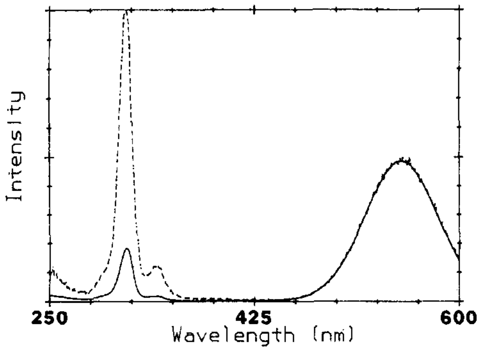

Figure 1. Excitation spectra of $Rh_2b_4^{2+}$ in CH_3CN at 20 °C taken with the emission monochromator set to observe the phosphorescence ($^3A_{2u} \rightarrow {}^1A_{1g}$, 800 nm, - - -) and the fluorescence ($^1A_{2u} \rightarrow {}^1A_{1g}$, 660 nm, —). The spectra are corrected for variations in the excitation light intensity, and the displayed intensity is arbitrary. The spectra have been scaled to give the same intensity at the maximum of the visible absorption peak (553 nm) for convenience of display.

of the fluorescent $^1A_{2u}$ state ($\phi_{ic} \approx 0.15$), yet it does not appreciably decrease the quantum yield of the phosphorescence. This implies that there is a highly efficient intersystem crossing pathway somewhere above the relaxed $^1A_{2u}$ state. Indeed, in $Rh_2b_4^{2+}$ it is reasonable to expect facile intersystem crossing from ^1E_u to ^3E_u, as these states have been shown to be strongly spin-orbit coupled.[3,9,21] Though it is less obvious why there would be such large spin-orbit coupling in these cases, it is possible that the intersystem crossing occurs from a ligand field state or a charge-transfer state which lies somewhere in energy between the ^1E_u state and the $^1A_{2u}$ state. Rice and Gray[3] have shown in polarized absorption spectra of single crystals of $(Rh_2b_4)[B(Ph)_4]_2$ that there are at least two weakly absorbing states whose energies lie between the two strongly absorbing states.

The low internal conversion yield after excitation into the ^1E_u absorption has been confirmed by transient absorption experiments. Excitation of $Rh_2b_4^{2+}$ with a 7-ns, 532-nm pulse from a Nd:YAG laser gives transient absorption which occurs during the laser pulse and which has been assigned as due to absorption from the lowest excited singlet state to upper singlet states ($^1A_{2u} \rightarrow S_n$).[12] This is followed by longer lived absorption which is due to absorption from the lowest triplet ($^3A_{2u}$) to higher triplet states.[1,2] Upon excitation at 355 nm with the same optical geometry, optical density of sample at the exciting wavelength, and number of photons per pulse, the longer lived excited triplet-state absorption signal size is the same to within 10%. However, here no obvious excited singlet-state absorption is seen to occur during the laser pulse. From the lack of clear singlet excited-state absorption signal upon excitation at 355 nm, it can be estimated that the $^1A_{2u}$ population is at least 5 times smaller that the $^1A_{2u}$ population resulting from 532-nm excitation. This is further evidence that upper state excitation does not lead to efficient population of the lowest singlet while it does lead to efficient population of the lowest triplet.

Attempts were made to observe emission directly from the upper excited states, ^1E_u and ^3E_u, by exciting directly into the ^1E_u state at 318 nm. However, the emission signal was impossible to differentiate from emission from ultraviolet-absorbing impurities and scattering from the sample and solvent. Thus, the 532-nm line from the Nd:YAG laser was used to initiate sequential two-photon absorption and subsequent emission. This technique has been shown to be more sensitive than direct one-photon absorption in the detection of weak emissions from upper excited states.[22-24] In the present case, $Rh_2b_4^{2+}$ in CH_3CN at 20 °C did not give emission between 320 and 390 nm which increased as the square of the laser power following excitation at 532 nm. Laser energies between 50 μJ/pulse and 5 mJ/pulse were used. From this and the lack of a clear signal upon direct excitation at 318 nm using a conventional fluorometer, the emission yield can conservatively be estimated to be less than 10^{-4}. This value, and the Strickler-Berg calculated lifetime, give an upper limit to the lifetime of the ^1E_u state of approximately 10^{-13} s.

