shorter than the center to nitrogen distance (C_t–N) for an unconstrained planar porphyrin, estimated by Hoard to be 2.01 Å,[22] the porphinato ligand may distort to give the so-called ruffled structure of D_{2d} symmetry.[19] In this case the pyrrole units swivel about the metal–nitrogen bonds giving a square-planar array of nitrogens which lie in the average plane of the porphinato ligand while permitting a shortening of the metal-ligand distances d(M–N). The most familiar example of the effect of ruffling is provided by Ni(OEP) which can be crystallized in two forms; one has a planar porphyrin core and d(M–N) = 1.958 Å while the other has a severely ruffled core with d(M–N) = 1.929 Å. Several bands in the RR spectrum of the planar form are shifted to lower frequencies in the spectrum of the ruffled form.[23]

In the present study, the nickel complex, which has been shown to exist as the D_{4h} form in an argon matrix or as a thin film at ~15 K,[23] exhibits the highest frequencies for all of the metal-sensitive bands. Only slightly lower frequencies are observed for Co(OEP), implying that no significant degree of distortion has occurred. The frequency shifts for the copper (d^9) and zinc (d^{10}) complexes are easily accounted for by core expansion which is associated with occupation of the $d_{x^2-y^2}$ orbital, the frequency for Zn(OEP) being even lower than that of Cu(OEP). Ruffling evidently plays only a minor role in frequency lowering for these species since, at least in the case of tetraphenylporphinatozinc(II), Zn(TPP), the porphinato ligand has been shown to be planar.[19]

The very low frequencies observed for the metal-sensitive bands of the manganese complex may be explained by partial occupation of the $d_{x^2-y^2}$ for this high-spin, d^5 configuration. Furthermore, relative to copper (d^9), this effect is magnified by the expansion of d orbitals resulting from decreased effective nuclear charge. Again, these lowered frequencies must be attributed to core expansion since, in the case of the Mn(TPP), the porphyrin core assumes a planar configuration.[19]

Consideration of the data for the iron complex provides further evidence of the importance of ruffling in determining frequencies of metal-sensitive bands. This complex takes the intermediate spin state and consequently has an empty $d_{x^2-y^2}$ orbital.[19] Nevertheless, large frequency shifts are seen for the two high-frequency bands (1575 and 1501 cm^{-1} in the nickel complex). The short Fe–N bonds expected for this four-coordinate species give rise to severe ruffling of the porphinato ligand,[19] thus accounting for the substantial shifts which are observed. The effect of ruffling on lower frequency modes (below 1100 cm^{-1}) is relatively small.

Although any of the mechanisms discussed above may be invoked to explain the observed metal sensitivity of various bands, core expansion associated with $d_{x^2-y^2}$ occupancy appears to be most important.[21] In any case, both the core expansion and pyrrole tilting mechanisms predict that largest frequency shifts will be observed for those modes which contain the greatest contributions from methine bridge stretching and deformation. It is therefore satisfying that those bands which exhibit greatest metal sensitivity may be reasonably assigned to $\nu(C_\alpha - C_m)$ on the basis of relative frequencies and deuterium shifts.

Acknowledgment. The authors thank Professor Thomas Spiro of Princeton University for providing the sample of ($NaNO_2$-^{15}N). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation, and to the Graduate School of the University of Kentucky for partial support of this work. The work performed at Marquette University was supported by the National Science Foundation Grants PCM8114676 and CHE-8205522.

Registry No. Ni(OEP), 24803-99-4; Ni(^{15}N-OEP), 86119-71-3; Ni(OEP-d_4), 55835-59-1; Ni(^{15}N-OEP-d_4), 86119-72-4; Co(OEP), 17632-19-8; Cu(OEP), 14409-63-3; Fe(OEP), 61085-06-1; Mn(OEP), 51321-25-6; Zn(OEP), 17632-18-7.

