large confidence limits for the four parameter fit indicate that a greater density of more accurate data over a larger range of pulse separations is required to determine even four parameters precisely from relaxation experiments such as these.

Using a computer program written to follow the treatment of proton cross-correlations for this geometry,[3] we calculate to first approximation (isotropic overall tumbling) that the intramolecular reorientation rate of the methyl group is large compared to that for overall tumbling. In this case theory indeed predicts a biexponential curve with preexponential terms $A_1 = 0.833$ and $A_2 = 0.167$ with $\lambda_2^{-1} \gg \lambda_1^{-1}$.[13] The initial slope ($\lambda_{\text{init}}^{-1} = 0.873$ sec) gives the relaxation time in the absence of cross-correlation. Exact comparison with theory, however, awaits a full treatment of the effect of a spin-rotation relaxation mechanism in the presence of dipole cross-correlations. It is clear that experiments on ^{13}C relaxation of the methyl carbon should confirm the interpretation of the data presented above. We have shown this to be true and it will be discussed as part of a more complete study of ^1H and ^{13}C relaxation in tetragastrin presented in a forthcoming publication.

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Gas Phase Proton Affinities of Molecules in Excited Electronic States by Ion Cyclotron Resonance Spectroscopy

Sir:

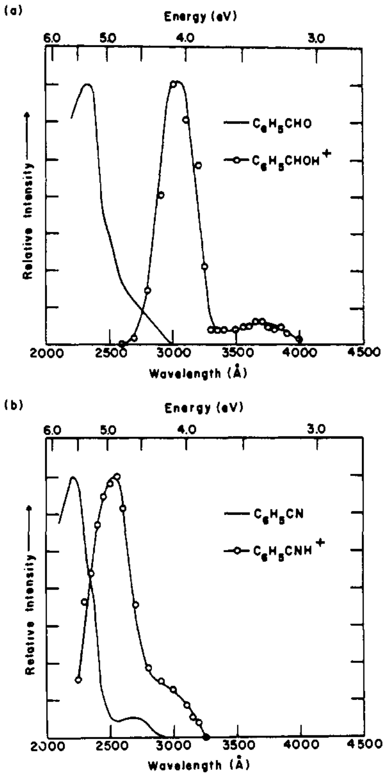
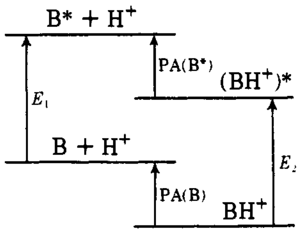


Figure 1. (a) Comparison of the gas phase absorption spectrum of benzaldehyde with the photodissociation spectrum of its conjugate acid. (b) Comparison of the gas phase absorption spectrum of cyanobenzene with the photodissociation spectrum of its conjugate acid. The absorption spectra of the neutrals were recorded at low resolution to facilitate comparison.

Scheme I



We wish to 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 (ICR).[1] The factors important in determining acid-base properties of molecules in the gas phase have been elucidated in the past several years. In the absence of complications due to solvation, the energetics of protonation can be directly related to electron distributions in neutral molecules and their conjugate acids and bases. Changes in electron distribution which accompany electronic excitation can be probed by determining the energetics of protonation in the excited state. The determination of proton affinities of molecules in excited electronic states follows directly from the thermochemical cycle (Scheme I).[2,3] In accordance with eq 1,

$$\mathrm{PA(B^*)} = \mathrm{PA(B)} + (E_1 - E_2) \qquad (1)$$

PA(B*) can be calculated if the proton affinity of B in its ground state, PA(B), and the excitation energies of the base, E_1, and its conjugate acid, E_2, are known.

ICR techniques have been developed for examining photodissociation of ions in the gas phase,[4-6] the phenomenon being generalized in eq 2.

$$A^+ + h\nu \rightarrow B^+ + C \qquad (2)$$

These experiments yield the product of the extinction coefficient and the quantum yield for dissociation as a function of wavelength (relative photodissociation probability.) A comparison of the absorption spectrum of a molecule with the relative photodissociation probability of its conjugate acid reveals in many instances quite similar spectra, which may be analyzed to determine E_1, E_2, and hence PA(B*).

