J. Phys. Chem. **1982**, *86*, 900-903

Hydrogen Bonding. 13. Infrared Study of the HF_2^- Anion in *p*-Toluidinium and Tetraalkylammonium Hydrogen Difluorides

Kenneth M. Harmon* and Ronald R. Lovelace

Department of Chemistry, Oakland University, Rochester, Michigan 48063 (Received: June 24, 1981)

The use of isotopic dilution has allowed analysis of the infrared spectrum of the HF_2^- ion in tetramethylammonium hydrogen difluoride. The F–H–F hydrogen bond in this salt is stronger than that in potassium hydrogen difluoride. This conflicts with published thermochemical data; however, this contradiction may be resolved when lattice expansion and cation-to-anion hydrogen-bonding effects are considered. The $C_{\infty v}$ HF_2^- ion in *p*-toluidinium hydrogen difluoride shows much weaker hydrogen bonding than the $D_{\infty h}$ ions in the potassium and tetramethylammonium ion salts, and an infrared spectrum similar to those of the unsymmetrically hydrogen-bonded $H_2F_3^-$, $H_3F_4^-$, and $H_4F_5^-$ ions.

Introduction

Potassium hydrogen difluoride has been extensively studied by a wide variety of spectroscopic, diffraction, and thermochemical techniques.[1] The crystal structure is similar to that of cesium chloride; each HF_2^- ion has eight potassium ion neighbors, four associated with each fluorine. The ion has $D_{\infty h}$ symmetry and lies at a D_{4h} site; under these selection rules the antisymmetric stretching ($\nu_3(a_{2u})$) and bending ($\nu_2(e_u)$) bands are observed[2] at 1473 and 1233 cm^{-1}, respectively (Figure 1), while the symmetric stretching band ($\nu_1(a_{1g})$) is forbidden. The symmetric stretch may be seen in the Raman spectrum[3] at 600 cm^{-1}.

Neutron diffraction studies[4] show that the HF_2^- ion in *p*-toluidinium hydrogen difluoride has $C_{\infty v}$ symmetry with one short and one long F–H distance; this ion lies at a C_1 site, so all vibrations are allowed and the degeneracy of the bending band is lifted.[5] This ion shows a very broad antisymmetric stretch centered at 1730 cm^{-1}, two bending bands at 1195 and 1122 cm^{-1}, and a band associated with the F···F motion at 527 cm^{-1} (Figures 1 and 2; Table I).

We previously noted[6] that tetrapropylammonium hydrogen difluoride appeared to give a third type of HF_2^- spectrum and tentatively assigned a band at 1915 cm^{-1} to ν_3 and bands at 1315 and 1255 cm^{-1} to ν_2. The infrared spectrum (Figure 1) is, at first examination, significantly different from that of either of the salts discussed above.

We recently observed that tetramethylammonium hydrogen difluoride has (Figure 3A) an infrared spectrum essentially identical—with the exception of cation bands—with that of the tetrapropylammonium ion salt. The hydrogen-bond energy of the HF_2^- ion in tetramethylammonium hydrogen difluoride was reported as 155 kJ mol^{-1} by Harrell and McDaniel from vapor pressure measurements,[7] and this has been taken as the standard experimental value against which calculations of hydrogen-bond energy in other salts such as potassium hydrogen difluoride are compared.[1] It is thus critical to determine whether the ions in the tetramethylammonium and potassium salts are actually different types; if they do not have the same structure, comparisons of calculated and experimental energies would not be meaningful. This work was carried out to investigate the nature of the HF_2^- ion in tetramethylammonium hydrogen difluoride.

TABLE I: Low-Temperature Infrared Spectra of Unsymmetrically Hydrogen-Bonded Complex Hydrogen Fluoride Anions[a-c]

ion	temp, K	FHF stretch	FHF bend	F···F stretch
HF_2^-	10[d,e]	1730 (bs)	1195 (s), 1122 (s)	527 (vs)
$H_2F_3^-$	12[f]	1800 (bs)	1115-1000[g]	490 (sh), 460 (vs)
$H_3F_4^-$	18[f]	1750 (bs)	1200-1000[h]	480 (sh), 450 (vs)
$H_4F_5^-$	14[f]	1780 (bs)	1200-875[i]	455 (vs), 409 (vs)

[a] Nujol mulls on AgCl plates with KBr windows. [b] Units are cm^{-1} (wavenumbers). [c] Symbols used: broad, b; strong, s; very strong, vs. [d] For *p*-toluidinium hydrogen difluoride. [e] Also shows $2\nu_2$ at 2424 and 2259 cm^{-1}. [f] For potassium ion salts; for complete vibrational analysis and band assignments see ref 9. [g] Four bands. [h] Six bands. [h] Eight bands.