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Time-Resolved Resonance Raman Observation of Tetrafluoro-*p*-benzosemiquinone Anion Radical[1]

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Time-resolved resonance Raman spectroscopy has been used to examine tetrafluoro-*p*-benzosemiquinone radical anion produced in the pulse radiolytic oxidation of tetrafluorohydroquinone in aqueous solution. This radical is much more reactive than *p*-benzosemiquinone and is observed to decay on the millisecond time scale in both Raman and pulse radiolytic experiments. For the Raman experiments excitation was on the red edge of the moderately strong absorption band of this radical at 430 nm. Two resonance-enhanced Raman bands are exhibited at 1556 and 1677 cm^{-1} and are assigned to the in-phase CO and symmetrical CC stretch vibrations. These frequencies are considerably higher than the corresponding values of 1435 and 1620 cm^{-1} observed in this radical's protonated counterpart. The relatively large increase in the CO stretch frequency, in particular, indicates that fluorination induces a substantial increase in the quinoid character of this radical.

The *p*-benzosemiquinone radical anion (PBSQ; $C_6H_4O_2^{-}\cdot$) and related radicals have been studied extensively by optical absorption and electron spin resonance spectroscopy employing chemical, electrochemical, pho-

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tochemical, and radiation chemical techniques for their generation.[2] We have recently reported the resonance Raman spectra of PBSQ[3] and certain of its halogen derivatives.[4] These latter radicals persist for seconds at millimolar concentrations and, therefore, can be readily observed by Raman methods in either continuous or pulsed radiolytic oxidation of aqueous solutions of the hydroquinones. However, in analogous attempts to examine the Raman spectrum of tetrafluoro-*p*-benzosemiquinone radical anion (TFPBSQ; $C_6F_4O_2^{-}\cdot$) no interpretable spectrum was observable, apparently because the steady-state radical concentration was too low. ESR studies[5] show conclusively that tetrafluorohydroquinone is readily oxidizable to TFPBSQ under the conditions of the present experiments, either directly by OH or by secondary oxidants such as Br_2^-, so that at short times sufficiently high concentrations should be available for direct observation by Raman techniques such as applied in a previous study on *p*-aminophenoxyl radicals.[6] These ESR studies show, unequivocally, that in basic solution, the two oxygen atoms of TFPBSQ are chemically equivalent and that the unpaired spin is distributed in much the same way as in PBSQ so that the radical can be presumed to be in the anionic form. Since the vibrational frequencies depend on the total electronic distribution rather than that of the unpaired spin density, one would particularly like to have comparative Raman data on these important radicals. We have employed pulse radiolytic methods to generate sufficiently high concentrations to allow their observation by time-resolved resonance Raman techniques and report the results here.

Experimental Section

In the initial experiments the Raman spectrum of TFPBSQ produced by pulse radiolysis was examined by using photomultiplier detection methods similar to those employed in previous studies of other *p*-benzosemiquinone radical anions.[4] An electron pulse (2.3 MeV; 50 mA; 1 μs) from a Van de Graaff accelerator was used for irradiation. The absorbed dose was ~10^4 rd per pulse, which should produce an initial radical concentration of ~50 μM. Since the photomultiplier (RCA 31034A) does not recover for ~100 ms from saturation by the intense Cerenkov pulse, a fast electromechanical shutter (Vincent Associates, Uniblitz Model 225L) was introduced between the Raman cell and the spectrograph. With appropriate synchronization it was found possible to carry out Raman experiments at times longer than ~1 ms after the electron pulse. In later experiments a gated optical multichannel analyzer (OMA; Princeton Applied Research 1420) was used to examine the signals at times down to ~3 μs after the pulse, as in our previous study on the *p*-aminophenoxyl radical.[6] A Molectron DL 300 dye laser pumped by a UV 1000 pulsed nitrogen laser was used as the excitation source and a 0.85-m Czerny-Turner Spex monochromator with a holographic grating (1800 grooves/mm) as the dispersion element. The exciting laser beam passed through the irradiation region within 1 mm from the exit window of the Raman cell. Time resolution was obtained by delaying the laser pulse with respect to the electron pulse. With photomultiplier detection the signal was sampled by a 1S1 Tektronix oscilloscope which was gated at the peak of the laser pulse. The output of the sampling unit was digitized and processed by a LSI 11/2 microcomputer and the data were stored on disk files on a PDP 11/55 computer for further processing. The LSI 11/2 was also used to scan the spectrum, control the experiment, and carry out signal averaging tasks. With the OMA 700 channels of data covering a region of ~450 cm^{-1} were collected and averaged in a PAR 1215 controller. In both cases data were collected at the rate of 7.5 experiments per second.

