most of the ions and neutrals examined in this study are monosubstituted benzenes. The detailed characterization of excited electronic states of these species remains controversial. In particular, for the neutral species, the two lowest singlet $\pi \rightarrow \pi^*$ excitations have been interpreted in two ways. The observation that the UV spectra of substituted benzenes are largely uniform and greatly resemble that of the parent compound, despite the reduction in symmetry and perturbation of the electronic system by the substituent, has led to the suggestion that these bands correspond to the benzene transitions shifted to lower energies.[48] Using this interpretation, bands corresponding to the benzene 203.5-nm primary band ($^1A_{1g} \rightarrow {}^1B_{1u}$) and to the 256-nm secondary band ($^1A_{1g} \rightarrow$

Table I. Spectroscopic and Thermochemical Data Related to Proton Affinities of Electronically Excited States of Selected Neutral Bases

		Neutral		Conjugate acid			
Compd	PA(B)[a]	λ_{max}[b]	Rel[c] intensity	λ_{max}[b]	Rel[c] intensity	PA(B*)[a]	ΔPA[a]
Benzaldehyde	198.1	232	1.00	303	1.00	227.1	29
	198.1	275[d]	0.11	368	0.09	224.1	26
Cyanobenzene	194.1	224	1.00	254	1.00	209.1	15
	194.1	274	0.07	293	0.20	201.1	7
Acetophenone	203.1	230	1.00	305	1.00	233.1	30
	203.1	275	0.05	355	0.24	226.1	23
Nitrobenzene	191.6	240	1.00	357	1.00	230.6	39
	191.6	280	0.12	~400	0.19	222.6	31
Pyridine	218.1	250	1.00	250	1.00	218.1	0
	218.1	275	*e*	*f*	*f*	<218.1	<0
Benzene	181.4	201[g]	1.00	245	0.25	204.4	23
	181.4	253[g]	0.03	330	1.00	207.4	26
Mesitylene	197	212	1.00	250	0.60	217	20
	197	264	0.02	355	1.00	225	28
Anisole	198.4	216	1.00	260	1.00	220.4	22
	198.4	268	0.20	340	0.14	220.4	22

[a] PA(B) and PA(B*) in kilocalories per mole. ΔPA = PA(B*) − PA(B); values for PA(B) are relative to $PA(NH_3) = 202.3 \pm 2$ kcal/mol (J. F. Wolf, I. Koppel, R. W. Taft, R. H. Staley, and J. L. Beauchamp, unpublished results). [b] Wavelength, ±10 nm for conjugate acid spectra. [c] Band intensities relative to the more intense peak, which is assigned a value of 1.00. [d] These bands are low-intensity shoulders for which λ_{max} is difficult to define precisely. An error of 10 nm introduces an uncertainty of approximately 5 kcal/mol in ΔPA. [e] Unresolved band. [f] Band not observed. [g] K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965).

$^1B_{2u}$) are found usually shifted in a regular way in monosubstituted benzenes such that the ratios of λ_{max} for the secondary and primary bands are $\lambda_{sec}/\lambda_{prim} \simeq 1.24$. These transitions can be assigned $^1A_1 \rightarrow {}^1B_2$ and $^1A_1 \rightarrow {}^1B_1$ in the lower C_{2v} symmetry. More recently it has been suggested that for certain substituents these transitions correspond to internal charge transfer bands in which electron density shifts either from the ring to the substituent or from the substituent to the ring depending on the nature of the substituent.[10b,49] Similar interpretations can also be applied to ionic monosubstituted benzenes such as benzoyl cation[36] and phenoxide anion.[10b]

If internal charge transfer is important in these species, dramatic effects on their acid-base properties in their lowest excited states are expected. Hence, the present studies provide further information relating to the nature of the electronic excitations.

Experimental Section

ICR instrumentation and experimental techniques for studying photochemical processes involving ions in the gas phase have been previously described in detail.[32,34-36] Methods for generating alkali ion complexes have also been described.[27] Pressures utilized for these experiments were typically 10^{-7} Torr and ion trapping times approached 2 s. A 2.5-kW mercury-xenon arc lamp was used in conjunction with a 0.25-m Bausch and Lomb monochromator set for a resolution of 10 nm, except for Li^+ complexes with nitrosobenzene, ferrocene, and *p*-methoxybenzaldehyde, for which 13-nm resolution was used, to obtain photodissociation spectra. Neutral absorption spectra were obtained on a Cary 17 using a 1-cm quartz gas cell. Except for pyridine and ferrocene, spectra reported in figures were recorded at low resolution to facilitate comparison with the ion spectra. All chemicals were commercial samples of high purity, and were used as supplied except for freeze-pump-thaw cycles to remove noncondensable gases. Mass spectrometry revealed no detectable impurities.

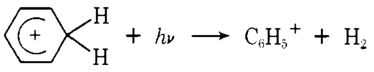
Results

Excited-State Basicities with H⁺ as the Reference Acid. The gas-phase spectra of several bases B and their conjugate acids BH^+ between 200 and 400 nm are displayed in Figures 2-6 and summarized in Table I. The spectra of the cations were obtained by monitoring their disappearance as a function of wavelength. In several instances (eq 14-18) the photoproducts were investigated.

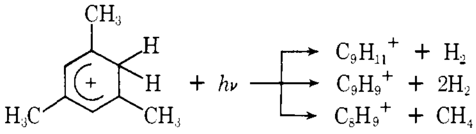
$$C_6H_5CHOH^+ + h\nu \rightarrow C_7H_7^+ + CO \quad (14)$$

$$C_6H_5CNH^+ + h\nu \rightarrow C_6H_5^+ + HCN \quad (15)$$

$$C_5H_5NH^+ + h\nu \rightarrow C_5H_4N^+ + H_2 \quad (16)$$



(17)



(18a)
(18b)
(18c)

For simplicity throughout this paper we use W_0 to denote the ground state and W_1 and W_2 (when applicable) to indicate the first and second strongly allowed states observed for the above bases and their conjugate acids.

Figures 2 and 3 compare the neutral absorption spectra of benzaldehyde, cyanobenzene, acetophenone, and nitrobenzene to the photodissociation spectra of their conjugate acids. These species have all been shown in other studies to be substituent protonated.[50] Due to the similarity in the band shapes of the neutral molecules and their conjugate acids, vertical excitation energies are used to determine E_1 and E_2 in eq 5 without introducing large errors.