Experimental Section

Alfa potassium hydrogen difluoride was used as supplied. Tetrapropylammonium[6] and *p*-toluidinium[5] hydrogen difluorides were prepared as previously described. Tetramethylammonium hydrogen difluoride was prepared by carefully neutralizing a portion of Eastman Kodak tetramethylammonium hydroxide (10% in H_2O) with hydrofluoric acid and then adding an additional portion of hydrofluoric acid equal to the first. Water was removed in vacuo, and the crystals were dried for 5 days in vacuo at 65 °C; titration showed $(CH_3)_4NF{\cdot}0.95HF$. Tetramethylammonium hydrogen-*d* difluoride was prepared by reacting tetramethylammonium chloride with silver oxide in D_2O to give a solution of the deuteriooxide and then treating this solution as above with DF in D_2O. The infrared spectrum of the dried crystals was identical with that of the hydrogen difluoride with expected isotope shifts. An isotope-diluted sample of tetramethylammonium hydrogen difluoride was prepared by dissolu-

---

(1) For a recent review, see J. Emsley, *Chem. Soc. Rev.*, **9**, 91 (1980), and reference therein.

(2) L. Jones and R. A. Penneman, *J. Chem. Phys.*, **22**, 781 (1954).

(3) P. Dawson, M. M. Hargreave, and G. R. Wilkinson, *Spectrochim. Acta, Part A*, **31**, 1055 (1975).

(4) J. M. Williams and L. F. Schneemeyer, *J. Am. Chem. Soc.*, **95**, 5780 (1973).

(5) K. M. Harmon, S. L. Madeira, and R. W. Carling, *Inorg. Chem.*, **13**, 1260 (1974).

(6) K. M. Harmon, I. Gennick, S. L. Madeira, and D. L. Duffy, *J. Org. Chem.*, **39**, 2809 (1974).

(7) S. A. Harrell and D. H. McDaniel, *J. Am. Chem. Soc.*, **86**, 4497 (1964).

0022-3654/82/2086-0900$01.25/0

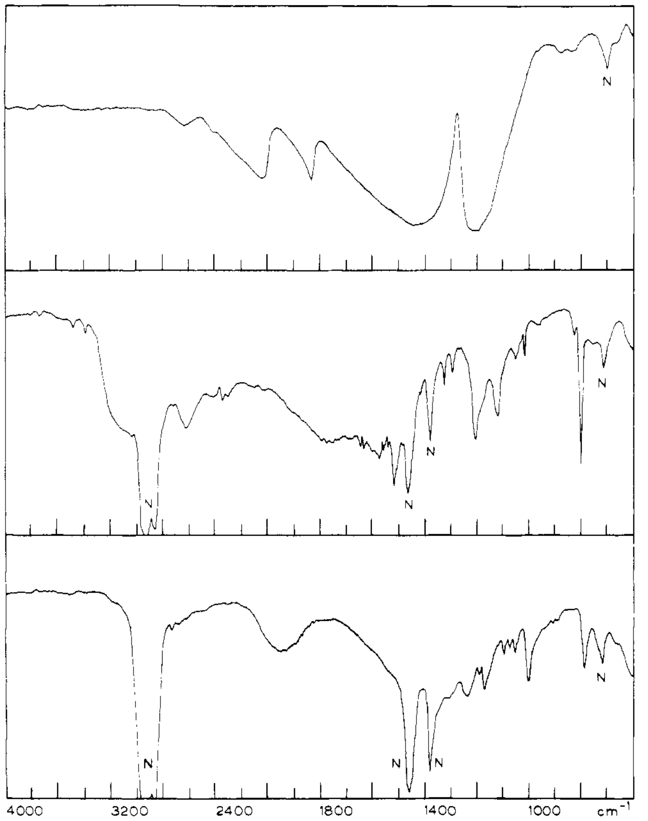

Figure 1. Infrared spectra of hydrogen difluoride salts: (top) potassium (Fluorolube mull above 1300 cm^{-1} and Nujol mull below 1300 cm^{-1} on AgCl plates), (center) *p*-toluidinium (Nujol mull on AgCl plates), and (bottom) tetrapropylammonium (Nujol mull on NaCl plates). Peaks marked N are from Nujol. Ordinate in %*T*.