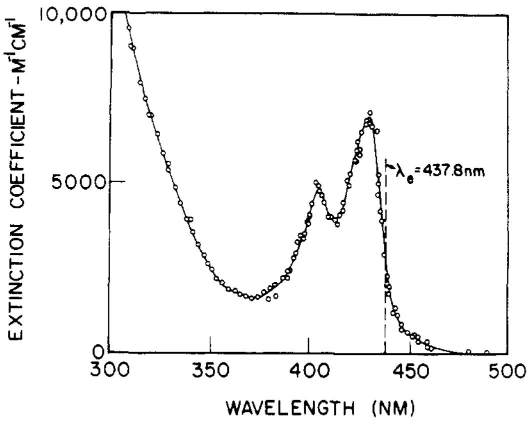

Figure 1. Absorption spectrum of tetrafluoro-*p*-benzosemiquinone radical anion. The radical was produced by pulse radiolysis of a basic solution of tetrafluorohydroquinone in water (5 × 10^{-4} M; pH ~10.5) and observed 16–20 μs after the electron pulse. λ_e shows the wavelength of the probe dye laser (437.8 nm) used in the Raman experiments.

The Raman cell was a cylindrical Suprasil quartz cell of ~0.1-mL volume through which a N_2O-saturated solution of tetrafluorohydroquinone (Alpha Products; pH ~ 10.5) was flowed at the rate of 0.2 cm^3 s^{-1}. Residence time of the solution in the Raman cell was ~0.5 s so that the solutions were on average subjected to three to four pulses.

Raman spectra of crystalline tetrafluoroquinone and tetrafluorohydroquinone were taken with a Spex Ramalog spectrometer using argon ion laser excitation at 514.5 nm. The growth and decay and optical absorption spectra of TFPBSQ were examined at the Radiation Laboratory's linear accelerator pulse radiolysis facility using methods similar to those previously described.[7] In this case the initial radical concentration was ~5 × 10^{-6} M.

Results and Discussion

The absorption spectrum of TFPBSQ obtained 10–20 μs after the pulse irradiation of a 5 × 10^{-4} M basic (pH ~10.5) solution of tetrafluorohydroquinone in N_2O-saturated water is given in Figure 1. A rate constant of 3.1 × 10^9 M^{-1} s^{-1} was obtained for oxidation of the tetrafluorohydroquinone by OH from observation on the growth of the absorption at 430 nm. A similar absorption was observed for oxidation by Br_2^-, produced in N_2O-saturated 0.1 M KBr solutions, with the rate constant in this case measured to be 7.4 × 10^8 M^{-1} s^{-1}. The ESR spectra obtained during the continuous irradiation of similar solutions show that in both cases TFPBSQ is the predominant radical present at millisecond times.[5] The ESR experiments show that oxidation by Br_2^- is somewhat cleaner in that other radicals are present at levels less than 1% whereas oxidation by OH results in contributions from

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(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2397 from the Notre Dame Radiation Laboratory.

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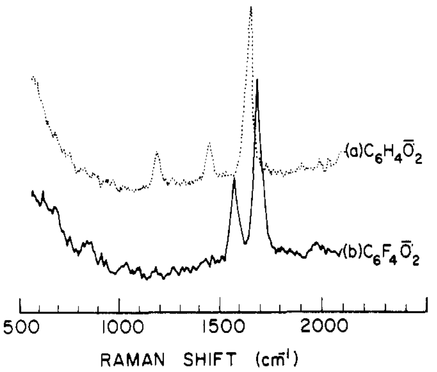

Figure 2. Resonance Raman spectrum of tetrafluoro-*p*-benzosemiquinone radical anion (λ_e = 437.8 nm) observed by photomultiplier detection methods 1 ms after its creation by microsecond electron pulse radiolysis of a basic solution of tetrafluorohydroquinone (2 × 10^{-3} M; pH 10.5) in water. The dotted lines show the Raman spectrum of *p*-benzosemiquinone anion obtained under similar conditions. Band positions are indicated in Table I.

other radicals at the ~5% level. In the latter case one expects that side reactions resulting from OH attack at the fluorine positions will produce some of the trioxo radical but neither the optical nor the Raman experiments indicate any important contributions from that radical.

