intense broad bands above 9.0 eV ionization energy mainly arising from unpyrolyzed DMSCB (Figure 1a).

The adiabatic first ionization potential of DMSE determined in this work, 7.71 ± 0.03 eV, should allow a determination of the heat of formation of $(Me_2Si=CH_2)^+$ from the known heat of formation of the neutral molecule. However, although the vibrational structure in Figure 3 was regularly spaced and could be assigned to vibrational excitation of the ion, contributions from ionization of a vibrationally excited neutral molecule to Figure 3 cannot be ruled out. Hence the measured adiabatic IP is regarded as a lower limit for the true adiabatic IP. The heat of formation of neutral DMSE has recently been determined from the proton affinity of Me₂Si=CH₂ measured by ion cyclotron resonance spectroscopy.²⁷ However, the value derived from this work depends on the heat of formation of the trimethylsilyl ion. A more precise value for this

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quantity than that used in the original work (ref 27) is. however, available which lowers the heat of formation of Me₂Si=CH₂, $\Delta H_{f}^{\circ}_{298}$, to 2 ± 9 kJ mol⁻¹.^{28,29} This latter value combined with the lower limit for the adiabatic IP determined in this work yields a lower limit for the heat of formation of $(Me_2Si=CH_2)^+$ of 745 ± 11 kJ mol⁻¹.

In conclusion, the main piece of information to be derived from this investigation is an improved value for the first ionization potential of the DMSE molecule. The figure obtained is significantly lower than that measured in a previous PES investigation³ but is in reasonable agreement with estimates obtained by electron impact mass spectrometry.^{4,5}

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Vibronic Absorption Spectra of Naphthalene and Substituted Naphthalene Cations in Solid Argon

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Naphthalene and methyl- and halonaphthalene cations have been produced by one- and two-photon matrix photoionization techniques and trapped in solid argon for absorption spectroscopic study. Five transitions in the visible and ultraviolet regions have been assigned to the radical cations. The argon matrix absorption spectra are in agreement with photoelectron and photodissociation spectra, absorption spectra of the ions in Freon glasses, and simple HMO calculations. Substituent effects were observed for the origins of the five transitions. The repeating vibronic intervals in the red N⁺ transitions due to the C(9)-C(10) stretching fundamentals for this group of substituted naphthalene cations are 40-50 cm⁻¹ above the Raman fundamentals for the molecules whereas the vibronic intervals due to ring deformation modes are up to 30 cm⁻¹ below the appropriate Raman fundamentals, and vibronic intervals in the sharp UV band are 30-45 cm⁻¹ below Raman fundamentals, which correlate with HMO π bond orders.

Introduction

A substantial amount of research has been done recently on the optical spectroscopy of molecular cations in noble gas matrices. These studies have included a variety of cations such as hexafluorobenzene,¹ fluorine-substituted benzene,² diacetylene,³ methylene chloride,⁴ carbon tetrachloride,⁵ cycloheptatriene,⁶ and styrene cations.⁷ The former studies of more stable cations have relied heavily on gas-phase emission and photoelectron spectra for identification of the cation carrier whereas the latter studies of photosensitive cations have involved photochemistry and employed gas-phase photodissociation and photoelectron spectra for identification of the cation spectrum.

Naphthalene has been studied extensively by photoelectron spectroscopy.⁸⁻¹¹ Absorption spectra of the naphthalene cation (hereafter N⁺) and methyl-substituted naphthalene cations have been observed in a variety of glassy matrices,¹²⁻¹⁴ and a preliminary argon matrix absorption spectrum has been communicated.¹⁵ Owing to the high endothermicity of N⁺ photodissociation,¹⁶ N⁺ has

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not been observed by one-photon photodissociation spectroscopy, but the two methylnaphthalene cation isomers have been studied and used as models for assignment of the N⁺ electronic states.¹⁷ In more recent work, however, two- and four-photon dissociation spectra of N⁺ have been observed.¹⁸ Gas-phase emission spectra of N⁺ have not been detected presumably because the transition between the lowest excited state $({}^{2}B_{1u})$ and the ground state $({}^{2}A_{u})$ of N⁺ is not electric dipole allowed;¹⁹ however, the resonance Raman spectrum of N⁺ in Freon glass has been observed.²⁰ The vibronic absorption spectrum of N⁺ in noble gas matrices provides both vibrational and electronic data, which may be compared to spectra of substituted naphthalene cations and the naphthalene molecule in order to gain a better understanding of the effect of ionization on the molecular orbitals and the vibrational potential functions of the molecules.

Experimental Section

The cryogenic apparatus and vacuum ultraviolet photoionization sources used in the present study have been described previously.^{5,21,22} Since naphthalene solid has only 1 torr of vapor pressure at 53 °C,²³ naphthalene was placed in a 0.25-in. Swaglok tee behind a fine needle valve (Nupro, SS4MG) affixed directly onto the vacuum vessel and final 10 cm length of 0.125-in. o.d. stainless steel spray-on line. After suitable outgassing, naphthalene and substituted naphthalenes were sublimed through the needle valve at room temperature (20 °C) onto the sapphire window at 20 ± 2 K along with argon flowing through a 3-mm orifice microwave-powered discharge tube at about 1 mM/h for 4-10-h periods. Visible-ultraviolet spectra were recorded on a Cary 17 spectrometer during and after sample deposition. Sample preparation in this manner gave a strong structured, naphthalene absorption peaking at 272 nm. On the basis of comparison of absorbances in the experiments to be described below using dilute equilibrium vapor samples, the naphthalene concentration is on the order of 1:300 in the matrices prepared with the sample needle valve opened two turns and 1:600 in similar samples formed with the needle valve opened one turn. Samples were photolyzed with a filtered high-pressure mercury arc for 30-min periods to characterize the product photochemistry.

A new two-photon technique for preparing matrix-isolated cations was developed during the course of this work.²⁴ Naphthalene vapor in equilibrium with the solid at room temperature (about 0.05 torr)²³ was mixed with CCl_4 and argon in a 2-L can to give an Ar: $CCl_4:N =$ 3000:4:1 sample. This mixture was deposited at about 2 mM/h for 3 h and photolyzed for 15-s to 30-min periods by a focussed, water-filtered high-pressure (1000 W) mercury arc positioned 20 cm from the sample. Spectra were recorded before and after each irradiation. Substituted naphthalene samples were prepared in a similar manner, but owing to the lower substituted naphthalene vapor pressure, these samples were slightly more dilute;

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TABLE I: Vibronic Absorptions and Vibrational Spacings for Naphthalene Cations in Solid Argon at 20 K