Similar results as those discussed above were seen for the complex $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) both in fluid solution and in a low-temperature glass. This, and similar work on isoelectronic Ir(I) complexes,[25] show that in dinuclear d^8–d^8 complexes upper state intersystem crossing kinetically competes with internal conversion. Thus, the large spin-orbit coupling possible in transition-metal complexes can lead to very rapid intersystem crossing. It appears that the intersystem crossing rate varies by orders of magnitude within these complexes, depending on the state. For $Rh_2b_4^{2+}$ the intersystem crossing rate constant from the lowest singlet state ($^1A_{2u}$) is 8×10^8 s^{-1}, the reciprocal of the fluorescence lifetime, while the intersystem crossing rate constant is probably greater than 10^{13} s^{-1} for intersystem crossing from the ^1E_u upper excited state.

Acknowledgment. We thank Ms. Janet L. Marshall and Professor Harry B. Gray for useful discussions through the course of this work and the National Science Foundation for partial financial support (PMC83-17044).

---

(21) Isci, H.; Mason, W. R. *Inorg. Chem.* **1975**, *14*, 913.
(22) Orner, G. C.; Topp, M. R. *Chem. Phys. Lett.* **1975**, *36*, 295.
(23) Topp, M. R.; Lin, H.-L. *Chem. Phys. Lett.* **1977**, *47*, 442.
(24) Topp, M. R.; Lin, H.-R. *Chem. Phys.* **1981**, *60*, 47.
(25) Marshall, J. L., unpublished results.

Production of $HO_2\cdot$ in the Track of High-Energy Carbon Ions[1]

Jay A. LaVerne and Robert H. Schuler*

Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556
(Received: June 25, 1985)

The radiation chemical yields of $HO_2\cdot$ produced by irradiating water with ^{12}C ions of 37–100-MeV initial energy have been determined. These data have been combined with previous values for lower energy carbon and helium ions to obtain the differential yields over the range 2–102 eV/Å. The close similarity between the yields for helium and carbon ions of the same LET suggests that the reaction volume of interest extends somewhat beyond the track core, especially for helium. LET appears to be a useful parameter to describe the production of $HO_2\cdot$ in the tracks of heavy particles.

Recently we have reported measurements on the radiation chemical production of $HO_2\cdot$ from water in the track of carbon ions with energies up to 35 MeV.[2] The differential $HO_2\cdot$ yield observed at 25 MeV, where the LET (linear energy transfer) for

0022-3654/85/2089-4171$01.50/0 © 1985 American Chemical Society

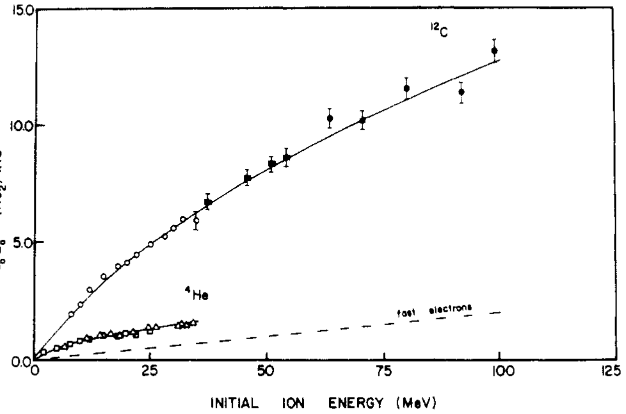

Figure 1. Yield of $HO_2\cdot$ (G_0E_0) as a function of initial ion energy (E_0) for (●) ^{12}C, this work; (○) ^{12}C and (□) ^4He, ref 2; (△) ^4He ref 7. The dashed line gives the yield of $HO_2\cdot$ for fast electrons ($G(HO_2\cdot) = 0.020$; ref 5). Error limits, as indicated in this work, correspond to an uncertainty in particle range of ±0.3 mg/cm² and oxygen analysis of ±4%.

carbon ions is 52 eV/Å, is 0.15. This yield is about a factor of 2 lower than at the Bragg peak of carbon ions but still considerably higher than the yield of 0.02 found with fast electrons.[3-5] This observed decrease in yield with increased particle energy is less pronounced than for H_2 production from benzene,[6] indicating that, in the present case, the yield is less critically dependent on initial local deposition of energy within the track. In order to understand these track processes in more detail it becomes important to extend previous studies to more energetic heavy ions having lower LET's. We have initiated such a program to examine radiation chemical processes with the heavy ions available at the Argonne National Laboratory ATLAS facility and report here initial studies on $HO_2\cdot$ production from water in the tracks of carbon ions with energies up to 100 MeV.