The absorption spectrum given in Figure 1 shows the characteristic features of a semiquinone radical with maxima at 430 and 404 nm which, as in PBSQ, can be assigned to the (0,0) and (0,1) vibronic transitions. The difference corresponds to a vibrational frequency of 1475 ± 100 cm^{-1} in the excited state. For the most intense bands the extinction coefficient (6850 M^{-1} cm^{-1} at 430 nm) is similar to that observed for PBSQ (6200 M^{-1} cm^{-7} at 430 nm). The Raman experiments described below were mainly carried out at 437.0 nm (Coumarin 120 dye) on the red edge of the principal absorption where the extinction coefficient is ~3000 M^{-1} cm^{-1}.

The Raman spectrum shown in Figure 2 was obtained in the pulse irradiation of a 2 mM solution of tetrafluorohydroquinone at 1 ms with photomultiplier detection using the Spex as a double monochromator. It represents 25 scans of the spectrum with data being taken every 1.5 cm^{-1}. A Raman spectrum of PBSQ obtained under similar conditions, which is essentially identical with that previously reported,[3] is shown for comparison. TFPBSQ exhibits two prominent Raman bands corresponding to vibrational frequencies of 1556 and 1677 cm^{-1} which are similar to those assigned to the in-phase CO (1435 cm^{-1}) and symmetrical CC (1620 cm^{-1}) stretch vibration in PBSQ. No other bands of similar intensity are observed in the 600–1400-cm^{-1} region, confirming the previous assignment of the band at 1161 cm^{-1} in PBSQ to a CH (bending) vibration. A weak combination band is observed at 1964 cm^{-1}. Similar spectra were also observed by using OMA detection.

The Raman signal from TFPBSQ decays on the millisecond time scale as is shown in Figure 3. While the initial decay is quite rapid, the kinetics are obviously complicated since the signal remaining at 128 ms (~20%) is appreciably greater than the 2–3% expected if the initial decay rate represented second-order reactions. One, of course, expects that the semiquinone radicals will, at least in part, disproportionate

$$SQ\cdot + SQ\cdot \rightleftharpoons HQ + Q \qquad (1)$$

to form the fluorinated quinone and hydroquinone. From Raman experiments on a 5 mM tetrafluorohydroquinone solution, where the semiquinone signal decays by a factor of 2–3 between 10 μs and 100 ms, we estimate that the equilibrium constant for reaction 1 is ~100. Whether or not a true equilibrium is reached is, however, not clear. Optical pulse radiolysis experiments also show that TFPBSQ decays on the millisecond time scale. The observed decay rate, however, depends on the dose and solute concentration. The decay kinetics, as monitored both by absorption spectrophotometry and by Raman techniques, are found to be very complicated and are not, at the moment, completely understood. From the optical experiments at relatively high concentrations of the hydroquinone (>1 mM) the initial decay appears to involve, at least in part, reaction with trace impurities, in which case the rate constant for reaction with the impurities must be >10^8 M^{-1} s^{-1}. For a solution 10^{-4} M in tetrahydroquinone, where such reactions should be relatively unimportant and the equilibrium of reaction 1 should be to the right, the median lifetime at a radical concentration of 4 × 10^{-6} M was found to be ~20 ms, indicating a rate constant for disproportionation of ~10^7 M^{-1} s^{-1}. The decay observed for TFPBSQ at millisecond times contrasts with the lack of such a decay for PBSQ and makes it clear that the fluorinated radical is much more reactive than its protonated counterpart. Resolution of the kinetics and ac-