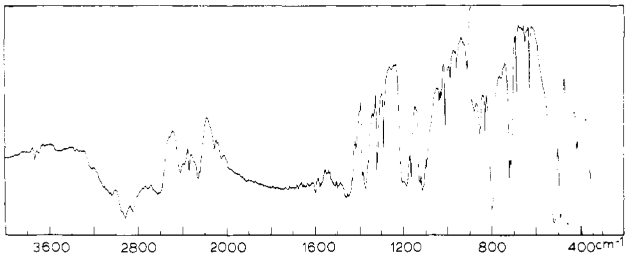

Figure 2. Infrared spectrum at 10 K of *p*-toluidinium hydrogen difluoride (Nujol mull on AgCl plates with KBr windows). Oridnate in %*T*.

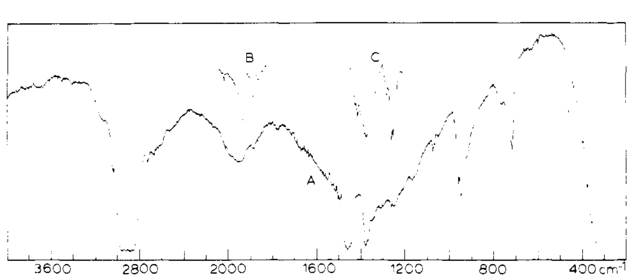

Figure 3. Infrared spectra of tetramethylammonium hydrogen difluoride: (A) pure sample (Nujol mull), (B) isotopically diluted sample (Nujol mull), and (C) isotopically diluted sample (hexachlorobutadiene mull). All spectra on AgCl plates at 300 K. Ordinate in %*T*.

tion of the salt in a 1:9 H_2O-in-D_2O mixture, which was then dried as above. Tetramethylammonium bromide and hexabromostannate were prepared as previously described.[8]

Teflon, polyethylene, or stainless-steel lab ware was used at all times. All operations were carried out in a glovebox under dry nitrogen. Infrared spectra were recorded on Beckman IR-33 and Perkin-Elmer Model 283 spectrophotometers. A Displex CSW-202 two-stage helium refrigerator was used for the low-temperature spectrum.

Results and Discussion

p-Toluidinium Hydrogen Difluoride. We have previously reported[9] detailed correlation of low-temperature infrared spectra with crystal structure for potassium dihydrogen trifluoride, trihydrogen tetrafluoride, and tetrahydrogen pentafluoride. The anions in these salts consist respectively of two, three, and four hydrogen fluorides bound to central fluoride by unsymmetrical (proton closer to terminal fluorine) hydrogen bonds. The FHF stretching region of all of these ions is a broad, featureless absorption centered between 1800 and 1700 cm^{-1}, which is unchanged on cooling to 12–18 K. The FHF bending regions of these ions resolve at 12–18 K into complex sets of lines whose patterns are determined by ion point and site symmetry; these bending bands are found variously in the 1100–900-cm^{-1} region. The symmetric F···F stretching modes of these ions appear as weak bands between 500 and 400 cm^{-1}, which become much more intense on cooling.

The infrared spectrum of the hydrogen difluoride ion in *p*-toluidinium hydrogen difluoride (Figures 1 and 2; Table I) is extremely similar to those of the dihydrogen trifluoride, trihydrogen tetrafluoride, and tetrahydrogen pentafluoride ions and also shows identical effects on cooling. The broad ν_3 band remains unchanged at 10 K, ν_2 is sharply resolved, and ν_1 increases dramatically in intensity. The spectral characteristics of the hydrogen difluoride ion in *p*-toluidinium hydrogen difluoride demonstrate this ion to be the first member of the sequence of unsymmetrically hydrogen-bonded ions, $HF_2^-(C_{\infty v})$, $H_2F_3^-(C_{2v})$, $H_3F_4^-(C_{3v})$, and $H_4F_5^-(T_d)$, which consists of progressively one to four hydrogen fluorides H-bonded to a "central" fluoride. This confirms the unsymmetrical nature of the ion, as determined by Williams and Schneemeyer,[4] in contrast to other claims, based on NMR[10] and X-ray[11] studies, that the proton is centered.

