14.36). Support for this also comes from the x-ray structural analysis of $Mn(CO)_5^-$ where the equatorial Mn–C bond lengths are slightly shorter (0.02 Å) than the corresponding axial bond lengths.[26]

(26) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **11,** 1109 (1972).

(27) A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, **14,** 365 (1975).

(28) The force field computed which fits this assignment is $k_1 = 15.20$, $k_2 = 14.55$, $k_3 = 13.71$, $k_{c'} = k_{c''} = 0.35_3$, $k_c = k_{cc} = 0.32_6$, and $k_t = 0.59_4$.

(29) This is contrary to the assignment involving an axial interaction where the intensity pattern observed is in very poor agreement with that computed. This is particularly noticeable when one examines the diethyl ether spectrum which is predominantly the contact ion species.

(30) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67,** 1722 (1963); T. L. Fabry and R. M. Fuoss, *ibid.*, **68,** 907 (1964).

(31) E. C. Ashby, F. R. Dobbs, and H. P. Hopkins, Jr., *J. Am. Chem. Soc.*, **97,** 3158 (1975).

(32) C. J. Pedersen, *J. Am. Chem. Soc.*, **89,** 7017 (1967); *ibid.*, **92,** 386 (1970); *ibid.*, **92,** 391 (1970).

(33) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74,** 351 (1974); H. K. Frensdorff, *J. Am. Chem. Soc.*, **93,** 600 (1971).

(34) "Solvolytic Displacement Reactions", A. Streitwieser, Jr., McGraw-Hill, New York, N.Y., 1962.

(35) N. Ivanoff and M. Magat, *J. Chim. Phys. Phys.-Chim. Biol.*, **47,** 914 (1950); E. Bauer and M. Magat, *ibid.*, **47,** 922 (1950).

Photochemistry of Organic Ions in the Gas Phase. Comparison of the Gas Phase Photodissociation and Solution Absorption Spectra of Benzoyl Cation, Protonated Benzene, and Protonated Mesitylene

B. S. Freiser and J. L. Beauchamp*[1]

Contribution No. 5148 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.

Received July 31, 1975

Abstract: The gas phase photodissociation spectra of benzoyl cation, protonated benzene, and protonated mesitylene are reported and compared to their solution absorption spectra. Each ion exhibits two maxima in the wavelength region 2000–4000 Å. The values of λ_{max} for the benzoyl cation ($C_6H_5CO^+ + h\nu \rightarrow C_6H_5^+ + CO$) are 260 ± 10 nm ($\sigma \simeq 0.15$ Å^2) and 310 ± 10 nm ($\sigma \simeq 0.04$ Å^2), for protonated benzene ($C_6H_7^+ + h\nu \rightarrow C_6H_5^+ + H_2$) 245 ± 10 nm ($\sigma \simeq 0.02$ Å) and 330 ± 10 nm ($\sigma \simeq 0.08$ Å^2), and for protonated mesitylene ($C_9H_{13}^+ + h\nu \rightarrow$ products) 250 ± 10 nm ($\sigma \simeq 0.06$ Å^2) and 355 ± 10 nm ($\sigma \simeq 0.10$ Å^2). With the exception of protonated benzene, excellent agreement between the solution absorption spectra and gas phase photodissociation spectra is observed. The lack of agreement for protonated benzene is attributed to other absorbing species present in solution. From a comparison of the gas phase and solution spectra, it can be inferred that the quantum yields for photodissociation do not vary significantly with wavelength and are thus very likely close to unity. In addition, there is no detectable solvent shift for any of the observed transitions.

Solvent shift is an effective spectroscopic tool both for determining the character of absorption bands in organic molecules and for yielding insight into the intermolecular forces between solute and solvent.[2] In general solvent shifts serve as a sensitive probe of the change in charge distribution which accompanies electronic excitation. It is possible, for example, to distinguish $n \rightarrow \pi^*$ transitions from $\pi \rightarrow \pi^*$ transitions in azo compounds, aldehydes, ketones, and thioketones by using solvents having a range of dielectric constants.[3] The highly specific solvent shifts observed in the presence of hydroxylic solvents are useful to identify transitions involving an n-donor site and can be interpreted to yield hydrogen bond strengths.[4] In the extreme cases where the solvent effects a change in the chemical species present, solvent shift enables the study of acid–base equilibria, tautomeric equilibria, and complex formation.[5]