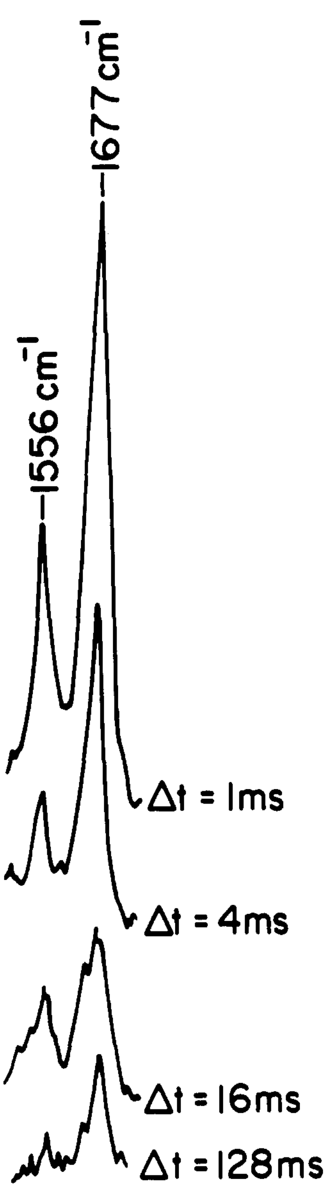

Figure 3. Decay of the Raman spectra of Figure 2 as a function of time between the irradiation pulse and the probe laser.

TABLE I: Comparison of the Raman Frequencies (cm^{-1}) in Hydroquinone, *p*-Benzosemiquinone, and *p*-Benzoquinone

	CC stretch	CO stretch	CX bend
$C_6H_4(OH)_2$ [a]	1609	1260	1166
$C_6F_4(OH)_2$ [b]	1670	1314	[c]
$C_6H_4O_2^{-}\cdot$ [b]	1620	1435	1161
$C_6F_4O_2^{-}\cdot$ [b]	1677	1556	277[d]
$C_6H_4O_2$ [e]	1667	1686	1147
$C_6F_4O_2$ [b]	1704	1734	271

[a] Hidalgo, A., Otero, C. *Spectrochim. Acta* 1960, *16*, 528. [b] Present work. [c] No band is observed in the 250-300-cm^{-1} region. [d] Derived from the combination band at 1954 cm^{-1}. [e] Anno, T. *J. Chem. Phys.* 1965, *42*, 932.

curate determination of the appropriate equilibrium and rate constants await further experimentation after the Raman techniques are made more quantitative. One should point out here that low-frequency noise does not contribute in the case of the Raman observations so that time-resolved Raman experiments are particularly well suited to measurements on the millisecond and longer time scale where ambient noise levels are bothersome in the case of the absorption experiments.

The phenyl CC stretch vibration (Wilson mode 8a) appears very strongly in the resonance Raman spectrum of PBSQ at 1620 cm^{-1}.[3,4] In the other tetrahalogen derivatives a reduction in this frequency to ~1590 cm^{-1} is observed[4] so that the 8a vibration in TFPBSQ might be expected in the region 1590–1620 cm^{-1}. However, no Raman band in this frequency region is observed in the present study. The strong Raman band at 1677 cm^{-1} is similar in relative intensity to that found for PBSQ at 1620 cm^{-1} and undoubtedly represents the 8a CC stretch mode, particularly since no other vibration is expected in this frequency region. While this increase in frequency of 57 cm^{-1} initially appears to be rather high, it is pointed out that fluorine substitution increases the 8a ring stretching frequency in benzene[8] by 55 cm^{-1} (whereas chlorine substitution reduces the frequency by 84 cm^{-1}).[9] We conclude that the difference in the frequencies noted here reflects a change in the CC bond character in the semiquinones much the same as in benzene. We have examined the Raman spectra of crystalline tetrafluoroquinone and tetrafluorohydroquinone by conventional methods and report the appropriate frequencies in Table I. As is indicated, upon fluorination of hydroquinone and quinone the CC stretching frequency increases by 61 and 37 cm^{-1}, respectively, so that the increase observed here is very reasonable. Using PBSQ as a model, interpolation between the data for the hydroquinones and quinones gives an expected CC stretching frequency for TFPBSQ of 1676 cm^{-1}, essentially identical with the value observed here. In each of these cases, attraction of the electrons into the ring system by the highly electronegative fluorine atoms appears to increase the strength of the CC bonds, and thus increase the vibrational frequency. It might also be argued that the 8a frequency could be increased because of a coupling with an appropriate CF stretching mode. However, such a coupling should impart a partial CC stretch character to the CF stretching vibration making it resonance Raman active. As indicated above, we do not observe any Raman band with an appropriate frequency that can be assigned to a CF stretching vibration so that this type of coupling cannot be of major importance.