The most pronounced effect of excitation on base strength is observed for the W_2 state of nitrobenzene, estimated to be 39 kcal/mol more basic than the ground state. This would correspond to an increase of about 28 p*K* units! Similar but smaller increases in proton affinity are calculated for the excited states of benzaldehyde, cyanobenzene, acetophenone, and the W_1 state of nitrobenzene (Table I).

Protonated aniline was not observed to undergo photodissociation. This suggests, but is not proof, that the spectrum lies to higher energies (unattainable with the present apparatus) as is observed for the absorption spectrum of anilinium in solution.[51] The lowest π → π* bands of the free base are observed with λ_{max} 230 and 282 nm in the gas phase.

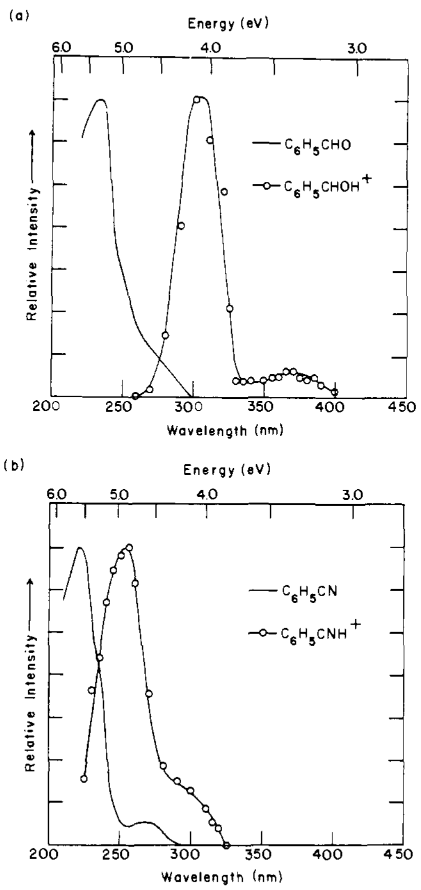


Figure 2. (a) Comparison of the gas-phase absorption spectrum of benzaldehyde with the photodissociation spectrum of its conjugate acid. (b) Comparison of the gas-phase absorption spectrum of cyanobenzene with the photodissociation spectrum of its conjugate acid.

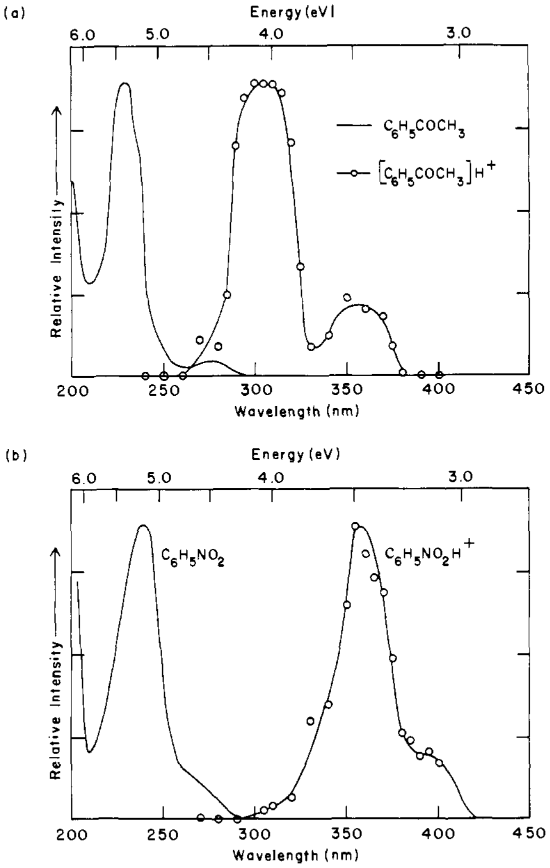


Figure 3. (a) Comparison of the gas-phase absorption spectrum of acetophenone with the photodissociation spectrum of its conjugate acid. (b) Comparison of the gas-phase absorption spectrum of nitrobenzene with the photodissociation spectrum of its conjugate acid.

Figure 4 compares the gas-phase spectrum of pyridine with the photodissociation spectrum of the protonated species obtained by monitoring reaction 16. The long wavelength tail ascribed to the n → π^* transition[52] is not observed in the protonated species. The $\pi \rightarrow \pi^*$ transition,[52] however, shows no shift, indicating no change in base strength in the excited state.

Figures 5 and 6 compare the gas-phase absorption spectra of benzene, mesitylene, and anisole to the photodissociation spectra of their conjugate acids. These species have been shown to be ring protonated.[50,53] Ring protonation occurs in the para position for anisole.[53] Assuming correlation, as previous solution studies suggest,[4] substantial increases in proton affinity are calculated for the excited states of these species with, for example, $\Delta PA = 26$ and 23 kcal/mol being noted for the W_1 and W_2 excited states in benzene.

As noted above, excitation energies of negative ions can be obtained by monitoring either photodissociation or photodetachment processes, and used in conjunction with eq 4 to yield excited-state base strengths. The specific examples mentioned here are observed to undergo photodetachment.

The photodetachment threshold is frequently a good estimate of the electron affinity.[38-40] Recent photodetachment experiments by J. H. Richardson have indicated that complex molecular ions can be expected to exhibit unusual photodetachment cross sections arising from transitions to excited electronic states of the ion.[40] The use of these excitation energies to elucidate excited-state properties of anionic bases was not considered. The photodetachment spectra of a series of phenoxides as well as thiophenoxide provide an interesting application of this analysis. Superimposed on a long tail extending to longer wavelengths is a peak at 332 nm in the case of phenoxide ions, which is also observed in solution[54] (ca. 300 nm). This feature is attributed to a $\pi \rightarrow \pi^*$ transition to an excited electronic state of the ion. The photodetachment cross section for the ions o-$CH_3C_6H_4O^-$, o-$ClC_6H_4O^-$, m-$ClC_6H_4O^-$, and $C_6H_5S^-$ were also reported[40] to have an excitation maximum very near 330 nm (Table II). The lowest transitions in the absorption spectra for the corresponding phenols are nearly identical with each other,[55] with thiophenol being only slightly different.[56]

An analysis of the spectra indicate that the first two $\pi \rightarrow \pi^*$ transitions in phenolate correspond to the first two in phenol.[10b,40] It is therefore probable that the maximum at 330 nm in phenolate corresponds to the transition $W_0 \rightarrow W_1$ and that $W_0 \rightarrow W_2$ is at shorter wavelengths. The W_1 state in phenol lies at 270 nm and using eq 5 one obtains a $\Delta PA(B)$ of -20 kcal/mol, that is, a decrease in basicity in the excited state. Identical results are noted for the other species in Table II.