The methods used here are essentially identical with those of our previous study.[2] Particle currents of 1 nA of fully stripped carbon ions ($^{12}C^{6+}$) with energies up to 110 MeV accelerated at ATLAS were used. Ion energy was determined to ±0.3 MeV before each run by using a solid-state detector on a portion of the beam elastically scattered with a gold foil. The solid-state detector was calibrated by using a magnetically analyzed particle beam whose energy was determined absolutely in terms of the magnetic parameters. Dosimetry was in terms of the integrated current and particle energy after taking into account energy loss in the window system and is, in general, known absolutely to ±3%. $HO_2\cdot$ production was determined from measurements of the O_2 yield from 10 mM cupric sulfate–1 mM ferrous sulfate solutions in 10 mN H_2SO_4 solutions using triply distilled water. Molecular oxygen was determined by bubbling helium through the radiolysis cell and through a Hersch electrochemical cell. The Hersch cell current was integrated after each irradiation to give a measure of the total oxygen produced to ±4%.

The $HO_2\cdot$ produced per particle (G_0E_0) is given in Figure 1 as a function of carbon ion energy. Figure 1 also shows results previously reported for low-energy carbon ions[2] and helium ions.[2,3,7] The present determination of the yield for 37 MeV carbon ions (0.18 molecules/100 eV) agrees within experimental error with values obtained at the Notre Dame heavy ion accelerator and it is seen in Figure 1 that the present results smoothly extend those of the previous study. Of particular importance is the slope of the plot of Figure 1 which gives the differential yield, G_i = ($d(G_0E_0/dE_0)$), for carbon ions with LET's over the range 20–100 eV/Å. The combined data were fitted by using polynomial regression methods to give an approximate dependence of G_i as a function of LET. This dependence was then adjusted to optimize overall agreement between the experimental results and the integral $\int_0^{E_0} G_i \, dE$ which is shown as a solid line in Figure 1. The resultant differential yields are plotted as a function of LET in Figure 2 and compared with similar data for helium ions. For ions having an LET of 20 eV/Å the differential yield for carbon ions (0.084) is only slightly lower than for helium ions (0.109) but still a factor of 4 higher than for fast electrons. It is seen that track effects are still very important for carbon ions having LET's in the 20 eV/Å range.

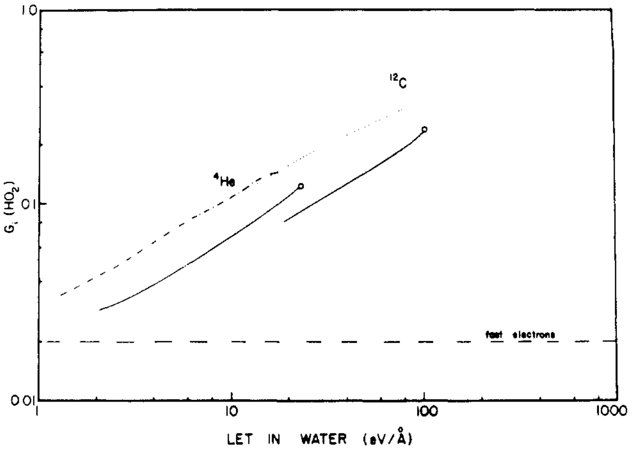

Figure 2. Differential $HO_2\cdot$ yield, G_i, as a function of LET for carbon and helium ions as determined from the slopes of Figure 1. The open points represent G_i at the Bragg maxima. The dashed line shows the limiting fast electron value. The differential $HO_2\cdot$ yield pertinent to the core is shown as a function of core LET by a dotted line for carbon and a dot-dashed line for helium ions.

The differential yields were corrected for the energy loss to high-energy δ rays which remove energy from the core but contribute only a minimum to $HO_2\cdot$ production.[8] For each track segment, δ rays were divided into several energy groups from 100 eV to the kinematic maximum and the fraction of energy loss to each group was calculated by using Rutherford cross sections. Secondary electrons of energy less than 100 eV were assumed to remain in the track and contribute to the core LET. A correction was made for the fraction of the energy of the more energetic secondaries which also contribute to the core. The total number of $HO_2\cdot$ radicals produced per unit track length was corrected for that produced by the δ rays, assuming 0.02 molecules/100 eV for the latter. The dependence of $G(HO_2\cdot)_C$ pertinent to the core is shown in Figure 2 as a function of energy remaining in the track core expressed in units of LET. It is very surprising that the core yields for carbon and helium ions at LET's of ~20 eV/Å are so similar when the radius of the track core of the carbon ion is approximately 3.6 times that of the helium ion.[6,9] For 2-MeV helium ions, because of the higher initial density of energy deposition, the initial concentration of radicals in the core should be more than an order of magnitude greater than the value of ~1 M estimated for 100 MeV carbon ions. However, this does not take into account the diffusion of precursors during $HO_2\cdot$ formation. The fact that the differential $HO_2\cdot$ yields are similar at a given LET shows that $HO_2\cdot$ production is not totally determined by the initial radical concentration within the track core, but rather that diffusion becomes important so that the reaction volume of interest extends somewhat beyond the track core, at least for helium. This result contrasts with the conclusions from studies of H_2 production from benzene.[6] Insofar as the present description is correct, LET is, in fact, a valid parameter to describe the phenomenology of radiation processes within heavy ion tracks.