The other principal band observed here (1556 cm^{-1}) can be readily assigned to the CO stretching frequency. This frequency is, however, 121 cm^{-1} higher than that observed in PBSQ, an increase which is about twice the effect on the CO stretch observed for fluorination of quinone and hydroquinone and considerably greater than the increase of 24 cm^{-1} observed for the chlorinated benzosemiquinone.[4] This anomalously large increase indicates a very large inductive effect of the fluorine which results in a substantial increase in the quinoid character of the radical. It is noted that the absorption maxima corresponding to the (0,0) transitions are almost identical for PBSQ and TFPBSQ so that the ground and excited electronic states are affected similarly to first order by fluorine substitution. This fact manifests that the dominant effect of fluorine on the electronic configuration is on the σ rather than the π electrons.[10] The ESR data[5] manifest rather minor changes in the distribution of unpaired spin density. The fluorine hyperfine constants for this radical are small (3.95 G) and of the magnitude expected from the 2.36 G observed for the protons in PBSQ. There cannot be any significant unpaired spin density on the fluorine atoms although the substantial increase in G factor (2.004 56 for PBSQ and 2.004 88 for TFPBSQ) shows that the fluorine atoms are sensed by the spin system. The increase in the hyperfine constants of the ring carbon atoms at the fluorinated position (from 0.75 G for PBSQ to 1.47 G for TFPBSQ) indicates some attraction of the unpaired electron into the ring. More importantly splitting by the carbon atom at the oxygenated positions is not observable (<0.5 G) so that the unpaired spin density at these positions cannot change appreciably and can be, in fact, estimated to increase somewhat (by ~0.02). From the ESR data it would appear that withdrawal of unpaired spin from the oxygen atoms onto the ring is insufficient to account for the large increase observed in the CO stretching frequency. This latter frequency will, of course, be sensitive to the distribution of the total electron population over the radical whereas the hyperfine data reflect only changes in the distribution of the unpaired electron. Comparison of the Raman and ESR data, therefore, qualitatively indicates that in addition to the effect on the unpaired electron fluorine substitution attracts appreciable charge to the ring from the oxygen atoms, a conclusion which is, of course, not surprising.

The Raman–Franck–Condon overlap between the vibrational wave functions of the ground and excited electronic states is large[3] for the 8a phenyl mode of PBSQ which is highly resonance enhanced in Raman. The CO stretching vibration also contributes to the Raman–Franck–Condon overlap and appears prominently in the resonance Raman spectrum of PBSQ. The CF stretch vibrations are expected[8,11,12] in the region 1200–1500 cm^{-1} but are not observed in the resonance-enhanced spectrum, indicating negligible mixing with the CO and CC modes and also a minimal role of the fluorine π electrons in the electronic excitation in resonance. In PBSQ the CH bonding mode (1161 cm^{-1}) derives its resonance Raman intensity from mixing in of the CC stretch character. In TFPBSQ the corresponding CF planar bend is expected to occur at ~270 cm^{-1}, as in some fluorinated benzenes,[8,11,12] but the Raman spectrum in this region could not be obtained because of strong scattered background. However, we observed a weak band at 1954 cm^{-1} which can

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be explained as a combination of the CC stretch (1677 cm^{-1}) with a 277-cm^{-1} vibration, which can be assigned to the CF planar bend. The apparent lack of resonance Raman enhancement of the ring breathing mode (not observed in either PBSQ or TFPBSQ) shows that the excited-state ordering of the $^{2}B_{1u}$ and $^{2}A_{u}$ states is not affected by the fluorine substitution and the electronic transition in resonance is $^{2}B_{3g}$–$^{2}B_{1u}$. The peak separation ~1475 cm^{-1} in the electronic absorption spectrum is assigned to the 8a frequency in the excited ($^{2}B_{1u}$) electronic state and is, as expected, slightly greater than the separation of 1394 cm^{-1} noted[4] for the protonated radical.