$N-h_s^+$			$N-d_8^+$			
λ, nm	$\nu, {\rm cm}^{-1}$	$\Delta \nu$, cm ⁻¹	λ , nm	ν , cm ⁻¹	$\Delta \nu,$ cm ⁻¹	
675.2	14810 ± 2^{a}	0	671.8	14885 ± 2	0	
653.0	15314 ± 2	504	650.6	15370 ± 2	485	
642.5	15564 ± 2	754	640.6	15610 ± 2	725	
638.7	15657 ± 2	846*	630.7	15855 ± 2	485	
632.2	15818 ± 2	504	613.2	$16\ 308\ \pm\ 2$	1423	
616.0	$16\ 234\ \pm\ 2$	1424	595.5	16793 ± 2	484	
597.5	16736 ± 2	502	587.4	$17\ 024 \pm 2$	716	
586.0	17065 ± 2	830*	578.8	$17\ 277\ \pm\ 2$	484	
580.1	$17\ 238\ \pm\ 2$	502	564.0	$17\ 730 \pm 2$	1422	
572.5	17467 ± 2	1233*	549.0	$18\ 215 \pm 2$	485	
566.4	17655 ± 2	1421	542.2	18443 ± 2	713	
550.8	18155 ± 2	500	534.9	18695 ± 2	480	
536.2	18650 ± 2	495	522.2	19150 ± 2	1420	
524.3	19073 ± 2	1421	509.5	19627 ± 2	487	
511.1	19566 ± 2	496				
460.9	21697 ± 10^{a}	0	458.1	21 829 ± 10	0	
453.3	22060 ± 10	364	444.8	22482 ± 10	653	
445.8	22432 ± 10	735	439.1	22774 ± 10	945	
439.0	22779 ± 10	1082	428.6	$23\ 332\ \pm\ 10$	1502	
			442.0	23697 ± 10	922	
381.1	$26\ 240\ \pm\ 20^a$	0	379.0	26 385 ± 20	0	
366.1	$27\ 315\ \pm\ 20$	1075	367.3	$27\ 226\ \pm\ 20$	840	
			361.6	$27~655 \pm 20$	1270	
307.6	$32\ 510\ \pm\ 10^a$	0	306.5	32637 ± 10	0	
303.3	32992 ± 10	482	302.1	33102 ± 10	464	
301.0	33223 ± 10	713	300.4	$33\ 289\ \pm\ 10$	652	
298.6	33490 ± 10	980	298.6	33490 ± 10	852	
292.4	$34\ 290\ \pm\ 10$	1690	292.0	$34\ 247\ \pm\ 10$	1610	
274.6	36417 ± 20^a	0	273.6	$36\ 550\ \pm\ 20$	0	
269.2	37147 ± 20	730	268.4	$37\ 258\ \pm\ 20$	708	
267.2	37425 ± 20	1008	267.3	$37\ 411\ \pm\ 20$	861	

^a Full-width at half-maximum for the origin bands are 60, 140, 400, 60, and 200 cm⁻¹, respectively, with increasing transition energy.

in these cases, the Ar:CCl₄ ratio was maintained at 500:1 and the substituted naphthalene dilution in argon was >3000:1.

The naphthalene and substituted naphthalene samples were obtained from Aldrich Chemical Co. and used without purification with the following exceptions: 2-fluoronaphthalene was supplied by Peninsular Chemresearch, 2-chloronaphthalene was obtained from ICN Pharmaceuticals, and 2-methylnaphthalene was recrystallized twice from the melt.

Results

Observations from naphthalene and substituted naphthalene experiments will be described in turn.

Naphthalene. The first series of experiments was performed with naphthalene (hereafter N) vapor effusing through the needle valve apparatus and codeposited with argon from a 3-mm orifice discharge tube.¹⁵ In one experiment, naphthalene vapor was codeposited with argon and no discharge for 2 h with an approximate Ar:N ratio of 300:1; a strong, structured N absorption was observed peaking at 272 nm (A = 0.50), a weak, structured system appeared at 309 nm (A = 0.03), and no additional absorption was observed out to 800 nm. This sample was photolyzed for 1 h with the mercury arc through a water filter and a weak absorption system was observed beginning at 675 nm ($A \approx 0.01$). When the subliming N vapor was exposed to argon discharge radiation, a strong 675.2 \pm 0.1 nm product band (A = 0.17) and associated structure were observed along with weaker bands at 461 (A = 0.01) and 381 nm (A = 0.03), which are listed in Table I.



Figure 1. Absorption spectra from 250 to 700 nm of naphthalene samples in solid argon at 20 K: (a) Ar:CCl₄:N = 3000:4:1; (b) sample in (a) after 15-s exposure to 220-1000-nm high-pressure mercury arc radiation; and (c) Ar:CCl₄:N- d_8 = 2000:4:1 sample after 5-min exposure to 220-1000-nm radiation.

Photolysis with 420–1000-nm radiation from the highpressure mercury arc for 30 min reduced these bands to 60% of their initial absorbances, and a like treatment with 290–1000-nm radiation further reduced the bands to 35%. Photolysis of a similar product sample (675.2 nm, A = 0.11, spectrum illustrated in ref 15) with 500–1000-nm radiation reduced these bands to 95% and a like treatment with the full arc (water filter, 220–1000-nm output) reduced the bands to 30% of their initial absorbances. One experiment was performed with krypton as the discharge and matrix gas; the product origin shifted to 679.4 \pm 0.1 nm; the vibronic bands and intervals are given in Table II. An experiment with xenon as the discharge and matrix gas gave no observable products.

A group of experiments was done with $Ar:CCl_4:N =$ 300:4:1 samples and only mercury arc photolysis to complement the above studies. A 15-s exposure to 220-1000-nm radiation produced the intense product spectrum shown in Figure 1b; the new bands and associated structure are listed in Table I. Spectra of this sample (a) before and (b) after photolysis show the growth of new product band progressions starting at 675.2 (A = 0.48), 460.9 (A= 0.028), 381.1 (A = 0.12), 307.6 (A = 0.78), and 274.6 nm (A = 0.9) at the expense of the N precursor absorption systems beginning at 313.3 (stronger band at 309.5 nm) and 272 nm, which were reduced by 70%. No absorption was observed out to 2000 nm. Photolysis for an additional 5 min increased the product bands by 15%, and an additional 25-min irradiation had no measurable effect on the product yield. Similar photochemical formation of product was obtained in the other studies. In another experiment, a 5-min irradiation of an Ar:CCl₄:N = 2000:4:1 sample gave the same product yield reported above, and no absorption was detected in the 2000-700-nm region. Warming the sample to 45 K over a 5-min period with the vacuum vessel isolated from the vacuum system reduced the product bands to 40% of their initial absorbances and

TABLE II: Vibronic Absorptions and VibrationalSpacings for Naphthalene Cations inSolid Krypton at 25 K

N-h _s +			N-d ₈ +			
λ, nm	ν , cm ⁻¹	$\Delta \nu$, cm ⁻¹	λ, nm	ν, cm ⁻¹	$\Delta \nu$, cm ⁻¹	
679.4 656.8 646.4 642.2 635.8 619.4 600.7 588.9 583.0 569.3 553.4 465.8 384.6	$14 719 \pm 4 \\15 225 \pm 4 \\15 470 \pm 4 \\15 571 \pm 4 \\15 728 \pm 4 \\16 145 \pm 4 \\16 647 \pm 4 \\16 647 \pm 4 \\16 681 \pm 4 \\17 153 \pm 4 \\17 565 \pm 4 \\18 070 \pm 4 \\21 468 \pm 20 \\26 240 \pm 40 \\22 512 0 = 20 \\26 240 \pm 40 \\20 26 26 20 \\20 26 20 \\20 26 20 \\20 26 20 \\20 20 20 \\20 20 20 \\20 20 20 \\20 20 20 \\20 20 \\20 20 20 \\20 \\$	0 506 751 852* 503 1426 502 836* 506 1420 505	675.8 654.6 644.7 634.6 616.6 599.0 590.7 582.3 567.0	14 797 15 277 15 511 15 758 16 218 16 695 16 929 17 173 17 637	0 480 714 481 1421 477 711 478 1419	
309.3 276.7	$32\ 510\ \pm\ 20$ $36\ 140\ \pm\ 40$					

produced a weak broad 900–1160-nm band centered at 1020 nm ($A \sim 0.01$). Photolysis for another 5 min increased the sharp product absorptions by 50% without affecting the 1020-nm absorption. Sample warming to 50 K over a 5-min period broadened the sharp product bands and reduced their intensities, increased the broad 1020-nm band (to A = 0.025), and produced a new weak broad 566-nm band (A = 0.006) replacing the sharp product absorption in this region. Another experiment was done with a krypton sample, Kr:CCl₄:N = 1000:2:1, which was deposited at 25 K and irradiated for 20-s and 5-min periods. The 679.4-nm origin increased threefold on the final photolysis to A = 0.083, the product band origins are given in Table II, and the spectrum is compared with the argon