Excited-State Basicities with Li^+ as the Reference Acid. Changes in basicity in excited states have been determined using Li^+ as the reference acid. The compounds, for which spectra are reported in this study, form Li^+ complexes directly (i.e., bimolecularly) via the reaction

$$B + Li^+ \rightarrow BLi^+ \qquad (19)$$

at low pressures (ca. 10^{-7} Torr), indicating a minimum lifetime of approximately 150 ms.[57] During the 2-s trapping time, 10-20 collisions with the neutral species stabilize and deactivate the complex.

Figures 7-11 compare the gas-phase absorption spectra of several bases to the photodissociation spectra of the corresponding Li^+ complexes obtained by monitoring process 9

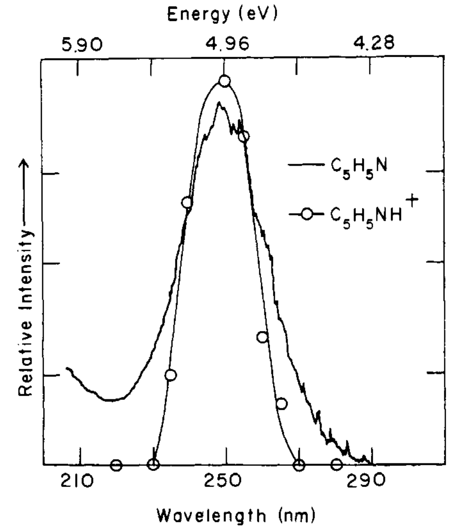


Figure 4. Comparison of the gas-phase absorption spectrum of pyridine with the photodissociation spectrum of its conjugate acid.

Table II. Spectroscopic and Thermochemical Data Related to Proton Affinities of Electronically Excited States of Selected Anionic Bases

Compd	Anion,[a] λ_{max}[b]	Neutral (conjugate acid), λ_{max}[b]	$\Delta PA(B)$[c]
Phenol	332	270[d]	−20
o-Methylphenol	330	268[e]	−20
o-Chlorophenol	340	276[e]	−20
m-Chlorophenol	330	270[e]	−20
Thiophenol	332	270[d]	−20

[a] Data on anions from ref 40. [b] Wavelength, ±10 nm. [c] $\Delta PA(B) = PA(B^*) - PA(B)$ in kilocalories per mole. [d] K. Kumura and S. Nagakura, *Mol. Phys.*, 9, 117 (1965). [e] Reference 55.

between 200 and 700 nm. Due to the similarity of the band shapes in the spectra of the neutral molecules and their complexes, vertical energies are again used instead of adiabatic energies to estimate $E_1 - E_2$, and therefore $\Delta D(B\text{-}Li^+)$ in eq 8 without introducing large errors. The results are summarized in Table III.

Appreciable shifts are observed for both transitions in benzaldehyde, nitrobenzene, acetophenone, and nitrosobenzene (Figures 7 and 8), with the most pronounced effect for the W_2 state of nitrobenzene, indicating an increase in Li^+ binding energy of 32 kcal/mol relative to the ground state. In comparison, however, no significant shifts are observed for the corresponding transitions in cyanobenzene and aniline (Figure 9). Interestingly, complexes of Li^+ with benzene and fluorobenzene were not observed to photodissociate appreciably over this wavelength region.

The spectrum of the Li^+ complex with *p*-methoxybenzaldehyde is shown to be similar in shape but shifted to lower energies relative to the uncomplexed neutral (Figure 10). That only the low-energy absorption is present, and none at higher energies relative to the neutral spectrum, indicates that Li^+ is bound entirely to CHO, CHO being much more basic than OCH_3. Furthermore, the changes in excited-state base strengths for the W_1 and W_2 states in *p*-methoxybenzaldehyde are identical with those in benzaldehyde (Table III).

Figure 11 compares the photodissociation spectrum of the Li^+ complex of ferrocene to the absorption spectrum of ferrocene vapor at 35 °C obtained by McGlynn et al.[58] The Roman numerals in the vapor spectrum were used by the authors of the previous work and are used here to facilitate the comparison. Bands VI, VIII, and IX appear to be present in the photodissociation spectrum of the complex with only minor shifts noted relative to the vapor spectrum (Table III). No other absorptions in the complex were noted between 220 and 700 nm (45 500–14 288 cm^{-1}). There is no evidence that band XII, interpreted as a ligand to the metal ($L \rightarrow M$)[59,60] transition with an extinction coefficient of greater than 30 000 L mol^{-1} cm^{-1}, is shifted to the red and observed in the spectrum of Li^+ complex at the wavelengths studied.

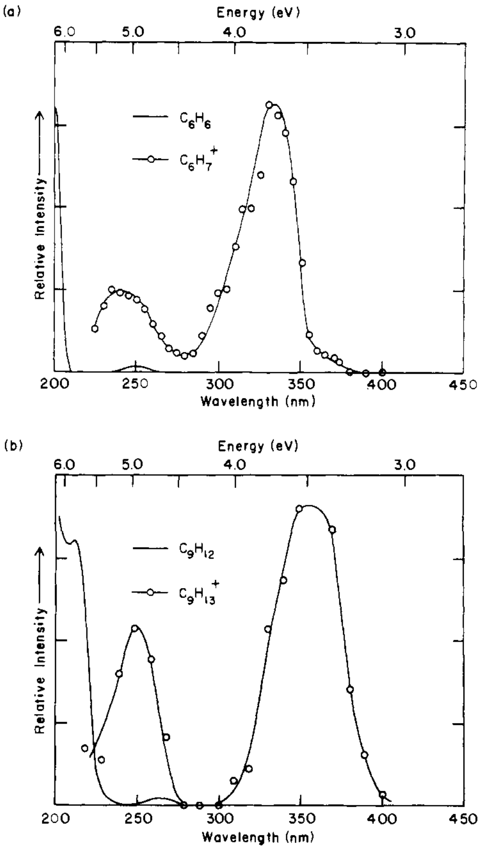


Figure 5. (a) Comparison of the gas-phase absorption spectrum of benzene with the photodissociation spectrum of its conjugate acid. (b) Comparison of the gas-phase absorption spectrum of mesitylene with the photodissociation spectrum of its conjugate acid.