The present experiments demonstrate that it is possible to use photomultiplier detection methods to carry out time-resolved, resonance-enhanced Raman studies of radiation-produced radicals at times longer than ~ milliseconds. For experiments at shorter times one must use some form of a gated detector, such as is available with an OMA, to avoid saturation of the detection system by the Cerekov pulse. Use of a single-channel device allows the use of a double monochromator as the dispersive element and in certain cases has some advantage over the OMA at the expense of multichannel collection of data. In laser flash photolysis experiments it should be possible to use photomultiplier detection methods where the photolytic source can be discriminated against by filters or other methods.

Registry No. $C_6F_4(OH)_2$, 771-63-1; $C_6H_4O_2^{-}\cdot$, 3225-29-4; $C_6F_4O_2^{-}\cdot$, 42439-31-6; $C_6F_4O_2$, 527-21-9.

Pulse-Rate Effects in the Photochemistry of Gas-Phase Bromobenzene Ions. A Study of Ion Relaxation Mechanisms

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Two-proton photochemistry of gas-phase bromobenzene ion using a repetitively pulsed light source was studied in the ion cyclotron resonance (ICR) spectrometer and modeled by numerical integration of the kinetic equations. Theoretical modeling and experiment were in excellent agreement, showing as expected that effects of pulse rate depend strongly on the relation of pulse rate and ion relaxation rates. Effects attributable to infrared radiative relaxation of ions were clearly evident, and this relaxation was found to have a rate between 1 and 3 s^{-1}.

Introduction

It is easy to contain gas-phase ions in an ion trap for periods of many seconds or longer. This has opened the opportunity of studying photochemical and other reactive processes on a time scale of unprecedented slowness for laboratory study of isolated molecular species. Processes which have been of particular interest in these studies are slow relaxation processes of long-lived excited ions by collisional[1] or infrared-radiative[2] mechanisms.

An exceptionally interesting experiment is the sequential two-photon photodissociation of ions by a repetitively pulsed light source. Interpretation of such results is a demanding test of our understanding of the interplay of kinetic processes under isolated-ion conditions. In an earlier exploration of these possibilities, using iodobenzene ion,[3] the fundamental point was made that a periodically pulsed light source is equivalent to a continuous source when the pulse rate is faster than the fastest ion relaxation mechanism but that distinctive pulse-rate-dependent effects are expected for pulse rates slower than relaxation. Described here is a much more comprehensive examination of the photochemistry of bromobenzene ion with a pulsed light source, in which the interplay of periodic excitation, collisional and fluorescent relaxation, and finite ion trapping time is sorted out in some detail. It will be seen that our conceptual model of ion two-photon photochemistry gives an excellent quantitative understanding of these observations, and provides in addition a confirmation that the radiative relaxation rate of this ion, which has been controversial, is not faster than 3 s^{-1}.

The observation of infrared fluorescence from gas-phase molecules has a long history.[4,5] But for gas-phase ions, determination of the rate of radiative decay is not straightforward, and recently the process of two-photon photodissociation has been explored as an indirect route to characterizing radiative relaxation. Freiser and Beauchamp first observed and correctly interpreted two-photon dissociation in benzene ion.[6] Subsequent quantitative kinetic analyses of the process in cyanobenzene ion[7] and bromobenzene ion[2,8] made evident the possibility of exploiting such observations to characterize relaxation processes in excited ions. van Velzen and van der Hart[9] reported the first serious effort to separate out the radiative contribution to relaxation of excited ions, and calculated several radiative relaxation rates, including a value of 7 ± 3 s^{-1} for bromobenzene ion. The very high-quality data of this work showed deviations from simple two-photon kinetics, and a more complicated mechanism was postulated to account for the deviations. Values of 14 s^{-1} for

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