Figure 2. Absorption spectra for naphthalene cations in solid argon, krypton, and xenon matrices plotted on a wave number scale by using a Nicolet 1180 computer and Zeta plotter: (a) Ar:CCl₄:N \approx 2000:4:1 sample at 20 K subjected to mercury arc photolysis for 15 s; (b) Kr:CCl₄:N \approx 1000:2:1 sample at 25 K subjected to mercury arc photolysis for 5 min; and (c) Xe:CCl₄:N \approx 1000:2:1 sample deposited at 50 K with concurrent xenon resonance radiation.

matrix spectrum in Figure 2 by using a wave number scale. Similar mercury arc photolysis of a xenon sample, Xe:C-Cl₄:N = 1000:2:1, deposited at 35 K, failed to give product absorptions. However, new product absorptions appeared when an identical xenon sample was deposited concurrently with xenon resonance radiation for 4 h. A new band system was observed at 692.0 (140-cm⁻¹ half-width, A =0.018), 668.5, 629.8, 610.5, and 578.0 ± 0.1 nm, which is shown in Figure 2, and a broad CCl₄⁺ band⁵ was observed at 470 nm (A = 0.08). Photolysis with 630–1000-nm radiation for 2 min had no effect on the absorptions; a 1-min photolysis with 290–1000-nm light, however, destroyed all product absorptions including product absorption near 310.5 nm overlapping N absorption at 311.5 nm.

Two experiments with $C_{10}D_8$ vapor and argon resonance photoionization produced a strong red system beginning at 671.8 nm (A = 0.20) with the structure listed in Table I and weaker bands at 458 (A = 0.008) and 379 nm (A =0.04). An experiment with krypton as the discharge and matrix gas produced the red system with the origin displaced to 675.8 nm; the vibronic bands are given in Table II. A final experiment with a 5-min mercury arc photolysis of an Ar:CCl₄:N- $d_8 = 2000:4:1$ sample produced the strong red system beginning at 671.8 (A = 0.64), 458.1 (A = 0.038), 379.0 (A = 0.16), 306.5 (A = 1.3), and 273.6 nm (A = 1.5);this spectrum is shown in Figure 2a and the absorption bands are listed in Table I; no absorptions were observed out out to 2000 nm. A faint white luminescence was observed from this sample during warming through 30–50 K.

Methylnaphthalenes. Three experiments were done with 1-methylnaphthalene vapor effusing through the needle valve at one and two turns and argon resonance



Figure 3. Comparison of absorption spectra of samples prepared by codepositing naphthalene, quinoline, and substituted naphthalenes and argon at 20 K with concurrent argon resonances photoionization: (a) naphthalene, (b) quinoline, (c) 2-methylnaphthalene, (d) 1-methylnaphthalene, (e) 1-fluoronaphthalene, (f) 1-chloronaphalene, and (g) 1-bromonaphthalene.

photoionization, which should give and Ar:MeN ratio between 300:1 and 1000:1. The spectrum from the most productive of these runs is illustrated in Figure 3d; a band system was observed beginning at 712.7 nm (A = 0.06) and weaker bands were found at 453 and 383 nm. This sample was exposed to 500–1000-nm photolysis for 30 min which reduced the absorptions to 60% of their initial absorbances, and a like treatment with 290–1000-nm radiation reduced the bands to 15%. In another experiment, 420– 1000-nm photolysis reduced the bands to 35% of their original intensities.

An argon matrix containing 1-MeN vapor (>3000:1) with CCl_4 (Ar: $CCl_4 = 500:1$) was subjected to mercury arc photolysis (220–1000 nm) for 15 s and the 712-nm band system was observed (A = 0.015). A further 10-min irradiation of this sample produced the spectrum illustrated in Figure 4c with band systems starting at 712.7 (A = 0.10), 452.6 (A = 0.018), 383.5 (A = 0.09), 309.6 (A = 0.25), and 276.3 nm (A = 0.6) which are given in Table III. The 1-MeN precursor absorptions were reduced to 25% of their original absorbances which made observation of the two ultraviolet product absorptions possible. Irradiation for 60 min increased these bands by 30%; a final photolysis with 500–1000-nm filtered radiation for 15 min reduced the bands by 10% and a 3-h exposure to this radiation decreased the bands another 5%.

Two experiments were done with argon resonance radiation and 2-methylnaphthalene vapor effusing through the needle valve at one and two turns. The spectrum from the best run is illustrated in Figure 3c; new band origins were observed at 671.0 (A = 0.083), 473.1 (A = 0.017), and 384.7 nm (A = 0.045); no product absorption was found between 1300 and 1800 nm, although the 713-nm absorption, produced from the 1-MeN isomer present as an impurity, was observed (A = 0.01) in these experiments. Photolysis of this sample with 420–1000-nm radiation for 30 min decreased the product bands by 70%, and exposure to 290–1000-nm light decreased the bands to 18% of their initial absorbances.



Figure 4. Absorption spectra from 250 to 700 nm of methylnaphthalene samples in solid argon at 20 K with added CCi₄ (Ar:CCi₄ = 500:1): (a) Ar:2-MeN > 3000:1; (b) sample in (a) after 5-min exposure to 220-1000-nm mercury arc radiation; and (c) Ar:1-MeN > 3000:1 sample after 10-min exposure to mercury arc radiation.

A 6-mmol sample of 2-MeN and CCl₄ was deposited for 3 h and the spectrum is illustrated in Figure 4a. This sample was irradiated by the mercury arc for 5 min and the resulting spectrum is shown in Figure 4b; approximately 75% of the 2-MeN precursor absorbance was destroyed and new product band systems appeared at 671.1 (A = 0.21), 473.1 (A = 0.055), 384.7 (A = 0.14), 312.0 (A = 0.83), and 279.7 nm (A = 0.4), which are listed in Table III. Photolysis with 340-1000-nm light for 30 min reduced the product bands by 10%.

Fluoronaphthalenes. Two experiments were performed with 1-fluoronaphthalene and argon resonance radiation with precursor vapor effusing through the needle valve set at one and two turns, respectively. New vibronic band systems were observed with origins at 687.6 (A = 0.06) and 379.5 nm (A = 0.06), which are illustrated in Figure 3e. A red shoulder, located at 693 nm on the origin band, is repeated on the other members of the progression. One experiment was done with this precursor and added carbon tetrachloride by using mercury arc photolysis. Irradiation for 5 min produced the 687.7-nm system (A = 0.17) which increased (to A = 0.23) after 30 min of irradiation; this system and other product bands at 440.5 (A = 0.02), 379.4 (A = 0.22), 308.6 $(A \approx 0.2)$, and 272.2 nm $(A \approx 0.9)$ are illustrated in Figure 5c and listed in Table IV. The red shoulder at 693 nm on the strong 687.7-nm band, analogous red shoulders on other members of the progression, and a 446-nm shoulder on the 440.5-nm absorption were destroyed by sample warming to 45 K which decreased the product bands by 40%. Irradiation for an additional 5 min restored the series of red shoulders on the dominant absorption progression.