Numerous examples of electronic absorption spectra of carbocations in solution are available in the literature.[6] These experiments are usually performed in superacid media having extremely low nucleophilicity where the ions are stable. In many instances it has been observed that the ions are so strongly solvated that the spectra are independent of the counterion present.[7]

Gas phase absorption spectra provide the standard by which absolute solvent shifts of carbocations can be determined. However, obtaining these spectra directly is rendered virtually impossible by the difficulties associated with producing and maintaining the required ion densities.[8] Ion cyclotron resonance spectroscopy (ICR)[9] provides the desired spectroscopic information from photodissociation spectra obtained by determining the wavelength dependence of processes such as generalized in eq 1.[10-12] Absorption maxima determined by

$$A^+ + h\nu \rightarrow B^+ + C \qquad (1)$$

this method should yield an intrinsic measure of the vertical transition energies of the ion since the photodissociation spectrum is free of all effects due to solvent, counterions, and any other neutral or ionic species which absorb in the region of interest. A meaningful comparison to the theoretical transition energies in addition to solvent shift data may therefore be obtained. Band intensities in photodissociation spectra depend, however, not only on the intrinsic transition probability or gas phase extinction coefficient, $\epsilon_g(\lambda)$, but also on the photodissociation quantum yield, $\varphi_d(\lambda)$. The measured quantity is the photodissociation cross section, $\sigma_d(\lambda)$, which is proportional to the product of these variables (eq. 2). If the quantum

$$\sigma_d(\lambda) \propto \epsilon_g(\lambda)\varphi_d(\lambda) \qquad (2)$$

yield for photodissociation is relatively constant over an absorption band (Figure 1, band I), then $\sigma_d(\lambda)$ will reflect the absorption spectrum and directly yield the vertical excitation energy. If, on the other hand, φ_d varies significantly over an absorption band (Figure 1, band II), then $\sigma_d(\lambda)$ will not yield exactly the vertical excitation energy. The latter would occur, for example, in the vicinity of the thermodynamic threshold for dissociation, below which $\varphi_d(\lambda) = 0$.

To explore these ideas and investigate solvent effects on excitation energies of carbocations we have undertaken a study of the photodissociation spectra of species for which solution spectra are already available. We wish to report results for

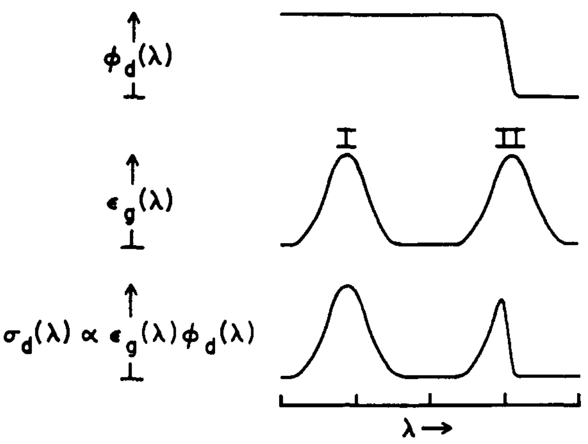


Figure 1. Comparison of expected photodissociation cross section $\sigma_d(\lambda)$ and absorption spectrum $\epsilon_g(\lambda)$ for cases where the photodissociation quantum yield $\varphi_d(\lambda)$ is constant (I) and varying (II) over the absorption band.

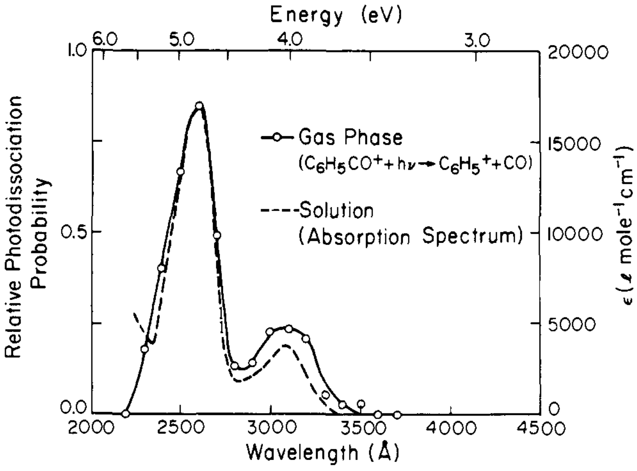


Figure 2. Comparison of the gas phase photodissociation spectrum of benzoyl cation to the uv absorption spectrum obtained in solution.