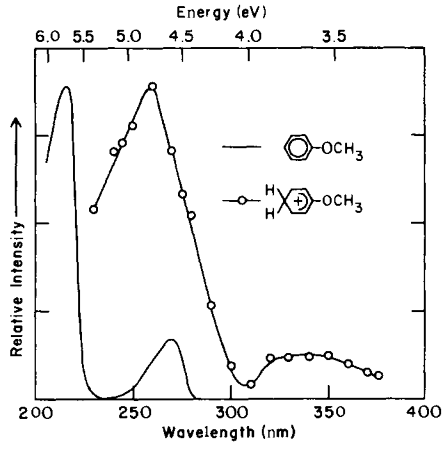


Figure 6. Comparison of the gas-phase absorption spectrum of anisole with the photodissociation spectrum of its conjugate acid.

Figure 8 compares the gas-phase absorption spectra of acetophenone and nitrosobenzene to the photodissociation spectra of both their corresponding Li^+ complexes and Li^+ bound

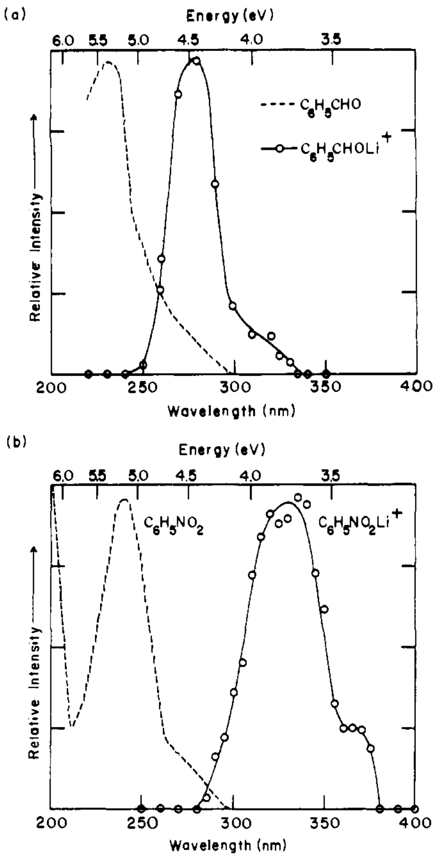


Figure 7. (a) Comparison of the gas-phase absorption spectrum of benzaldehyde with the photodissociation spectrum of the corresponding Li^+ complex. (b) Comparison of the gas-phase absorption spectrum of nitrobenzene with the photodissociation spectrum of the corresponding Li^+ complex.

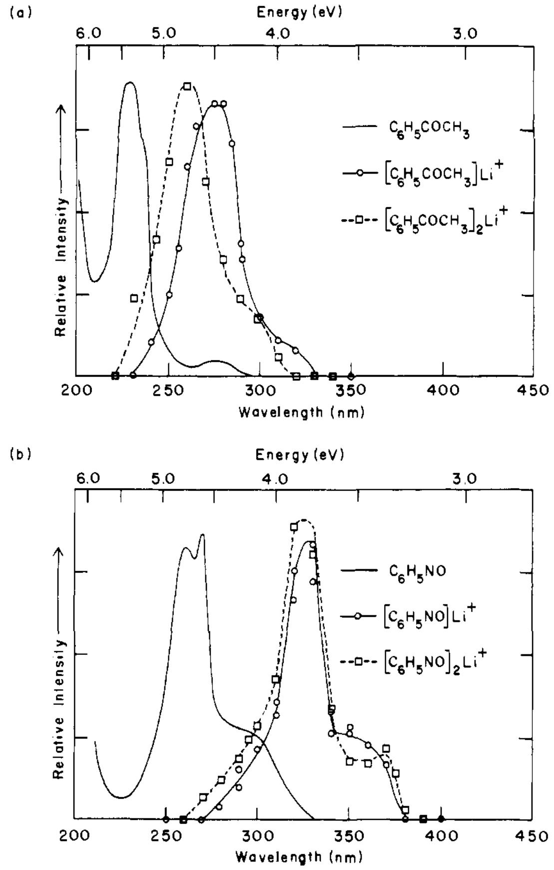


Figure 8. (a) Comparison of the gas-phase absorption spectrum of acetophenone with both the photodissociation spectrum of the corresponding Li^+ complex and Li^+ bound dimer. (b) Comparison of the gas-phase absorption spectrum of nitrosobenzene with both the photodissociation spectrum of the corresponding Li^+ complex and Li^+ bound dimer.

dimer complexes. The latter were obtained by monitoring the appearance of BLi^+ product in process 11, since monitoring the disappearance of the dimer complex directly was hampered by the limited mass range of the present apparatus. The spectra of the neutral, monomer, and dimer are similar in appearance for acetophenone (Figure 8a) and nitrosobenzene (Figure 8b) with only small shifts to higher energy noted for both W_1 and W_2 in the dimer complex of acetophenone relative to the monomer and to lower energy for W_1 in nitrosobenzene. These results are summarized in Table IV.

Excited-State Acidities. The gas-phase spectra of $C_6H_5CO^+$ and $C_6H_5CHOH^+$, obtained by monitoring reactions 20 and

$$C_6H_5CO^+ + h\nu \rightarrow C_6H_5^+ + CO \qquad (20)$$

14, and of their corresponding conjugate bases C_6H_5CHO and $C_6H_5CH_2OH$ between 200 and 400 nm are displayed in Figure 12 and summarized in Table V. Using eq 13 and the data from the figure, the changes in the bond dissociation energies for the cation acids in excited states relative to their ground states for the processes

$$C_6H_5CO^+ + H^- \rightarrow C_6H_5CHO \qquad (21)$$

$$C_6H_5CHOH^+ + H^- \rightarrow C_6H_5CH_2OH \qquad (22)$$

may be estimated. The results are summarized in Table V and indicate, for example, that benzoyl cation has a lower $\bar{D}(R^+\text{-}H^-)$ in its two excited states (decreased acidity) relative to its ground state by about 13 kcal/mol.