---

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2733 from the Notre Dame Radiation Laboratory.

(2) LaVerne, J. A.; Burns, W. G.; Schuler, R. H. *J. Phys. Chem.* **1985**, *89*, 242.

(3) Baverstock, K. J.; Burns, W. G. *Nature (London)* **1976**, *260*, 316.

(4) Hart, E. J. *Radiat. Res.* **1955**, *2*, 33.

(5) Bjergbakke, E.; Hart, E. J. *Radiat. Res.* **1971**, *45*, 261.

(6) LaVerne, J. A.; Schuler, R. H. *J. Phys. Chem.* **1984**, *88*, 1200.

(7) Burns, W. G.; May, R.; Baverstock, K. F. *Radiat. Res.* **1981**, *86*, 1.

(8) Burns, W. G., private communication.

(9) Mozumder, A. *J. Chem. Phys.* **1974**, *60*, 1145.

J. Phys. Chem. 1985, 89, 4173–4175

Whether or not this is the case is, of course, determined by the lifetime of the reactants.

With further development of the ATLAS facility well-defined beams of carbon ions with energies up to 300 MeV, where the LET drops to $\sim$5 eV/Å, are expected to become available. We expect to extend our studies of track processes to these higher energy carbon ions and other massive ions in order to provide a more comprehensive picture of the radiation chemistry of water and aqueous systems.

Acknowledgment. We thank the operators of the ATLAS facility at Argonne National Laboratory for the accelerator operations and especially Dr. B. Glagola for his assistance with the energy measurements.

High Resolution Overtone Spectroscopy of H_2O in a Molecular Beam

C. Douketis, D. Anex, G. Ewing, and J. P. Reilly*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405 (Received: August 9, 1985)

$\Delta v = 4$ overtone transitions of water vapor have been observed in a supersonic molecular beam under conditions in which Doppler broadening is dramatically reduced yielding spectral line widths of 3 MHz. This experiment demonstrates that it is possible to spectrally interrogate molecular overtone line shapes under reduced congestion conditions with extremely high resolution.

The study of vibrational overtones in the ground electronic states of molecules is a well documented and rich area of molecular spectroscopy.[1] Research in this field extends back a full century.[2-8] Quite recently there has been renewed experimental interest in molecular overtones.[9-18] Several new methods, many of them based on laser light sources, have been developed to monitor these transitions. Recent theoretical interest in overtones has focussed on comparing local and normal-mode models for describing the vibration of polyatomic molecules, and on understanding the dynamics of molecules subsequent to their excitation.[19-31] This understanding should provide insight into related phenomena such as intramolecular energy redistribution, predissociation, gas–surface desorption, bond-selective photochemical processes, and infrared multiphoton absorption.

Molecules whose high overtone spectra have been studied thus far can be roughly divided into two groups: those that exhibit sharp (i.e., rotationally resolved) overtone rovibronic structure and those that exhibit broad contours. The former class includes diatomic molecules, C_2H_2, CH_4, NH_3, and H_2O, while the latter includes larger alkanes, alkenes, and aromatic molecules. One of the fundamental issues in this field involves the mechanistic origin of the broad overtone bands. Spectral congestion resulting from the high densities of rotational and vibrational states certainly must play a role. It has been hypothesized that the dominant reason why many line widths are so broad is that the lifetimes of these highly vibrationally excited molecules are ultrashort.[13] Alternatively one might suggest that Fermi resonance among myriad high vibrational levels of large molecules results in a distribution of oscillator strength over many overlapping transitions to produce unresolved diffuse overtone bands. Coupling between rotational and vibrational motions, which apparently affects radiationless relaxation rates,[32,33] may play an important role in determining overtone spectral structure. Two other sources of line broadening are dependent upon experimental conditions. Collisional broadening has generally been a factor in overtone spectroscopy particularly since the weakness of overtone absorption line strengths has led many researchers to study samples at either high gas-phase pressures or in condensed phases. However, with the development of ultrasensitive photoacoustic techniques, this problem has been overcome and overtone spectra of several molecules have been recorded under low pressure conditions. In contrast, Doppler broadening has never been eliminated from a high overtone absorption experiment. While the Doppler width of a single rovibrational line is in general quite narrow, overlapping of hundreds or thousands of closely spaced Doppler broadened

---

*Alfred P. Sloan Fellow and Camille & Henry Dreyfus Teacher Scholar

(1) G. Herzberg, "Molecular Spectra and Molecular Structure", Part II, Van Nostrand, New York, 1945.