Table I. Heats of Formation of Ions Employed to Calculate Photodissociation Thresholds

Ion	ΔH_f[a]	Footnote
$C_6H_5^+$	270 ± 3	*b*
$C_6H_7^+$	204 ± 2	*c*
$C_6H_5CO^+$	190 ± 5	*d*
$C_9H_{13}^+$	165 ± 3	*c*
$C_9H_{11}^+$	238 ± 10	*e*
$C_9H_9^+$	*f*	
$C_8H_9^+$	242 ± 10	*g*

[a] All data in kcal/mol at 298 K. [b] J. L. Beauchamp, *Adv. Mass Spectrom*, **8,** 717 (1974). [c] Calculated from PA(C_6H_6) = 182 kcal/mol and PA(mesitylene) = 197 kcal/mol: J. F. Wolf, I. Koppel, R. W. Taft, R. H. Staley, and J. L. Beauchamp, unpublished results. [d] Estimated from data summarized in *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969). [e] Estimated assuming a trimethyl phenyl cation structure. The value would be significantly lower for a dimethyl benzyl cation. [f] Structure uncertain. [g] Estimated assuming a dimethyl phenyl cation structure.

benzoyl cation, protonated benzene, and protonated mesitylene.

Experimental Section

The ICR instrumentation and experimental techniques for studying photochemical processes involving ions in the gas phase have been previously described in detail.[9,10,11,13] The total pressure for these experiments was approximately 1×10^{-7} Torr and the 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 100 Å. The benzaldehyde, benzene, and mesitylene were obtained from Matheson, Coleman, and Bell and D_2O (99.8%) from Columbia Organic Chemical Co., Inc. All were used as supplied except for freeze–pump–thaw cycles to remove noncondensable gases. The HCN was prepared by reaction of concentrated H_2SO_4 with KCN. Mass spectrometry revealed no detectable impurities in the samples used.

For the ion species considered in this work, there was no evident variation of apparent photodissociation cross section with the pressure of the neutral precursor, either alone or in mixtures with other molecules. This rules out the possibility of photon induced bimolecular reactions contributing to the disappearance of the photolyzed species.[12a]

Results

Benzoyl Cation. The major ions present at 70 eV in benzaldehyde include $C_6H_5CHO^+$, $C_6H_5CO^+$, $C_6H_5^+$, and $C_4H_3^+$. At long trapping times $C_6H_5CO^+$ and $C_6H_5CHOH^+$ predominate, the former being generated by reaction 3 in addition to electron impact. Protonated benzaldehyde results primarily as indicated in reaction 4. These ions remain unreactive with the parent neutral at the pressures used.

$$C_6H_5^+ + C_6H_5CHO \rightarrow C_6H_5CO^+ + C_6H_6 \tag{3}$$

$$C_6H_5CHO^+ + C_6H_5CHO \rightarrow C_6H_5CHOH^+ + C_6H_5CO \tag{4}$$

Upon irradiation the benzoyl cation undergoes the photoreaction 5, giving the photodissociation spectrum shown in

$$C_6H_5CO^+ + h\nu \rightarrow C_6H_5^+ + CO \tag{5}$$

Figure 2, obtained while continuously ejecting $C_6H_5^+$ to prevent reaction 3. No interference was observed from the photochemistry of other species present;[14] benzoyl cation and its precursors are not the product of another photoreaction. The values of λ_{max} for benzoyl cation are 260 ± 10 nm ($\sigma \simeq 0.15$ Å^2)[15] and 310 ± 10 nm ($\sigma \simeq 0.04$ Å^2). The observed onset for reaction 5 at 350 ± 10 nm (3.5 eV) is well above the calculated thermodynamic threshold of 2.3 eV (Table I) and is clearly spectroscopically determined. From a comparison of the solution[7] and gas phase spectra in Figure 2, it is evident that (a) there is no solvent shift and (b) the quantum yield for dissociation, $\varphi_d(\lambda)$, is relatively constant over the wavelength region considered. The latter conclusion is based on the assumption that the extinction coefficients in the gas phase and in solution do not differ significantly.