Two experiments were performed with 2-fluoronaphthalene samples doped with CCl_4 and mercury arc photolysis. After a 15-s irradiation, new product bands were observed; irradiation for 15 min tripled the yield, and irradiation for 1 h increased the yield a factor of 5. The final spectrum is illustrated in Figure 5b which may be compared with the original sample spectrum shown in

 TABLE III:
 Vibronic Absorptions and Vibrational

 Spacings for Methylnaphthalene Cations in Solid Argon

1-MeN ⁺			2-MeN⁺			
λ, nm	ν , cm ⁻¹	$\frac{\Delta \nu}{\mathrm{cm}^{-1}}$	λ, nm	ν , cm ⁻¹	$\Delta \nu$, cm ⁻¹	
712.7 687.3 665.2 646.7 626.1 608.1 592.4 575.0	$\begin{array}{c} 14\ 031\ \pm\ 10^{a}\\ 14\ 550\ \pm\ 10\\ 15\ 033\ \pm\ 10\\ 15\ 463\ \pm\ 10\\ 15\ 972\ \pm\ 10\\ 16\ 461\ \pm\ 10\\ 16\ 880\ \pm\ 10\\ 17\ 391\ \pm\ 10\\ \end{array}$	0 519 1002 1432 509 998 1417 511	671.0 651.6 633.8 612.4 596.3 581.5 563.4 549.5 537.0 521.5	$\begin{array}{c} 14 \ 903 \ \pm \ 6^{b} \\ 15 \ 347 \ \pm \ 6 \\ 15 \ 778 \ \pm \ 6 \\ 16 \ 329 \ \pm \ 6 \\ 16 \ 770 \ \pm \ 6 \\ 17 \ 197 \ \pm \ 6 \\ 17 \ 749 \ \pm \ 6 \\ 18 \ 198 \ \pm \ 6 \\ 18 \ 622 \ \pm \ 6 \\ 19 \ 175 \ \pm \ 6 \end{array}$	$\begin{array}{r} 0 \\ 444 \\ 431 \\ 1426 \\ 441 \\ 427 \\ 1420 \\ 449 \\ 424 \\ 1426 \end{array}$	
452.6 444.9 440.4 429.3 416.7	$\begin{array}{c} 22\ 095\ \pm\ 10\\ 22\ 477\ \pm\ 10\\ 22\ 707\ \pm\ 10\\ 23\ 294\ \pm\ 10\\ 23\ 998\ \pm\ 10 \end{array}$	0 382 612 1199 1903	473.1 463.1 452.8 441.0	$\begin{array}{c} 21\ 137\ \pm\ 10\\ 21\ 594\ \pm\ 10\\ 22\ 085\ \pm\ 10\\ 22\ 676\ \pm\ 10 \end{array}$	0 456 948 1539	
383.5 367.6 362.5 348.7	$\begin{array}{c} 26\ 076\ \pm\ 20\\ 27\ 203\ \pm\ 20\\ 27\ 586\ \pm\ 20\\ 28\ 678\ \pm\ 20\\ \end{array}$	0 1127 1510 2602	384.7 378.5 369.8 364.6 358.3	$\begin{array}{c} 25 \ 994 \ \pm \ 20 \\ 26 \ 420 \ \pm \ 20 \\ 27 \ 042 \ \pm \ 20 \\ 27 \ 427 \ \pm \ 20 \\ 27 \ 910 \ \pm \ 20 \end{array}$	0 426 1047 1433 1915	
309.6 305.0 303.3 300.5	$\begin{array}{c} 32\ 300\ \pm\ 10\\ 32\ 787\ \pm\ 10\\ 32\ 971\ \pm\ 10\\ 33\ 278\ \pm\ 10\\ 33\ 278\ \pm\ 10\\ \end{array}$	0 487 671 978	312.0 309.7 307.8 305.2 302.9 301.1 298.6 296.2	$\begin{array}{c} 32051\pm10\\ 32389\pm10\\ 32489\pm10\\ 32765\pm10\\ 33014\pm10\\ 33212\pm10\\ 33490\pm10\\ 33727\pm10 \end{array}$	0 ^c 238 437* 714* 963* 1160* 1438* 1676	
$\begin{array}{c} 276.3\\ 271.1\end{array}$	36 193 ± 20 36 887 ± 20	0 694	279.7 276.4 273.8	$\begin{array}{r} 35753\pm20\\ 36179\pm20\\ 36523\pm20 \end{array}$	0 427 770	

^a Full-width at half-maximum is 210 cm⁻¹. ^b Full-width at half-maximum is 160 cm⁻¹. ^c The vibronic origin for the 2-MeN precursor was observed at 316.7 nm and vibronic fine structure was observed within ±10 cm⁻¹ of spacings marked with an asterisk.



Figure 5. Absorption spectra from 250 to 700 nm of fluoronaphthalene samples in solid argon at 20 K with added CCl_4 (Ar: $CCl_4 = 500$:1): (a) Ar:2-FN > 3000:1; (b) sample in (a) after 60-min exposure to 220–1000-nm mercury arc radiation; and (c) Ar:1-FN > 3000:1 sample after 30-min exposure to mercury arc radiation.

 TABLE IV:
 Vibronic Absorptions and Vibrational

 Spacings for Fluoronaphthalene Cations in Solid Argon

1-FN ⁺			2-FN⁺			
λ , nm	ν , cm ⁻¹	$\frac{\Delta \nu}{\mathrm{cm}^{-1}}$	λ, nm	ν , cm ⁻¹	$\frac{\Delta \nu}{\mathrm{cm}^{-1}}$	
693 ^a	14 430		664.2ª	15 056		
687.7	14541 ± 10^{b}	0	657.7	15 205 ± 3 ^c	0	
662.6	15092 ± 10	551	640.3	15618 ± 3	413	
641.3	15 593 ± 10	1052	623.9	16028 ± 3	410	
625.9	15977 ± 10	1436	622.2	16072 ± 3	867	
605.1	16526 ± 10	549	601.1	16636±3	1431	
574.5	$17\ 406\ \pm\ 10$	1429	586.7	$17\ 044 \pm 3$	408	
556.9	17957 ± 10	551	574.9	$17\ 394 \pm 3$	758	
531.1	18829 ± 10	1423	573.1	17449 ± 3	405	
			554.0	$18\ 051\ \pm\ 3$	1415	
			541.7	18460 ± 3	409	
446 sh	22 422 ± 20		466.7	21 427 ± 10	0	
440.5	22701 ± 20	0	457.7	21848 ± 10	421	
422.8	23652 ± 20	951	449.5	$22\ 247\ \pm\ 10$	399	
			445.9	22427 ± 10	1000	
			434.8	22 999 ± 10	1572	
379.4	26357 ± 10	0	378.3	26 434 ± 10	0	
370.5	26 991 ± 10	634	372.2	26 867 ± 10	433	
365.0	27 397 ± 10	1040	364.2	27457 ± 10	1023	
			358.3	27 910 ± 10	453	
			351.8	28425 ± 10	968	
308.6	32404 ± 10	0	308.7	32 394 ± 10	0	
272.2	36 738 ± 20	0	276.3	36 193 ± 20	0	
267.0	37453 ± 20	715			-	

^a Origins of progressions due to matrix site. ^b Fullwidth at half-maximum is 190 cm⁻¹. ^c Full-width at halfmaximum is 30 cm⁻¹.

Figure 5a; the sharp product progressions are listed in Table IV. New absorption origins were observed at 675.7 nm (A = 0.27) with a resolved satellite origin at 664.2 (A = 0.14), 466.7 (A = 0.058), 378.3 (A = 0.17), 308.7 $(A \sim 0.3)$, and 276.3 nm $(A \sim 0.3)$; the latter two absorptions grew at the expense of precursor absorption in this region.



Figure 6. Visible and ultraviolet absorption spectra of 2-halonaphthalene samples in solid argon at 20 K with added CH₂Cl₂: (a) Ar:CH₂Cl₂:2-CIN \approx 3000:6:1; (b) sample in (a) after 35-min exposure to 220–1000-nm mercury arc radiation; (c) 2-BrN vapor codeposited with Ar:CH₂Cl₂ = 500:1 sample and argon from discharge resonance lamp giving Ar:2-BrN \approx 1000:1.