Comparison of Gas-Phase Excitation Spectra to Solution Absorption Spectra. Many of the ionic species for which gas-phase spectra have been obtained in this study have been observed in solution. We recently reported that the photodissociation spectra of benzoyl cation, protonated benzene, and protonated mesitylene were identical with the direct absorption spectra obtained in HF and BF_3 for benzoyl cation and concentrated H_2SO_4 for the latter ions.[36] In Table VI we include these examples, as well as several more for which the comparison can be made. It is apparent from the table that lack of a solvent shift is *not* a general rule. The maxima observed for the conjugate acids of benzaldehyde, acetophenone, and nitrobenzene in concentrated H_2SO_4 occur at shorter wavelengths compared to the corresponding maxima in the gas-phase spectra. Similarly, the maxima for phenoxide and thiophenoxide occur at shorter wavelength in solution than in the gas phase.

Discussion

Excited-State Base Strengths. The results from both the excited-state proton and Li^+ affinities are straightforward and suggest that the $W_0 \rightarrow W_1$ and $W_0 \rightarrow W_2$ transitions in benzaldehyde, acetophenone, nitrosobenzene, nitrobenzene, and *p*-methoxybenzaldehyde have large contributions due to internal charge transfer, as evidenced by large changes in base strength. The results for the same transitions in aniline and cyanobenzene, however, suggest no charge redistribution, which affects the Li^+ binding energy, and possibly minor rearrangement, which has a small effect on the proton binding energies.

The dominant attractive interactions between a positive ion and a neutral molecule are the ion-polarization and ion-dipole terms. Changes in polarizability and dipole moment which accompany electronic excitation will thus be reflected in changes in the ion binding energy and hence the inferred

Table III. Spectroscopic and Thermochemical Data Relating Li^+ Binding Energies of Excited Electronic States of Selected Bases

	Neutral		Complex		
Compd	λ_{max}[a]	Rel[b] intensity	λ_{max}[a]	Rel[b] intensity	$\Delta D(B\text{-}Li^+)$[c]
Benzaldehyde	232	1.00	280	1.00	21
	275	0.11	310	0.12	12
Nitrobenzene	240	1.00	330	1.00	32
	280	0.12	370	0.19	25
Cyanobenzene	224	1.00	225	1.00	1
	274	0.07	270	0.07	−1
Aniline	230	1.00	235	1.00	3
	282	0.19	280	0.21	−1
Acetophenone	230	1.00	275	1.00	20
	275	0.05	310	0.12	12
Nitrosobenzene	265	1.00	325	1.00	20
	300	0.37	360	0.27	16
p-Methoxy-	260	1.00	320	1.00	21
benzaldehyde	290	0.50	335	0.45	13
Ferrocene[d]	194				
	202				
	211				
	234		225[e]		−5
	244		250[e]		3
	266		280[e]		5

[a] Wavelength, ±10 nm. [b] Band intensities relative to the more intense peak, which is assigned a value of 1.00. [c] $\Delta D(B\text{-}Li^+) = D(B^*\text{-}Li^+) - D(B\text{-}Li^+)$ in kilocalories per mole. [d] Taken from ref 58. [e] Poorly resolved bands.

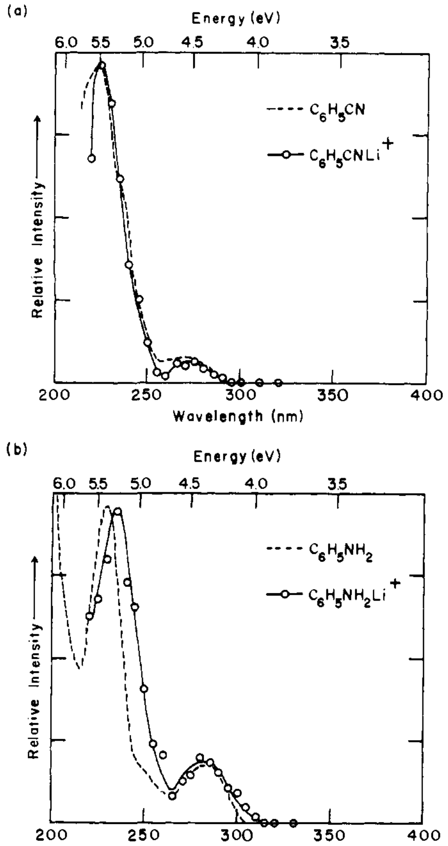


Figure 9. (a) Comparison of the gas-phase absorption spectrum of cyanobenzene with the photodissociation spectrum of the corresponding Li^+ complex. (b) Comparison of the gas-phase absorption spectrum of aniline with the photodissociation spectrum of the corresponding Li^+ complex.

acid-base properties of the excited state. The above findings are in qualitative agreement with the change in dipole moment measured for several of the transitions considered (Table VII).

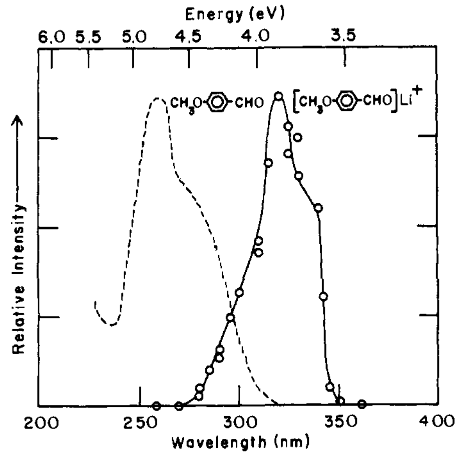


Figure 10. Comparison of the gas-phase absorption spectrum of *p*-methoxybenzaldehyde with the photodissociation spectrum of the corresponding Li^+ complex.

Changes of greater than 4 D were measured for nitrobenzene, benzaldehyde, and nitrosobenzene and less than 1 D for aniline and cyanobenzene.[10-12] Analysis of the solvent effects, as well as calculations on these systems leads to similar conclusions. The ICR method is thus useful to probe changes in excited-state dipole moments and has the advantage that, unlike direct determinations of excited-state moments,[11,12] the sign of change is evident.

No dissociation was observed for Li^+ complexes of benzene and fluorobenzene. Unlike the previous examples, it is likely that Li^+ is π bonded to the ring in these compounds. Although the effect of π-bonded Li^+ on the spectra could not be determined, it is possible that the lowest $\pi \rightarrow \pi^*$ transitions are blue shifted. This contrasts with the behavior observed with H^+, where the protonated benzene (benzenium ion) absorbs strongly and reflects the quite different bonding characteristics of H^+ and Li^+.