Protonated Benzene. Protonated benzene was formed in a 2:1 mixture of HCN and C_6H_6. At 70 eV both HCN^+ and H_2CN^+ reacted rapidly to form $C_6H_7^+$. Other ions produced by reactions in benzene itself[16] did not interfere. The photodissociation spectrum for the only observed process 6 is shown

$$C_6H_7^+ + h\nu \rightarrow C_6H_5^+ + H_2 \tag{6}$$

in Figure 3a. The values of λ_{max} for protonated benzene are 245 ± 10 nm ($\sigma \simeq 0.02$ Å^2) and 330 ± 10 nm ($\sigma \simeq 0.08$ Å^2). The onset at 380 ± 10 nm (3.3 eV) is near the expected thermodynamic threshold of 2.9 eV (Table I). Although the solution spectrum[17] (Figure 3b) also exhibits a peak at λ_{max} 330 nm, it differs significantly from the photodissociation spectrum at longer and shorter wavelengths. These differences are attributed to absorbing species other than protonated benzene in solution (see Discussion).

Protonated Mesitylene. The major ions present at 70 eV in mesitylene include $C_8H_9^+(P - CH_3)$, $C_9H_{12}^+(P)$, $C_6H_7^+$, $C_6H_5^+$, $C_7H_7^+$, and $C_8H_7^+$. The fragment ions react with

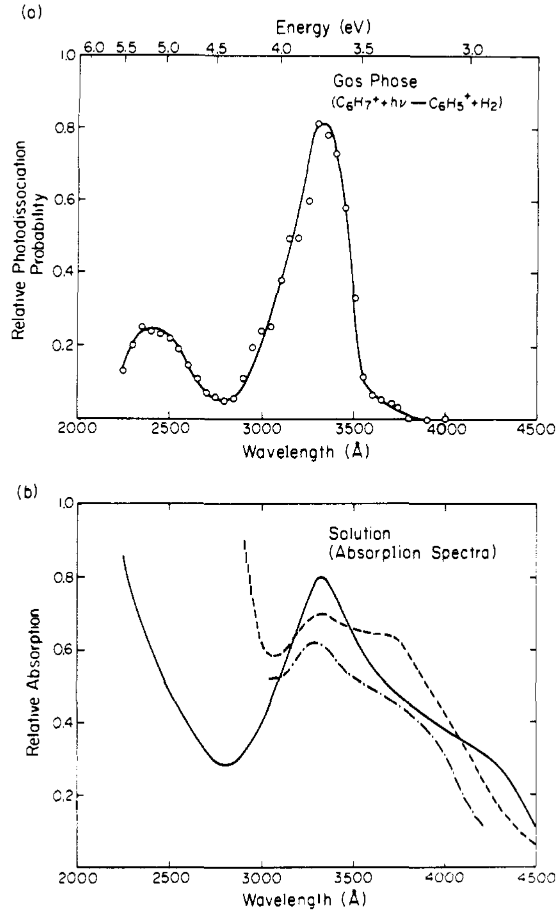


Figure 3. (a) Gas phase photodissociation spectrum of protonated benzene. (b) Solution absorption spectra obtained by several workers given in ref 17.

$$C_8H_9^+ + C_9H_{12} \longrightarrow C_9H_{11}^+ + C_8H_{10} \qquad (7)$$

$$\phantom{C_8H_9^+ + C_9H_{12}} \longrightarrow C_{17}H_{21}^+ \qquad (8)$$

$$C_6H_7^+ + C_9H_{12} \longrightarrow C_9H_{13}^+ + C_6H_6 \qquad (9)$$

$$C_6H_5^+ + C_9H_{12} \longrightarrow C_{10}H_{13}^+ + C_5H_4 \qquad (10)$$

$$\phantom{C_6H_5^+ + C_9H_{12}} \longrightarrow C_{14}H_{14}^+ + CH_3 \qquad (11)$$

$$C_7H_7^+ + C_9H_{12} \longrightarrow C_9H_{11}^+ + C_7H_8 \qquad (12)$$

$$C_8H_7^+ + C_9H_{12} \longrightarrow C_{11}H_{13}^+ + C_6H_6 \qquad (13)$$

mesitylene as shown in reactions 7–13. The species $C_9H_{11}^+$ further condenses by reactions 14 and 15. The parent ion re-

$$C_9H_{11}^+ + C_9H_{12} \longrightarrow C_{10}H_{13}^+ + C_8H_{10} \qquad (14)$$

$$\phantom{C_9H_{11}^+ + C_9H_{12}} \longrightarrow C_{18}H_{23}^+ \qquad (15)$$

mains unreactive with the parent neutral. To minimize any possible interferences from the photochemistry of the ions produced by these reactions, protonated mesitylene was prepared in a large excess of HCN. In particular, no significant contribution to $C_9H_{13}^+$ results from reaction 9. This avoids complications due to concomitant photodissociation of $C_6H_7^+$. In addition, the photodissociation spectrum of deuterated mesitylene formed in a mixture with D_2O yielded identical results.