Chloronaphthalenes. Two argon resonance photoionization experiments were done with 1-chloronaphthalene by using one and three turns on the needle valve admitting sample vapor; the spectrum in Figure 3f exhibits new broad bands at 746.5 (A = 0.07), 719.0, 675.5, 452, and 391 nm; sharp peaks at 675.2, 653.0, and 616.0 nm probably arise from N in the sample. These absorptions were reduced 50% by 290-1000-nm irradiation. Another study codepositing Ar:CH₂Cl₂ = 500:1 as an electron trap along with 1-ClN vapor substantially increased the product yield (746.5 nm, A = 0.22), which enabled sharp shoulders at 677.6 and 617.9 nm to be observed. Two studies were done

TABLE V:Vibronic Absorptions and VibrationalSpacings for 2-Halonaphthalene Cations in Solid Argon

	2-ClN⁺			2-BrN ⁺	
λ , nm	ν , cm ⁻¹	$\frac{\Delta \nu}{\mathrm{cm}^{-1}}$	λ, nm	ν , cm ⁻¹	$\frac{\Delta \nu}{\mathrm{cm}^{-1}}$
677.6	14758 ± 6	0	689.8	14 497 ± 6	0
661.8	15110 ± 6	352	677.2	14.767 ± 6	270
646.8	15461 ± 6	351	666.7	14999 ± 6	502
617.9	16184 ± 6	1426	663.8	15065 ± 6	568
604.9	16532 ± 6	348	655.0	15267 ± 6	770
568.0	$17\ 606\ \pm\ 6$	1422	652.3	15 330 ± 6	833
556.9	17957 ± 6	351	628.1	15921 ± 6	1424
			617.8	16186 ± 6	265
497.4	20105 ± 10	0	607.2	16469±6	548
461.4	$21\ 673\ \pm\ 10$	1568	599.6	16678 ± 6	757
			597.7	16731 ± 6	810
440.6	22696 ± 10	0	577.1	$17\ 328\ \pm\ 6$	1407
426.0	23474 ± 10	778	568.2	$17\ 599\ \pm\ 6$	271
			559.3	17879 ± 6	551
394.1	25374 ± 20	0	534.2	18720 ± 6	1392
387.8	25786 ± 20	412			
379.1	26 378 ± 20	1013			
373.5	26774 ± 20	1400	507	19724 ± 20	0
366.4	$27\ 293\ \pm\ 20$	1910			
317.2	$31\ 521\ \pm\ 10$	0	468.5	$21\ 345\ \pm\ 10$	0
313.7	31878 ± 10	357			
310.0	32258 ± 10	737	403.3	$24\ 795\ \pm\ 20$	0
306.8	32595 ± 10	1074	387.7	25793 ± 20	998
303.2	32982 ± 10	1461	382.0	$26\ 178\ \pm\ 20$	1383
300.2	33311 ± 10	1790			
296.9	33681 ± 10	2160	320.5	$31\ 201\ \pm\ 10$	0
			313.1	31939 ± 10	738
284.7	35125 ± 20	0	310.1	$32\ 248\ \pm\ 10$	1047
276.3	36193 ± 20	1068	305.9	32690 ± 10	1489

with CCl₄ doped samples and mercury arc photolysis; the 746.5- (A = 0.02) and 719.0-nm bands were observed, but stronger bands at 677.6, 617.9, and 317.2 nm dominated the product spectrum. A final experiment was done with 2-chloronaphthalene codeposited with Ar:CH₂Cl₂ = 500:1, and the spectrum is shown in Figure 6a; after a 35-min full mercury arc photolysis, six sharp new band systems appeared with origins at 677.6 (A = 0.32), 497.4 (A = 0.056), 440.6 (A = 0.013), 394.1 (A = 0.096), 317.2 (A = 0.50), and 284.7 nm (A = 0.28) which are illustrated in Figure 6b and listed in Table V.

Bromonaphthalenes. An argon resonance photoionization experiment with 1-bromonaphthalene vapor effusing through the needle valve at four turns for 10 h gave broad bands at 787.5 (A = 0.07), 761, 709, 688, 456, and 397 nm, which are illustrated in Figure 3g; these bands decreased slightly upon 290-1000-nm photolysis. Two experiments with mercury arc photolysis of a CCl₄ doped sample produced only a very weak broad 787.5-nm band (A = 0.002). An argon resonance photoionization experiment with 2bromonaphthalene codeposited with $Ar:CH_2Cl_2 = 500:1$ sample gave new band systems at 689.8 (A = 0.45), 507 (A= 0.015), 468.5 (A = 0.002), 403.3 (A = 0.07), and 320.5 nm (A = 0.35), which are illustrated in Figure 6c and listed in Table V; 290–1000-nm mercury arc photolysis reduced these bands to 80% and 220-1000-nm radiation reduced the bands to 30% of their initial absorbances. A final experiment with mercury arc photolysis of CH₂Cl₂ doped sample produced a lower yield and the two strongest new bands were observed at 689.8 (A = 0.06) and 320.5 nm (A= 0.04) above precursor at 319.7 nm.

Quinoline. Quinoline (C₉H₇N) vapor was codeposited with argon from the discharge tube in one experiment, and the product spectrum is contrasted in Figure 3b with that from a naphthalene study in Figure 3a. New product absorptions were found at 627.2 nm (A = 0.045), with associated structure at 608.0, 598.8, 576.0, 559.5, 460.6 (A

TABLE VI: Origin Bands (cm⁻¹) of the Five TransitionsObserved for Naphthalene and Substituted NaphthaleneCations in Solid Argon

molecular					
ion	1	2	3	4	5
N ⁺	14 810	21 697	26 240	32 510	36 417
$N-d_{8}^{+}$	$14\ 885$	21 8 29	26 385	32637	36 550
2-MeN ⁺	14903	21137	25994	32051	35753
1-MeN⁺	$14\ 031$	22095	26076	32300	36 193
$2 \cdot FN^+$	$15\ 205$	21427	$26\ 434$	$32\ 394$	36 193
$1 \cdot FN^+$	$14\;541$	22701	26357	32404	36 738
2-ClN⁺	14758	22696	25374	$31\ 521$	35125
1-ClN⁺	13394	$22\ 222$	25510		
2-BrN⁺	$14\ 497$	21345	24 795	$31\ 201$	
$1 \cdot BrN^*$	12698	$21\ 834$	25189		

= 0.009), and 385.0 nm (A = 0.03). Sharp absorptions at 520.6 (A = 0.025) and 472.5 nm (A = 0.007) due to the C₂⁻ anion²⁵ in the quinoline experiment were not observed in any of the naphthalene experiments.

Discussion

The new product absorptions will be identified and assigned and substituent effects on the vibronic spectra of substituted naphthalene cations will be considered.

Identification. The five band systems listed in Table VI are assigned to the naphthalene radical cation (N^+) for the following reasons:

(1) Three of these absorption systems were observed with two different techniques capable of forming positive ions. The first experiments employed argon resonance (11.6, 11.8 eV) photoionization²² which is capable of ionizing N during matrix condensation and trapping N⁺ in solid argon;¹⁵ in these studies the electron removed in ionization is probably trapped by a molecular fragment or another parent molecule. Later experiments used intense mercury arc radiation to perform two-color resonance photoionization²⁴ of N molecules isolated in solid argon with the relatively long-lived S1 state serving as an intermediate step in the photoionization processes.²⁶ In the latter experiments CCl_4 was added as an electron trap, and positive ion yields increased by a factor of 3 over singlephoton ionization experiments, giving further support to the product identification as a positive ion. The two highest energy absorption systems were obscured by precursor absorption in the first experiments, but the latter studies used one-tenth as much N, and the N⁺ absorptions were produced at the expense of N bands (Figure 1).