A complete understanding of the excited states of benzenium ion ($C_6H_7^+$) has not been achieved, as evidenced by the variety

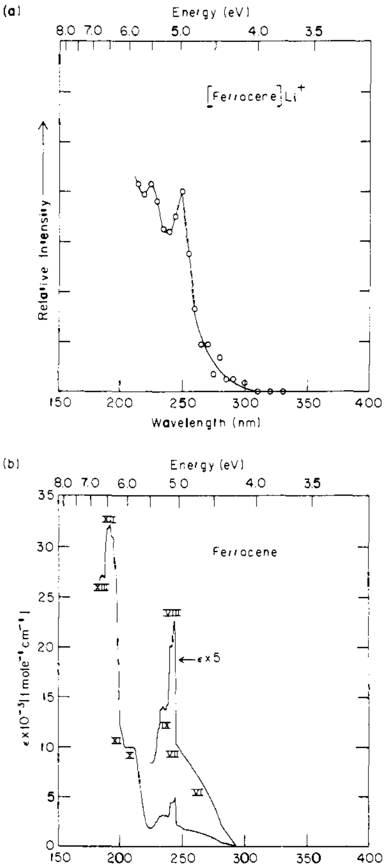


Figure 11. (a) Photodissociation spectrum of the Li^+ complex of ferrocene. (b) Absorption spectrum of ferrocene vapor at 35 °C (taken from ref 58). The Roman numerals were used by the authors of the previous work and are used here to facilitate comparison.

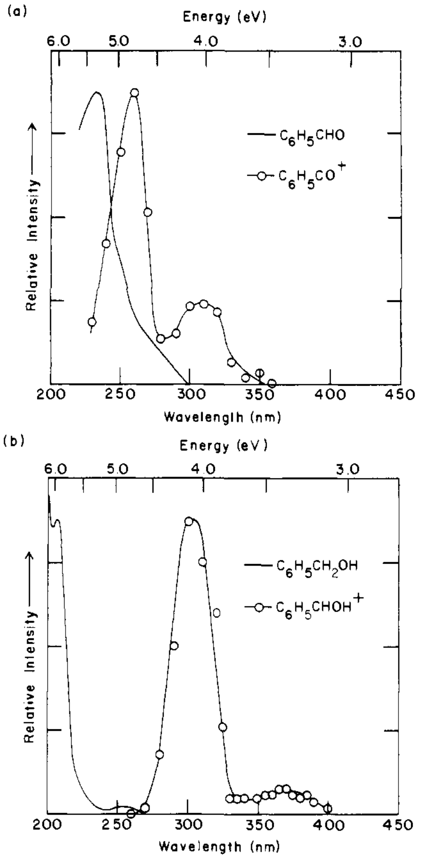
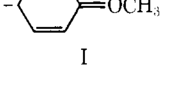


Figure 12. (a) Comparison of the photodissociation spectrum of benzoyl cation with the gas-phase absorption spectrum of its conjugate base, benzaldehyde. (b) Comparison of the photodissociation spectrum of protonated benzaldehyde with the gas-phase absorption spectrum of its conjugate base, benzyl alcohol.

of theoretical models proposed in the literature.[61-63] For this reason the large change in proton affinity estimated for the excited states in benzene as well as the following interpretations are also speculative. The ΔPA observed for benzene, mesitylene, and anisole are all comparable (Table I), indicating that the effect which the substituents CH_3O and CH_3 have on benzene is the same in its ground and excited states. This is somewhat contrary to studies indicating an increased quinoid like structure I in the excited state of anisole,[11] for example,



I

yet substantiates other evidence that the excitation is associated with at most a small contribution of electron density from CH_3O to the ring.[10b]

The spectroscopy of phenol and phenolate have been studied extensively in solution.[10b] For phenol, measurements of the change in dipole moment[11] as well as calculations[10b] indicate only a small internal charge-transfer component (substituent to ring) if any is involved in the first two singlet transitions of this molecule. The calculations predict an increase in the charge-transfer components upon ionization of phenol to phenolate, which is in qualitative agreement with the decrease in proton affinity noted for phenolate in its excited states (Table II). This arises since ionization of phenol to form phenolate results in a marked energy decrease of both the first two singlet $\pi \rightarrow \pi^*$ transitions. Similar results are obtained for thiophenolate.

Photodissociation of the Li^+ complex of *p*-methoxybenzaldehyde is illustrative of an application of these studies as a probe to determine binding sites in polyfunctional molecules. For a disubstituted benzene, attachment of Li^+ may initially occur at either site. If one site is considerably more basic than the other, ion molecule reactions will shortly produce all of the complexes having Li^+ bound at that site. If, however, the sites are comparable in basicity, ion molecule reactions will produce an equilibrium mixture of complexes bound at either site. The presence of one or both structural isomers can be detected by their unique excitation spectrum. The Li^+ complex of *p*-methoxybenzaldehyde was studied as an example. The two lowest singlet $\pi \rightarrow \pi^*$ excitations in this compound are expected to result in a net increase of negative charge on the aldehyde substituent (as observed for benzaldehyde). This would result in a shift to higher or lower energies of the transitions present in the neutral depending on whether Li^+ is bound to the CH_3O or CHO groups, respectively. Figure 10 shows that the spectrum of the Li^+ complex of *p*-methoxybenzaldehyde is shifted to lower energies than the isolated neutral. No absorptions to higher energies are noted. This result indicates that CHO is substantially more basic than CH_3O with respect to Li^+ as the reference acid. Although $D(\text{B-Li}^+)$ has not been measured directly for anisole or benzaldehyde, this result is in accord with the reported ordering of $D(\text{B-Li}^+)$ being higher for CH_3CHO than CH_3OCH_3.[27] Furthermore, while the methoxy shows its effects on the spectrum of benzaldehyde (both λ_{max} of *p*-methoxybenzaldehyde are at longer wavelengths than benzaldehyde, Table III), it does not enhance the change in Li^+ affinity $\Delta D(\text{B-Li}^+)$ compared to benzaldehyde (Table III). It is concluded that internal charge transfer from CH_3O to the ring is not an important component in the $\pi \rightarrow \pi^*$ transitions. These results are in accord with the relatively small changes in dipole moment observed for phenol and O-

Table IV. Spectroscopic and Thermochemical Data Comparing Li^+ Monomer and Dimer Complexes

	BLi^+		Li^+		
Compd	λ_{max}[a]	Rel[b] intensity	λ_{max}[a]	Rel[b] intensity	$\Delta D(BLi^+{-}B)$[c]
Acetophenone	275	1.00	262	1.00	−5
	310	0.12	295	0.22	−5
Nitrosobenzene	325	1.00	324	1.00	0
	360	0.27	368	0.21	2

[a] Wavelength, ±10 nm. [b] Band intensities relative to the more intense peak, which is assigned a value of 1.00. [c] $\Delta D(BLi^+{-}B) = D(BLi^{+*}{-}B) - D(BLi^+{-}B)$ in kilocalories per mole.