Addition of alkyl groups on protonated benzene is not expected to change the spectrum of the ion significantly.[18] This is observed in Figure 4 where both the photodissociation spectrum, obtained by monitoring the disappearance of $C_9H_{13}^+$ in reaction 16, and the solution spectrum of protonated

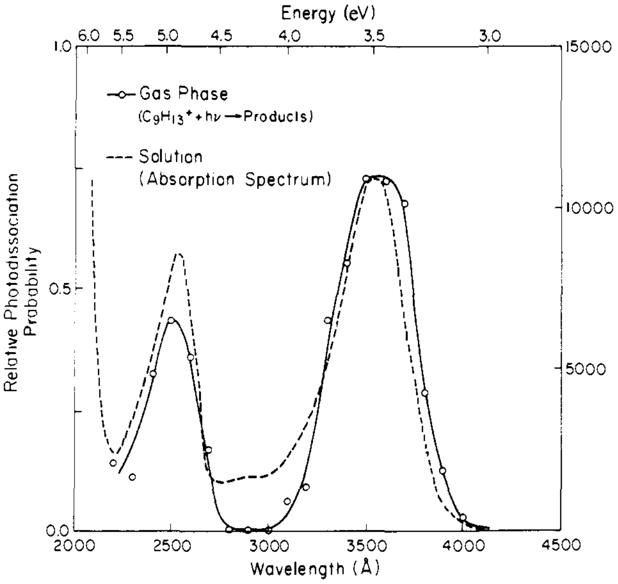


Figure 4. Comparison of the gas phase photodissociation spectrum of protonated mesitylene to the uv absorption spectrum obtained in solution.

$$C_9H_{13}^+ + h\nu \longrightarrow C_9H_{11}^+ + H_2 \qquad (16a)$$

$$\phantom{C_9H_{13}^+ + h\nu} \longrightarrow C_9H_9^+ + 2H_2 \qquad (16b)$$

$$\phantom{C_9H_{13}^+ + h\nu} \longrightarrow C_8H_9^+ + CH_4 \qquad (16c)$$

mesitylene are seen to be very similar in appearance to the photodissociation spectrum obtained for protonated benzene. The values of λ_{max} for protonated mesitylene are 250 ± 10 nm ($\sigma \simeq 0.06$ Å^2) and 355 ± 10 nm ($\sigma \simeq 0.10$ Å^2).

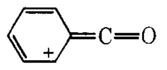
The solution and gas phase spectra are in excellent agreement except for the peak at low intensity in the solution spectrum at 290 nm. This feature was attributed by the authors to absorption of a neutral HF complex.[18] The relative intensities of the solution and gas phase spectra again indicate that the photodissociation quantum yield for reaction 16 is relatively constant over these energies.

Discussion

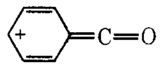
Benzoyl Cation. The observed transitions of the benzoyl cation can be assigned readily by a comparison to the characteristic uv bands in the spectra of benzene and its monosubstituted derivatives. Extensive studies on these compounds indicate that, despite the reduction of symmetry and perturbation of the electronic system by the substituent, the uv spectra of substituted benzenes are largely uniform and greatly resemble that of the parent compound.[19] Thus in monosubstituted benzenes, bands corresponding to the benzene 203.5 nm primary band ($^1A_{1g} \rightarrow {}^1B_{1u}$) and to the 256 nm secondary band ($^1A_{1g} \rightarrow {}^1B_{2u}$) are found. These bands are shifted in a regular way such that the ratios of λ_{max} for the secondary and primary bands are $\lambda_{sec}/\lambda_{prim} \simeq 1.24$. The solution and gas phase spectra of the benzoyl cation suggest that the transitions are those of the perturbed benzene with λ_{max} 260 nm and λ_{max} 310 nm corresponding to the benzene primary $^1A_{1g} \rightarrow {}^1B_{1u}$ transition (shifted to longer wavelength by 56 nm) and secondary $^1A_{1g} \rightarrow {}^1B_{2u}$ transition (shifted to longer wavelength by 54 nm), respectively. The ratio $\lambda_{sec}/\lambda_{prim} \simeq 1.2 \pm 0.1$ is in accord with the above. These transitions can be assigned $^1A_1 \rightarrow {}^1B_2$ and $^1A_1 \rightarrow {}^1B_1$ in the lower C_{2v} symmetry.