(2) The two visible band origin positions are in excellent agreement with photoelectron spectra (PES).8-11 The red absorption provides an excellent basis for comparison between PES and the sharp matrix absorption spectrum since sharp vertical PES band origins, which can be measured to ± 0.01 eV, were observed for the first and third ionic states of N⁺. The difference between the first and third PES band origins is 1.85 ± 0.02 eV which predicts an absorption band origin at $14920 \pm 160 \text{ cm}^{-1}$ in the gas phase, assuming no change in structure between the neutral molecule and the two ionic states. The argon matrix origin at 14810 ± 3 cm⁻¹ is in agreement within measurement error, which confirms the identification of N⁺ and indicates relatively little perturbation of N⁺ by the argon matrix. The blue absorption at 21697 ± 10 cm⁻¹ is also in excellent agreement with the $21859 \pm 160 \text{ cm}^{-1}$ difference between sharp origins of the first and fourth PES bands. The three ultraviolet bands are attributed to

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(26) Duncan, M. A.; Dietz, T. G.; Smalley, R. E. J. Chem. Phys. 1981, 75, 2118.



electron-promotion transitions with upper states not reached by PES, hence a comparison cannot be made.

(3) The first four transitions are in excellent agreement with the 690-, 467-, 387-, and 308-nm absorptions assigned to N⁺ produced by radiolysis of N in a Freon glass at 77 K.¹³ The small red shifts (42-400 cm⁻¹) are due to greater interaction with the more polarizable Freon medium. Vibronic structure is similar in the solid argon and solid Freon samples; the bands are a factor of 3 sharper in solid argon which facilitates more accurate vibronic measurements.

(4) The first three transitions are predicted reasonably well by simple Hückel molecular orbital theory.^{10,27} The 10 π molecular orbitals of N are given in Scheme I with HMO energies calculated by using $\beta = 2.77$ eV from the PES⁹ which scales the MO's to cation energies. The first three transitions are $d \rightarrow f$ (long-axis polarized, 16100 cm⁻¹ calculated), $c \rightarrow f$ (short-axis polarized, 22600 cm⁻¹ calculated), and $f \rightarrow g$ (short-axis polarized, 27600 cm⁻¹ calculated). The orbitally degenerate $f \rightarrow h$ and $e \rightarrow g$ transitions are calculated at 36300 cm⁻¹; more sophisticated configuration interaction calculations predict a 3000-cm⁻¹ splitting in these two transitions,^{13,28} in reasonable agreement with the two strong ultraviolet absorptions for N⁺. A very recent SCF-MO-CI calculation²⁹ for the N⁺ cation predicts transitions at 14430, 22730, 34480 and 37450 cm⁻¹, in excellent agreement with the present data; another SCF calculation also gives good results;¹⁰ however, a CNDO/S calculation³⁰ gives very poor agreement. The argon matrix absorption spectrum gives accurate relative intensities and line widths for five N⁺ transitions, which may be useful to test further calculations of electronic structure in aromatic systems.

(5) The sharp UV band origins at 32510 and 36417 cm⁻¹ are in agreement with the broad four-photon dissociation¹⁸ bands at 33 200 and 38 200 cm^{-1} for N⁺; the agreement would probably be better if origins were resolved for the broad PDS bands.

(6) The vibronic structure in the absorption systems, particularly the red band, and the $N-d_8^+$ counterpart



Figure 7. Comparison of 2-methylnaphthalene cation absorption spectra measured with different techniques: (a) gas-phase photodissociation spectrum, replotted from ref 17: (b) argon matrix absorption spectrum; and (c) Freon matrix absorption spectrum, reploted from figure used in ref 13.

spacings correspond closely with N and $N-d_8$ vibrational intervals.³¹ The small blue shifts in the origin bands upon deuteration range from 75 to 145 cm⁻¹; the weak S_1 origin of N at 313.2 nm exhibits a similar 102-cm⁻¹ blue shift upon deuteration. These shifts arise from differences in zeropoint vibrational energy and are compatable with the naphthalene cation assignment.

The spectrum of N⁺ in a krypton matrix shows increased bandwidths (about double) and red shifts compared to argon as is expected for the more polarizable medium. The higher energy transitions show larger red shifts than the first band owing to their greater interaction with the matrix. The N⁺ bandwidths and red shifts are increased still further in solid xenon.

The broad bands at 1020 and 566 nm are in excellent agreement with naphthalene dimer cation bands at 1031 and 575 nm in a butyl chloride glassy matrix at 77 K.¹² The increase in these bands at the expense of N⁺ monomer bands on warming the argon matrix sample supports the identification of $(N)_2^+$ in the argon matrix experiments. The near-IR band has been assigned to the intervalence transition, observed at 900 nm in similar benzene experiments,³² and the 566-nm band is probably the dimer counterpart of transition 1.

Five band systems given in Table VI are assigned to the 1-methyl- and 2-methylnaphthalene cations based on their similarity to the above N⁺ spectra, the spectra of these cations in Freon glasses,¹³ and PES which predict red absorptions in the same region.^{17,33} Additional comparisons with photodissociation spectra (PDS) of the gaseous cat-

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ions in an ICR trap¹⁷ confirm assignment of the five bands to the MeN⁺ isomers.

Figure 7 contrasts the PDS¹⁷ and argon matrix and Freon matrix¹³ absorption spectra of 2-MeN⁺. A number of important differences are apparent. The large bandwidths in the PDS (2500 cm^{-1} for the 15600- cm^{-1} band) completely obscure vibrational structure that is clearly observed in the solid-state spectra. This vibrational structure is characteristic of the cation itself, as verified by the present study, and is not caused by the solid environment, as suggested¹⁷ to explain the lack of vibrational structure in the PDS. It is the cold solid, however, that quenches excess internal energy, reduces the bandwidth, and makes possible the observation of vibronic structure in the matrix absorption bands. The present comparison of argon matrix absorption and PDS bandwidths and the earlier comparison with styrene cations⁷ suggest that excess internal energy contributes to the PDS bandwidth of ions produced by electron impact. Comparison of peak positions in the PDS and argon matrix is complicated by the great difference in bandwidths and the lack of band origins in the PDS. Agreement for the two visible transitions is within experimental error. Although the PDS peaks in the ultraviolet region are 1700, 1700, and 2100 cm⁻¹ higher than the argon matrix band origins for the 2-MeN⁺ isomer and 800, 300, and 1500 cm⁻¹ higher than the argon matrix band origins for the 1-MeN⁺ isomer, the onsets of the PDS bands correspond closely with the matrix band origins. Hence, part of this apparent difference is due to comparing centers of very broad bands with sharp vibronic origins and part is due to matrix interaction and resulting red shifts of the transitions, which is expected to be more pronounced with higher excited states of cations as the electron affinity of the cation state approaches the ionization energy of the solid argon host. The relative positions of the matrix absorptions for the two isomers should, however, be accurate and probably more reliable than measurements of the broad PDS bands. The two techniques agree on the relative energies of the strong first band but disagree on the three UV bands although the differences between MeN⁺ isomers in the UV are probably within PDS measurement errors. The two techniques do give reasonably consistent relative intensities within the five bands for each isomer.