Table I. Spectroscopic and Thermochemical Data Related to Proton Affinities of Electronically Excited States of Benzaldehyde, Cyanobenzene, and Pyridine

Base	$PA(B)^a$	Neutral $\lambda_{max}{}^b$	Neutral ϵ^c	Conjugate acid $\lambda_{max}{}^b$	Conjugate acid $\epsilon\phi^d$	$PA(B^*)^a$	ΔPA^a
Benzaldehyde	195	232	14 000	303	23 000	224	29
		275^e	1 000	368	2 000	221	26
Cyanobenzene	195	224	23 000	254	10 000	210	15
		274	650	293^e	2 000	202	7
Pyridine	219	250	2 000	250	4 000	219	0
		~275	*f*	*g*	*g*	<219	<0

[a] PA(B) and PA(B*) in kcal/mol. $\Delta PA = PA(B^*) - PA(B)$; values for PA(B) are relative to $PA(NH_3) = 202 \pm 1$ 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] Extinction coefficient in l. mol^{-1} cm^{-1}. Benzaldehyde and cyanobenzene values are from K. Kimura and S. Nagakura, *Theor. Chim. Acta,* 3, 164 (1965). [d] Product of extinction coefficient ϵ and quantum yield for dissociation ϕ in l. mol^{-1} cm^{-1}. Reported values are relative to a value of 16900 for benzoyl cation (see ref 4 for discussion). [e] 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. [f] Unresolved band. [g] Band not observed.

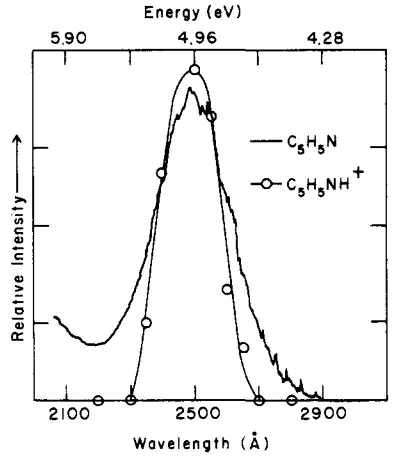


Figure 2. Comparison of the gas phase absorption spectrum of pyridine with the photodissociation spectrum of its conjugate acid.

We wish to report results for benzaldehyde, cyanobenzene, and pyridine.[7]

The gas phase spectra of these compounds and their conjugate acids between 2000 and 4000 Å are displayed in Figures 1 and 2 and summarized in Table I.[8] The spectra of the cations were obtained by monitoring reactions 3-5 as a function of wavelength at 100 Å resolution.

$$C_6H_5CHOH^+ + h\nu \rightarrow C_6H_7^+ + CO \quad (3)$$

$$C_6H_5CNH^+ + h\nu \rightarrow C_6H_5^+ + HCN \quad (4)$$

$$C_5H_5NH^+ + h\nu \rightarrow C_5H_4N^+ + H_2 \quad (5)$$

The uv spectra of substituted benzenes are largely uniform and greatly resemble those of the parent compound. Thus in monosubstituted benzenes the two lowest singlet $\pi \rightarrow \pi^*$ bands have been interpreted to correspond to the benzene 203.5-nm primary band and to the 256-nm secondary band, shifted in a regular way such that the ratios for the secondary to primary bands are $\lambda_{sec}/\lambda_{prim} \simeq 1.2$.[9] With electron accepting groups such as NO_2, CO_2H, CN, and CHO, these transitions may also have large contributions due to internal charge transfer from the ring to the substituent.[10] For simplicity we use W_0 to denote the ground state, and W_1 and W_2 to indicate the first and second strongly allowed states observed for benzaldehyde, cyanobenzene, and their conjugate acids in Figure 1.

Since proton affinities are thermodynamic quantities, E_1 and E_2 in eq 1 should correspond to adiabatic transition energies. However, due to the similarity in the band shapes in the spectra of the neutral molecules and their conjugate acids, vertical energies are used without introducing large errors.

The most pronounced effect of excitation on base strength is observed for the W_2 state of benzaldehyde, estimated to be 29 kcal/mol more basic than the ground state. This would correspond to an increase of about 21 p*K* units! Similar but smaller increases in proton affinity are calculated for the excited states of cyanobenzene and the W_1 state of benzaldehyde (Table I). These results are in qualitative agreement with studies indicating that these transitions have contributions due to internal charge transfer.[10]

The gas phase spectrum of pyridine comprises a $\pi \rightarrow \pi^*$ transition with $\lambda_{max} \simeq 250$ nm and a weaker $n \rightarrow \pi^*$ transition appearing as a shoulder at longer wavelengths.[11] Figure 2 compares the gas phase spectrum of pyridine with the photodissociation spectrum of the protonated species obtained by monitoring reaction 5. The long wavelength tail ascribed to the $n \rightarrow \pi^*$ transition is not observed in the protonated species, shifted to higher energies because of the involvement of the lone pair in the bond to hydrogen. The $\pi \rightarrow \pi^*$ transition, however, shows no shift, indicating no change in base strength in the excited state.

In summary ICR offers an elegant method for obtaining information about excited state acid-base properties from cation absorption data. Further work is in progress.

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