From the shift of the benzoyl $^1A_1 \rightarrow {}^1B_2$ transition relative to the primary band in benzene ($\Delta\lambda = 56$ nm) and using the correlations obtained by Doub and Vandenbelt,[19] one finds, not surprisingly, that $-CO^+$ is a powerful ortho-para director. A Hammett parameter $\Delta\sigma = \sigma_p - \sigma_m = -1.0$ is calculated, indicating a relatively large resonance effect of the substituent.

These findings are in accord with the downfield shifts of the para and ortho ^{13}C resonance observed by Olah et al. in the ^{13}C NMR spectrum of benzoyl cation,[20] and substantiates the importance of resonance structures A and B.



A



B

Protonated Benzene and Protonated Mesitylene. Extensive theoretical studies on the benzenium ion have to date yielded different results, depending on the model chosen. Calculations assuming strong hyperconjugation between the CH_2 group and the four π electrons of the ring predict that the two lowest singlet transitions would occur at 4000 Å ($^1A_1 \rightarrow {}^1B_2$) and 3200 Å ($^1A_1 \rightarrow {}^1A_1$) with the latter band being about twice as intense as the former.[21] These results *appeared* to be in good agreement with the solution spectra.[17,22]

An alternate approach by Stuart et al.[18] using the self consistent field formalism developed by Roothaan[23] and simplified by Pople[24] neglects hyperconjugation, assuming that the two π electrons withdrawn to form the methylene do not interact with the ring electrons. Including configuration interaction they predict that the two lowest lying transitions occur at 4000 and 2540 Å having oscillator strengths of 0.21 and 0.06, respectively.

The solution[18] and gas phase spectra for mesitylene provide support for the second approach. In addition, the gas phase spectrum of protonated benzene is consistent with these results and suggests that, although the long wavelength cutoff in the photodissociation spectrum is due at least in part to the thermodynamic threshold of reaction 6, most likely impurities were present in solution which obscured the true spectrum. The lack of agreement between the three determinations of the solution spectrum shown in Figure 3b provides additional support for this conclusion.

Lack of Solvent Shift. The absence of any solvent shifts in the spectra of the carbonium ions considered herein is a surprising and significant result in view of the apparent high degree of solvation by superacid media.[7] Although a general and comprehensive treatment of solvent effects on spectra have been given by Bayliss and McRae,[25] they do not consider any examples where a charge is present. It is expected that an electronic excitation would be accompanied by a change in the effective ion radius as well as a shift in the change distribution. Both of these effects cause a change in the solvation energetics and would likely result in a blue shift. The absence of such a shift may be due to a cancelation of effects. More gas phase spectra will have to be recorded before it can be concluded that the lack of solvent shifts for carbocations in acidic media is a general result.

Constant Photodissociation Quantum Yields. The results indicate that the quantum yield for dissociation of benzoyl cation and protonated mesitylene is relatively constant over the two bands observed in each spectrum. Cross-section measurements for the processes involved correspond to extinction coefficients comparable to those measured in solution, suggesting that the quantum yield for dissociation is near unity.[26] This result is reasonable since the quantum yield for dissociation would not be expected to remain constant if fragmentation were competing with another process, such as fluorescence. It thus appears that dissociation, whether directly from the excited state or from a vibrationally excited ground state, predominates. Interestingly, protonated mesitylene has been observed to fluoresce in solution[22] but no quantum yields were reported. Our results appear to have some precedence in the gas phase photochemical studies of benzene and alkyl substituted benzenes reported by Braun, Kato, and Lipsky.[27] They found that no emission or internal conversion to the emitting S_1 state was observed for these molecules in the vapor phase following excitation into higher bands and concluded that the upper electronic states undergo photochemical change with unit efficiency in the vapor or alternatively internally convert to the ground electronic state without resultant photochemistry.

In addition to the spectroscopy it is of interest to compare possible relationships between the photochemistry of ions in the gas phase and solution. In conjunction with recent studies of the absorption spectra of carbonium ions in magic acid, Olah and co-workers[7] attempted to photolyze $C_6H_5CO^+$ in solution with the hope of observing the elusive phenyl cation. Failure to observe this process in solution[28] leads to the conclusion that in this case collisional deactivation is fast relative to dissociation. Future comparisons of this sort will be fruitful.