Table V. Spectroscopic and Thermochemical Data Related to Excited-State Acidities of Selected Ions

		R^+		RH			
R^+	$D(R^+{-}H^-)$[a]	λ_{max}[b]	Rel[c] intensity	λ_{max}[b]	Rel[c] intensity	$D(R^{+*}{-}H^-)$[a]	$\Delta D(R^+{-}H^-)$[a]
$C_6H_5CO^+$	234	260	1.00	232	1.00	221	−13
	234	310	0.27	275	0.11	222	−12
$C_6H_5CHOH^+$	215	303	1.00	208[d]	1.00	172	−43
	215	368	0.09	258[d]	0.04	182	−33

[a] $D(R^+{-}H^-)$ and $D(R^{+*}{-}H^-)$, ±5 kcal/mol. $\Delta D(R^+{-}H^-) = D(R^{+*}{-}H^-) - D(A^+{-}H^-)$; values for $D(R^+{-}H^-)$ estimated from data summarized in NSRDS-NBS 26, U.S. Government Printing Office, Washington, D.C., 1969. [b] Wavelength, ±10 nm for cation spectra. [c] Band intensities relative to the more intense peak which is assigned a value of 1.00. [d] P. P. Shorygin, V. A. Petukhov, A. Kh. Khomenko, and E. A. Chernyshev, *Russ. J. Phys. Chem.*, **42,** 555 (1968).

Table VI. Comparison of the Gas-Phase Photoexcitation Spectra to the Solution Absorption Spectra

	Gas phase,	Solution			
Species	λ_{max}[a]	Solvent	λ_{max}[a]	Ref	$\Delta H_s(A^*) - \Delta H_s(A)$[b]
$C_6H_5CO^+$	260	H_2SO_4	260	*c*	0
	310		310	*c*	0
$C_9H_{13}^+$	250	HF, BF_3	250	*d*	0
	355		355	*d*	0
$C_6H_7^+$	245	HF, BF_3	*e*		
	330		330	*f*	0
$C_6H_5CHOH^+$	303	H_2SO_4	293	*g*	3
	368		323	*g*	11
$[C_6H_5COCH_3]H^+$	305	H_2SO_4	295	*g*	3
	355		322	*g*	8
$C_6H_5NO_2H^+$	357	H_2SO_4	*e*		
	~400		350	*h*	10
$C_5H_5NH^+$	250	HCl, C_2H_5OH	250	*i*	0
$C_6H_5O^-$	*e*	KOH, H_2O, CH_3OH	235	*j*	
	332		287	*j*	14
$C_6H_5S^-$	*e*	KOH, H_2O	263	*k*	
	332		302	*k*	9

[a] Wavelength, ±10 nm for gas-phase spectra. [b] $\Delta H_s(A^*) - \Delta H_s(A)$ in kilocalories per mole corresponds to the change in solvation energy of the ion between its excited and ground states. [c] G. A. Olah, C. U. Pittman Jr., R. Waack, and M. Doran, *J. Am. Chem. Soc.*, **88,** 1488 (1966). [d] Reference 61. [e] Band not observed. [f] V. H. Luther and G. Pockels, *Z. Electrochem.*, **59,** 159 (1955). [g] W. L. Paul, P. J. Kovi, and S. G. Schulman, *Spectrosc. Lett.*, **6,** 1 (1973). [h] S. G. Schulman, L. B. Sanders, and J. D. Winefordner, *Photochem. Photobiol.*, **13,** 381 (1971). [i] M. L. Swain, A. Eisner, C. F. Woodward, and B. A. Brice, *J. Am. Chem. Soc.*, **71,** 1341 (1949). [j] Reference 47. [k] J. S. Kwiatkowski, M. Berndt, and J. Fabian, *Acta Phys. Pol. A*, **38,** 365 (1970).

alkylated derivatives in their excited states.[10,11]

Not allowing for geometry changes, the symmetry of ferrocene dictates that its dipole moment in any of its states must be zero. hence there is no change in dipole moment upon excitation. The lack of substantial shifts noted for the excitation spectrum of the Li^+ complex, despite the fact that charge-transfer transitions are associated with large changes in polarizability, is a graphic illustration that a change in dipole moment rather than polarizability is the important factor. Large shifts are predicted to occur for nonsymmetric inorganic complexes, and can be used to detail the charge-transfer transitions in such compounds.

The photodissociation of Li^+ bound dimers yields information about changes in the absorption spectrum of an acid-base complex when an additional base is added. This information provides insight into the difference between purely gas-phase spectra and spectra obtained in solution. The effect of the second base is to weaken the interaction of Li^+ with the

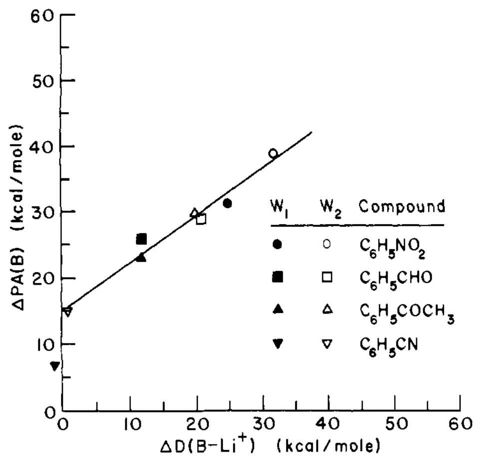


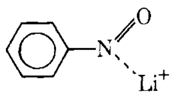
Figure 13. Comparison of the change in basicity upon excitation measured using H$^+$ as the reference acid to that measured using Li$^+$ as the reference acid.