The matrix photochemistry of N⁺ and MeN⁺ is consistent with the gas-phase observations. Photolysis with 500-nm cutoff radiation reduced N⁺ absorptions by 5% and MeN⁺ bands by 40%; irradiation with 420-nm light reduced N⁺ bands by 40% and MeN⁺ bands by 70%. Since N⁺ does not dissociate with the energy available in visible radiation,^{16,17} the reduction of N⁺ absorptions with visible photolysis is probably due to photobleaching, i.e., detachment of electrons from anion traps with subsequent neutralization of cations in the sample. Some of the decrease in MeN⁺ absorptions with visible photolysis is probably also due to photobleaching. However, the MeN⁺ cations were more photosensitive than N⁺ in these experiments, and this is attributed to photodissociation of the MeN⁺ cations, as observed in the gas-phase PDS experiments.17

The absorption bands for the 1-FN⁺ and 2-FN⁺ ions are identified and assigned by their close agreement with N⁺ and MeN⁺ absorptions. The ClN⁺ and BrN⁺ origins for the first transition are red shifted from the N⁺ and FN⁺ systems, which is typical behavior for the heavier halogen-substituted aromatic species;^{34,35} the transition origins

are given in Table VI. The spectrum of 1-ClN⁺ is complicated by the presence of sharp peaks due to N⁺ and 2-ClN⁺, which arise from these impurities in the original sample; likewise the spectrum of 1-BrN⁺ contains weak N^+ bands. The BrN⁺ cations are the most photosensitive cations studied here. The 2-ClN and 2-BrN precursors yielded substantially more parent cation upon two-photon ionization than their 1-substituted analogues; this suggests longer singlet lifetimes²⁴ for the 2-substituted precursors.

The new product absorptions in the quinoline experiment are appropriate for the quinoline cation. The quinoline cation transitions are near corresponding N⁺ bands, as might be expected. The PES⁹ of quinoline predicts a blue shift of about 0.1 eV for the red transition for quinoline cation as compared to N⁺, which is in accord with the matrix observations.

Assignments. Photoelectron spectra,⁸⁻¹¹ HMO,²⁷ and SCF-MO calculations¹³ support assignment of transition 1 (Table VI) to the $d \rightarrow f$ (long-axis polarized) and transition 2 to $c \rightarrow f$ (short-axis polarized) absorptions. Although the PES exhibits a weak peak near 11.4 eV,¹⁰ this peak does not necessarily correspond to an optically allowed transition. The weak PES peak near 11.4 eV probably arises from a σ -orbital ionization, and transition 3 (Table VI) is probably due to the $f \rightarrow g$ transition owing to agreement with simple HMO calculations for naphthalene scaled to the cation. The $e \rightarrow f$ transition is predicted from PES¹⁰ to be near 1666 nm; no absorption was observed from 800 to 2000 nm, which is consistent with the optically forbidden nature of this transition.

Transitions 4 and 5 (Table VI) are in the region HMO calculations predict for $f \rightarrow h$ and $e \rightarrow g$ transitions, but without more sophisticated calculations, specific state assignments cannot be made. It is tempting to assign transition 4 at 307.6 nm to the analogous naphthalene ${}^{1}A_{e}$ \rightarrow ¹B_{3u} transition observed beginning at 313.3 nm in solid argon and 312.3 nm in the gas phase; this corresponds to a ${}^{2}A_{u} \rightarrow {}^{2}B_{3g}$ transition for N⁺. The 592-cm⁻¹ blue shift for this transition between the same orbitals for the cation and neutral may be ascribed to increased effective nuclear attraction for the 9 π electrons in the cation as compared to the 10 π electrons in the molecule.

Following the halobenzene cations, the ClN⁺ and BrN⁺ cations are expected to exhibit strong $n_z \rightarrow \pi$ charge transfer transitions in the visible region.^{34,35} The bands at 497 and 507 nm in 2-ClN and 2-BrN experiments, respectively, are appropriate for this transition; however, these bands are slightly red shifted from the 470- and 505-nm $n_z \rightarrow \pi$ transitions for chlorobenzene and bromobenzene cations in solid argon.³⁵ The 440- and 497-nm transitions for 2-ClN⁺ are probably separated by interaction between the " 1^2B_{2g} " and "Cl $3p_2$ " upper states, which accounts for a blue shift in the 440-nm band from the N⁺ position and a red shift in the 497-nm band from the chlorobenzene cation position. The 1568-cm⁻¹ interval in the 497.4-nm transition is probably due to the C-C stretching mode observed at 1575 cm⁻¹ in the neutral molecule.³⁷ This interaction is less with the "Br 4p₂" upper state, and accordingly the weak 507-nm band for 2-BrN⁺ is near the bromobenzene cation position.

Two regularly repeating vibrational intervals were observed in the red N⁺ absorptions. The first interval, 1422 \pm 6 cm⁻¹, was unchanged upon deuterium substitution.

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⁽³³⁾ Schafer, W.; Schweig, A.; Vermeer, H.; Bicklehaupt, F.; de Graaf, H. J. Electron Spectrosc. Related Phenom. 1975, 6, 91.

This is in agreement with the $1420 \pm 40 \text{ cm}^{-1}$ interval in the first PES band,^{8,11} which is probably due to the C-(9)–C(10) stretching mode $\nu_4(a_g)$. The strong fundamental at 1376 cm⁻¹ in the Raman spectrum of $C_{10}H_8$ is complicated by Fermi resonance, but the strong fundamental for $C_{10}D_8$ is at 1380 cm^{-1.31} This fundamental has been observed at 1398 cm^{-1} for N⁺ in Freon glass.²⁰ The second repeated interval in the spectra was approximately 505 cm^{-1} for N- h_8^+ and 485 cm^{-1} for N- d_8^+ ; this corresponds to the $\nu_9(a_g)$ skeletal distortion observed in the Raman spectra for $N-h_8$ at 512 cm⁻¹ and $N-d_8$ at 491 cm^{-1,31} and N^+ in Freon glass at 511 cm⁻¹. The 754-cm⁻¹ interval corresponds to $\nu_8(a_g)$, the skeletal breathing mode observed at 758 and 769 cm⁻¹, respectively, in the Raman spectra of N and N^+ . The weaker bands with intervals noted by an asterisk in Table I are probably due to vibrational modes made vibronically allowed by y- or z-dipole radiation. Since there is disagreement in the literature on assignment of the weaker Raman fundamentals^{31,36} for N, it is pointless to speculate on mode assignments. Although the red band origins were displaced on going from argon to krypton to xenon matrices, the vibrational intervals were unchanged within the error of measurement.

The four higher energy transitions for N⁺ exhibit vibrational structure without the repeating feature characteristic of the red absorption. The fourth band exhibits a sharp origin and three sharp vibronic components 482, 713, and 980 \pm 20 cm⁻¹ above the origin; the deuterium counterparts were spaced 464, 652, and 852 \pm 20 cm⁻¹ above their origin. These intervals are 10–45 cm⁻¹ below the ν_9 , ν_8 , and $\nu_6(a_g)$ Raman fundamentals³¹ at 512, 758, and 1025 cm⁻¹, respectively, and their N-d₈ counterparts at 491, 694, and 862 cm⁻¹, which suggests these vibronic assignments.

It is interesting to note that the ν_8 and ν_9 vibronic intervals in the first N⁺ transition are $7-15 \text{ cm}^{-1}$ below the neutral molecule and ground-state cation Raman values, but the v_4 mode is 24-46 cm⁻¹ above the neutral molecule and ground-state cation values. π bond orders between carbon atoms calculated from the sum of the products of the HMO coefficients²⁴ show changes ranging from an increase of 0.12 for the 9-10 bond to a decrease of 0.14 for the 1-9 bond between the ground-state molecule and cation, and the $1{}^{2}B_{3g}$ state of the ion. This increase in π bond order for the 9–10 bond explains the increase in the ν_4 interval in the red absorption as compared to the Raman spectrum of the molecule and cation. The intervals in the fourth vibronic band are 30-45 cm⁻¹ below neutral molecule values. This larger decrease in vibrational fundamentals for the $2^{2}B_{3g}$ state of the ion may be explained by the net reduction in bonding π electrons for this 8-bonding and 1-antibonding electron configuration; π bond orders are decreased up to 0.17 in the $2^{2}B_{3g}$ state of the ion as compared to the ground-state molecule.