Acknowledgment. We gratefully acknowledge the assistance of R. L. Woodin in obtaining the photodissociation spectrum of protonated mesitylene. This work was supported in part by the Energy Research and Development Administration under Grant No. AT(04-3)767-8.

References and Notes

(1) Camille and Henry Dreyfus Teacher-Scholar, 1971–1976.
(2) For a general discussion of solvent effects see Jaffe and Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York, N.Y., 1962, Chapter 9.
(3) A. Burnaway, *Ber.*, **63,** 3155 (1930); *J. Chem. Soc.*, 1177 (1939); *ibid.*, 20 (1941).
(4) Reference 2, p. 187.
(5) Reference 2, pp. 192–195.
(6) A. Olah, C. U. Pittman, Jr., and M. C. R. Symons, "Carbonium Ions", Vol. I, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1968, Chapter 5.
(7) G. A. Olah, C. U. Pittman, Jr., R. Waack, and M. Doran, *J. Am. Chem. Soc.*, **88,** 1488 (1966).
(8) G. Herzberg, *Q. Rev., Chem. Soc.*, **25,** 201 (1971).
(9) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22,** 527 (1971).
(10) B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96,** 6160 (1974).
(11) B. S. Freiser and J. L. Beauchamp, *Chem. Phys. Lett.*, **35,** 35 (1975).
(12) (a) J. M. Kramer and R. C. Dunbar, *J. Am. Chem. Soc.*, **94,** 4346 (1972); (b) R. C. Dunbar, *ibid.*, **95,** 6190 (1973); (c) R. C. Dunbar and B. B. Hutchinson, *ibid.*, **96,** 3816 (1974).
(13) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43,** 509 (1972).
(14) Protonated benzaldehyde undergoes the photoreaction $C_6H_5CHOH^+ + h\nu \rightarrow C_6H_7^+ + CO$: B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98,** 265 (1976).
(15) All photodissociation cross sections, σ, calculated relative to the benzene cation value of 0.06 Å^2 observed for the reaction $C_6H_6^+ + h\nu \rightarrow C_6H_5^+ + H$ (ref 11).
(16) F. H. Field, P. Hamlet, and W. F. Libby, *J. Am. Chem. Soc.*, **89,** 6035 (1967).
(17) V. H. Luther and G. Pockels, *Z. Elektrochem.*, **59,** 159 (1955).
(18) G. Dallinga, E. L. Mackor, and A. A. V. Stuart, *Mol. Phys.*, **1,** 123 (1958).
(19) (a) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69,** 2714 (1947); (b) L. Doub and J. M. Vandenbelt, *ibid.*, **71,** 2414 (1949).
(20) G. A. Olah and P. W. Westerman, *J. Am. Chem. Soc.*, **95,** 3706 (1973).
(21) N. Muller, L. W. Picket, and R. S. Mulliken, *J. Am. Chem. Soc.*, **76,** 4770 (1954).
(22) C. Reid, *J. Am. Chem. Soc.*, **76,** 3264 (1954).
(23) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23,** 69 (1951).
(24) (a) J. A. Pople, *Trans. Faraday Soc.*, **49,** 1375 (1953); (b) J. A. Pople, *Proc. Phys. Soc., London, Sect. A*, **68,** 81 (1955).
(25) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58,** 1002, 1006 (1954).
(26) In units of l. mol^{-1} cm^{-1} the measured cross sections for benzoyl cation correspond to extinction coefficients ϵ 2400 (310 nm) and 9000 (260 nm), compared to ϵ 3800 and 17 000 for the same transitions in solution. For mesitylene the gas phase values are ϵ 6000 (355 nm) and 4000 (250 nm), compared to solution values of 12 000 and 9000. Thus the solution values are higher by a factor of ~2. No great significance can be attached to this difference since the difficulties associated with each measurement are substantial, mainly due to uncertainties in photon flux, photon beam-ion distribution overlap in the gas phase, and concentration measurement in solution. If $\varphi_d(\lambda)$ were significantly different from unity (e.g., 0.5) we would expect to observe more of a variation with wavelength.
(27) C. L. Braun, S. Kato, and S. Lipsky, *J. Chem. Phys.*, **39,** 1645 (1963).
(28) G. A. Olah, private communication.