(2) W. J. Russell and W. Lapraik, *J. Chem. Soc.*, **39**, 168 (1881).

(3) J. W. Ellis, *J. Opt. Soc. Am.*, **8**, 1 (1924).

(4) (a) R. Mecke, *Z. Phys.* **81**, 313 (1933); (b) W. Baumann and R. Mecke, *Z. Phys*, **81**, 445 (1933); (c) K. Freudenberg and R. Mecke, *Z. Phys.*, **81**, 465 (1933).

(5) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **8**, 469 (1936).

(6) G. Herzberg, F. Patat, and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937).

(7) E. H. Eyster, *J. Chem. Phys.*, **6**, 580 (1938).

(8) H. W. Thompson, *J. Chem. Phys.*, **7**, 453 (1939).

(9) The number of research groups working in this area is large. References 10–18 are representative of their work and contain extensive reference lists.

(10) (a) B. R. Henry, *Acc. Chem. Res.*, **10**, 207 (1977); (b) B. R. Henry, *J. Phys. Chem.*, **80**, 2160 (1976).

(11) R. L. Swofford, M. E. Long, and A. C. Albrecht, *J. Chem. Phys.*, **65**, 179 (1976).

(12) G. Stella, J. Gelfand, and W. K. Smith, *Chem. Phys. Lett.*, **39**, 146 (1976).

(13) R. G. Bray and M. J. Berry, *J. Chem. Phys.*, **71**, 4909 (1979).

(14) J. W. Perry and A. H. Zewail, *J. Chem. Phys.*, **70**, 582 (1979).

(15) G. A. West, R. P. Mariella, J. A. Pete, W. B. Hammond, and D. F. Heller, *J. Chem. Phys.*, **75**, 2006 (1981).

(16) J. S. Wong and C. B. Moore, *J. Chem. Phys.*, **77**, 603 (1982).

(17) G. J. Scherer, K. K. Lehmann, and W. Klemperer, *J. Chem. Phys.*, **78**, 2817 (1983).

(18) H. L. Fang, D. Meister, and R. L. Swofford, *J. Phys. Chem.*, **88**, 405 and 410 (1984).

(19) (a) W. Siebrand, *J. Chem. Phys.*, **46**, 330 (1967); **47**, 2411 (1967); (b) W. Siebrand and D. F. Williams, *J. Chem. Phys.* **49**, 1860 (1968); (c) B. R. Henry and W. Siebrand, *J. Chem. Phys.*, **49**, 5369 (1968).

(20) R. Wallace, *Chem. Phys.*, **11**, 189 (1975).

(21) M. L. Elert, P. R. Stannard, and W. M. Gelbart, *J. Chem. Phys.*, **67**, 5395 (1977).

(22) R. T. Lawton and M. S. Child, *Mol. Phys.*, **37**, 1799 (1979).

(23) (a) D. F. Heller, *Chem. Phys. Lett.*, **61**, 583 (1979); (b) D. F. Heller and S. Mukamel, *J. Chem. Phys.* **70**, 463 (1979).

(24) E. J. Heller and W. M. Gelbart, *J. Chem. Phys.*, **73**, 626 (1980).

(25) C. Jaffe and P. Brumer, *J. Chem. Phys.*, **73**, 5646 (1980).

(26) M. L. Sage and J. Jortner, *Adv. Chem. Phys.*, **47**, 293 (1981).

(27) (a) E. L. Sibert, III, W. P. Reinhardt, and J. T. Hynes, *J. Chem. Phys.*, **77**, 3583 and 3595 (1982); (b) E. L. Sibert, III, W. P. Reinhardt, and J. T. Hynes, *Chem. Phys. Lett.*, **92**, 455 (1982).

(28) I. Abram, A. de Martino, and R. Frey, *J. Chem. Phys.*, **76**, 5727 (1982).

(29) A. A. Ovchinnikov and N. S. Erikhman, *Sov. Phys. Usp.*, **25**, 738 (1982).

0022-3654/85/2089-4173$01.50/0