The sharp 312.0-nm transition 4 for 2-MeN⁺ exhibited sharp vibronic bands (Table III) which agree ($\pm 10 \text{ cm}^{-1}$) with similar vibronic intervals in the 316.7-nm transition for the precursor. This suggests that the upper states of the cation and molecule, which differ by a single π electron in the weakly bonding a_{2u} orbital, have similar vibrational potential functions. This point is substantiated by π bond order calculations for the N system, which exhibit an average increase of only 0.03 from the ¹B_{3u} state of the molecule to the 2²B_{3g} state of the cation.

The vibronic spectrum of 2-BrN⁺ contained a large number of active modes (Table V), owing to the reduced symmetry of the molecule. These intervals are near Raman fundamentals of the molecule³⁷ except for the C-

TABLE VII: Comparison of Repeated Vibronic Intervals (cm⁻¹) in the Red Absorption of Substituted Naphthalene Cations with Raman Fundamentals (cm⁻¹) of the Precursor Molecule

	C(9)-C(10) stretch		ring deformation		
	N	N ⁺	N	N+	
$\overline{\text{N-}h_s}$	1376	1422^{a}	512	505 ^a	
N-d [°]	1380	1422	491	485	
2-MeN	1383	1423	454	436	
1-MeN	1374	1425	515	514	
2-FN	1383	1424	422	410	
1-FN	1385	1436	570	550	
2-ClN	1382	1424	352	350	
1-ClN	1373	1410	534	512	
2-BrN	1377	1420	274,580	270,568	
1-BrN	1368	1406	473	440	

^a Average vibronic interval accuracy ± 6 to ± 20 cm⁻¹.

(9)-C(10) stretching mode which is increased 43 cm^{-1} in the cation; this mode is more anharmonic in 2-BrN⁺ than the other substituted naphthalene cations studied here.

Substituent Effects. A number of differences were observed in the spectra of substituted naphthalene cations as compared to naphthalene cation; some of these have been mentioned to support assignment of the spectra. Shifts in the origin band position as a function of substituent can be followed in Table VI. Substitution of methyl or fluorine at the 1-position red shifts transition 1 and blue shifts transition 2 whereas these substituents in the 2-position have the opposite effect. HMO π bond orders show that the positive hole is concentrated in the C(1)–C(2) region in the ground ${}^{2}A_{u}$ state of the N⁺ cation, in the C(1)–C(9) region in the excited ${}^{12}B_{3g}$ state, and in the C(2)-C(3) region in the higher $1^{2}B_{2g}$ state. A π conjugating substituent is expected to stabilize the electron deficient MO at the site of substitution, in agreement with the observed substituent effect on the band origins. Methyl substitution in both positions red shifts the three ultraviolet transitions. Changes in relative band intensity were also observed on substitution (see figures). The 1substituent reduced transition 2 intensity and enhanced transition 5 intensity, whereas the 2-substituent increased the relative intensity of transition 4.

The first vibrational interval in the red adsorption for N^+ and substituted N^+ cations ranges from 1406 to 1436 cm⁻¹ whereas the precursor fundamentals range from 1368 to 1385 cm^{-1,37-39} as summarized in Table VII. This represents a substantial $44 \pm 7 \text{ cm}^{-1}$ increase in the cation mode compared to the neutral, which may be rationalized by an increase in the C(9)–C(10) π bond order, in this transition, as explained for N^+ . The substituent effect on this C(9)-C(10) stretching mode for both cation and neutral is small. The second vibronic interval, however, shows a pronounced substituent effect for the cations ranging from 550 cm^{-1} for 1-FN⁺ to 440 cm^{-1} for 1-BrN⁺ and from 436 cm⁻¹ for 2-MeN⁺ to 270 cm⁻¹ for 2-BrN⁺. The cations exhibit ring deformation vibrational modes up to about 30 cm^{-1} below the precursor counterparts³⁷⁻³⁹ for this interval (Table VII), showing that ionization slightly reduces the ring deformation mode. The particular ring deformation mode active in the vibronic spectrum clearly depends upon the nature and position of the substituent.

Conclusions

Naphthalene and methyl- and halogen-substituted naphthalene cations have been produced by one- and

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two-photon matrix photoionization techniques and trapped in solid argon. Five absorptions in the visible and ultraviolet regions have been assigned to the radical cations. The argon matrix absorption spectra for the naphthalene cation are in agreement with photoelectron and photodissociation spectra, absorption spectra of the ions in Freon glasses, and simple HMO calculations. Substituent effects were noted for the origins of the five transitions and the vibronic spacings. The C(9)-C(10) stretching vibrational interval in the red cation transitions are $40-50 \text{ cm}^{-1}$ above Raman bands of the precursors and the ring deformation intervals are up to 30 cm⁻¹ below precursor values. The 2-substituted naphthalene cations gave sharper and stronger absorption bands than the 1-substituted species.

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Carbon-13 Hyperfine Constants, g Factors, and Electronic Structure of *m*-Benzosemiguinone Radical Anions¹

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The ^{13}C ESR spectra of the carboxylated *m*-benzosemiquinone radical anions produced in aqueous solution by in situ radiolysis techniques have been observed. Carboxyl substitution does not perturb the spin distribution appreciably so that ¹³C hyperfine constants can be readily assigned to *m*-benzosemiquinone. This radical is an odd-alternant species with appreciable spin density at the 4 and 6 positions of the ring system but very fittle at the 2 position. The large proton and ¹³C hyperfine constants and relatively low g factors of these radicals show that there is very little spin density on the oxygen atoms. •

Introduction

Oxidation of resorcinol in basic aqueous solution is known to produce the *m*-benzosemiquinone radical anion (I).² On the time scale of ESR experiments the protons



on the 4 and 6 positions are equivalent so that the unpaired spin density appears to be equally distributed between the two oxygen atoms in much the same way as in the ortho and para isomers. These two protons, however, have relatively large hyperfine constants (11.4 G) indicating that in contrast to its isomers a major fraction of the spin density is located on the ring. Electronically the two types of radicals are quite different; only in *m*-semiguinone do the oxygen atoms and the ring carbon atoms form an odd-alternant system. It is expected that the unpaired spin density will be located primarily on the oxygen atoms and on positions 2, 4, and 6 while the spin density at the 1, 3, and 5 positions will be small or negative. Chemically

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m-semiguinone is relatively reactive and behaves more like a substituted phenoxyl radical than like the other semiquinones. For example, in contrast to the latter it disappears rapidly in second-order processes and oxidizes ascorbic acid quite readily.³ However, the g factor (2.00383; see below) is considerably smaller than that of phenoxyl radical $(2.00461)^4$ so that there is clearly destructive interference between the contributions from the two oxygen atoms. It is useful to have ¹³C hyperfine data to provide further information on the electronic structure of this important radical. Attempts to examine it directly at natural abundance levels $(1.1\% {}^{13}C)$ with in situ irradiation techniques^{5,6} were unsuccessful because only relatively low concentrations were available as the result of its high reactivity. Because the rate constants for disappearance of the carboxyl derivatives are lower by 2 orders of magnitude,⁷ we have been able to produce a sufficiently high steady-state concentration to observe the ¹³C satellites of all the ring carbon atoms in the 2-carboxy, 4-carboxy-, and 5-carboxy-m-semiquinone and report the ESR parameters here. These data show that the electron distribution is perturbed by carboxyl substitution only to a minor extent. Assignments can be made to the individual carbon atoms and realistic estimates given for the ¹³C hyperfine constants in the unsubstituted radical. Of particular importance is the low spin density at the C₂ position as manifested by both the proton and ¹³C hyperfine constants. These data are particularly valuable in providing information on the contributions of local and remote spin density to the ¹³C hyperfine interactions in a well-defined system.

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