Table VII. Changes in Dipole Moment on Electronic Excitation ($\pi \rightarrow \pi^*$) in Several Substituted Benzenes

Compd	State	$\lvert\Delta\mu\rvert$[a]	Ref
Nitrobenzene	W$_1$	4.8	*b*
	W$_1$	3.9	*c*
	W$_2$	4.0	*b*
	W$_2$	7.6	*c*
Benzaldehyde	W$_1$	4.3	*b*
	W$_2$	3.5	*b*
Nitrosobenzene	W$_1$	9.1	*b*
Cyanobenzene	W$_1$	0.31	*d*
Aniline	W$_1$	0.85	*e*
Phenol	W$_1$	0.20	*e*
p-Fluorophenol	W$_1$	0.44	*e*
Fluorobenzene	W$_1$	0.3	*f*

[a] $\lvert\Delta\mu\rvert$ in debye is the absolute change in dipole moment. [b] Reference 10a. [c] Reference 10b. [d] Reference 12. [e] Reference 11. [f] Reference 13.

original base. Thus the shift in the spectra of the dimer complex is not expected to be as great as in the monomer complex relative to the isolated neutral. This is observed for the acetophenone system (Figure 8a). Even smaller shifts are expected for fully complexed Li$^+$ in solution.[64] The dimer and monomer complexes of nitrosobenzene, however, have the same absorption maxima (Figure 8b). This can be rationalized as follows. In comparing the changes of dipole moment in Table VII to the changes in ΔD(B-Li$^+$) in Table III, the largest change of dipole moment, 9.1 D for nitrosobenzene, is not manifest in the shifts observed with Li$^+$. Assuming that the dipole measurement is not in error, this suggests that Li$^+$ is bonded to nitrogen and not oxygen (species II), and experiences only a small component of the change in the dipole moment vector. The fact that the photoexcitation spectra of the dimer and monomer complex have the same maxima could then (accidentally) result from Li$^+$ bonding to oxygen in the dimer (species III). In this configuration, Li$^+$ experiences a larger change in dipole moment than in structure II (which would shift the spectra to longer wavelengths), but the second base weakens the interaction and counteracts the shift. The net effect is that the monomer and dimer spectra have the same maxima.



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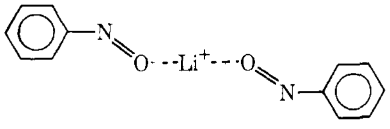

III

Excited-State Acid Strengths. From a comparison of benzoyl cation and protonated benzaldehyde to their respective conjugate bases (Figure 12 and summarized in Table V), it is observed that in both cases D(R$^+$-H$^-$) decreases in the excited state. Not surprisingly, this indicates that the $\pi \rightarrow \pi^*$ transitions in these cations involve transfer of electron density from the ring to the substituent. This is in complete accord with charge distribution calculations performed on benzoyl cation.[8]

Solvent Effects. Solvent effects (shifts) in absorption spectra arise mainly from two effects. First, the solvent configuration surrounding a specie in its ground state may not be the lowest energy configuration when the specie is in its excited state and, secondly, because the solvation energy for the species in the two states may differ.

The absence of any solvent shift for benzoyl cation, $C_6H_7^+$ and $C_9H_{13}^+$ in highly acidic media has already been noted with surprise.[36] The new examples listed in Table VI do, however, indicate that this will not always be the rule and suggest a plausible explanation for the lack of shift in the former examples. The spectra of $C_6H_5CHOH^+$, $[C_6H_5COCH_3]H^+$, and $C_6H_5NO_2H^+$ in H_2SO_4 are all shifted to higher energies relative to their gas-phase spectra. These ions all have acidic protons which upon going from the gas phase to solution become less acidic due to the increased interaction of the solvent. This effect is identical with that described for BLi$^+$ compared to B$_2$Li$^+$. The ions for which no shifts are observed *do not* possess acidic protons.

Comparison of ΔPA(B), Δ*D*(B-Li$^+$), and Changes in Dipole Moment. Figure 13 compares the change in basicity upon excitation determined using H$^+$ and Li$^+$ as reference acids. The data (although limited) follow the linear relationship

$$\Delta PA(B) = 0.76\Delta D(B\text{-}Li^+) + 15 \qquad (23)$$

where the thermodynamic quantities are in kilocalories per mole. There are two points of interest: (1) in Figure 13, ΔPA(B) is always greater than ΔD(B-Li$^+$); (2) the proton affinities of these compounds are all near 200 kcal/mol, while the D(B-Li$^+$) probably center near 50 kcal/mol. Except for cyanobenzene, ΔD(B-Li$^+$)/D(B-Li$^+$) is greater than ΔPA(B)/PA(B), indicating that while covalent bonding of H$^+$ enhances PA relative to D(B-Li$^+$), it does not play an important role in determining ΔPA(B). Thus, changes in basicity arise primarily from electrostatic interactions.

In comparing the changes of dipole moment in Table VII to the changes in PA (Table I) or changes in ΔD(B-Li$^+$) (Table III) a number of interesting points surface. As mentioned above, substantial changes in ΔD(B-Li$^+$) and ΔPA(B) are noted in these species whose change in dipole moment is >4 D, and little or no change in those species where the change in dipole moment is <1 D. Several inconsistencies are noted. For nitrobenzene and benzaldehyde the change in dipole moment for W$_1$ is greater than for W$_2$, which is the opposite expected from their spectral shifts. This could indicate either an enhanced role of polarization in the W$_2$ states of these molecules or an error in the dipole change determination. Also, as noted earlier, the largest change in dipole moment (Table VII) of 9.1 D for nitrosobenzene is not manifest in the spectral shifts observed with Li$^+$. This apparent inconsistency was explained above by invoking a nitrogen-bonded Li$^+$ complex.

Conclusions

A general method for obtaining information about excited-state acid-base properties has been described and applied to a number of interesting systems and problems. Since most previous studies have been confined to solution, the ICR technique brings a new dimension to the type of information which can be obtained. The spectra of ions in the gas phase allow an intrinsic measure of excited-state properties and frequently permits an evaluation of solvation effects. Using Li$^+$ and H$^+$ as "shift reagents" allows the study of changes in dipole moment and charge density with greater specificity and sensitivity than solvent shift studies. In contrast to direct determination of excited-state dipole moments, the present methodology yields in favorable instances the sign of the change in dipole moment.

Spectra of Li$^+$ bound dimers allow comparison to the lowest excitation in the monomer complexes. Information about internal solvation and structure in highly solvated complexes can be obtained.

While the present work has focused on monomer complexes, the data obtained with Li$^+$ bound dimers suggests many exciting extensions of the present work to more highly solvated acid-base complexes.

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