Tetramethylammonium Hydrogen Difluoride. Published spectra of potassium hydrogen difluoride[12] show two prominent bands at 1473 cm^{-1} (ν_3) and 1233 cm^{-1} (ν_2). Tetrapropylammonium,[6] tetraethylammonium,[14] and tetramethylammonium hydrogen difluorides also show two prominent anion absorptions, one near 1900 cm^{-1} and one near 1300 cm^{-1}. This led to the original assignment[6,14] of the 1900-cm^{-1} band to ν_3 and of the 1300-cm^{-1} band to ν_2. A shift of ν_3 from 1473 cm^{-1} in the potassium salt to near 1900 cm^{-1} in the tetraalkylammonium ion salts would indicate that the F–H–F hydrogen bond in the latter is weaker, in accord with thermochemical data (see below); however, if this were true, ν_2 would be expected to lie at lower frequencies in the tetraalkylammonium ion salts, which is the opposite of what is observed.

We now propose an alternative explanation of the tetraalkylammonium hydrogen difluoride spectra. In addition to the prominent ν_3 and ν_2 bands, the hydrogen difluoride

---

[8] K. M. Harmon, I. Gennick, and S. L. Madeira, *J. Phys. Chem.*, **78**, 2585 (1974).

[9] K. M. Harmon and I. Gennick, *J. Mol. Struct.* **38**, 97 (1977).

[10] J. Cousseau, L. Gouin, E. K. C. Pang, and J. A. S. Smith, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1015 (1977).

[11] W. A. Denne and M. F. Mackay, *J. Cryst. Mol. Struct.*, **1**, 311 (1971).

[12] For example, see ref 3 and 13.

[13] J. A. A. Ketelaar and W. Vedder, *J. Chem. Phys.*, **19**, 654 (1951).

[14] I. Gennick, K. M. Harmon, and J. Hartwig, *Inorg. Chem.*, **16**, 2241 (1977).

TABLE II: Vibrational Assignments for the $D_{\infty h}$ HF_2^- Ion in Various Salts[a,b]

vibration[c]	assignment[c]	$K^+HF_2^-$	$(C_3H_7)_4N^+HF_2^-$	$(CH_3)_4N^+HF_2^-$ [d]	$(CH_3)_4N^+DF_2^-$	ν_H/ν_D [e]
ν_{comb}	$(\nu_3 + \nu_1)$	2045 (w)	1960 (sh)	2038 (w)	f	
ν_{comb}	$(\nu_2 + \nu_1)$	1838 (w)	1915 (bs)	1933-1888 (s)	f	
$\nu_3(\sigma_u^+)$	FHF str	1473 (vs)	1315 (vs)[g]	1376 (vs)	977 (vs)	1.41
$\nu_2(\pi_u)$	FHF bend	1233 (vs)	1255 (vs)[g]	1264-1255 (vs)	900 (vs)	1.40
$\nu_1(\sigma_g^+)$	F···F str	600[h]	650[i]	650[i]	j	

[a] See footnotes a-c of Table I. [b] Additional symbols: weak, w; shoulder, sh. [c] Assignments from ref 3 and 13. [d] For isotopically diluted sample. [e] For tetramethylammonium hydrogen difluoride only. [f] Not observed, masked by cation and/or Nujol absorptions. [g] Approximate position, spectrum not well resolved. [h] From Raman spectrum.[3] [i] Inactive band, position inferred from combination bands. [j] Not observed.

ion in potassium hydrogen difluoride shows[2,13] two weak combination bands at 2045 and 1838 cm^{-1}. These bands, which are normally of very low intensity, show clearly in the spectrum of potassium hydrogen difluoride in Figure 1, which was taken of an extremely concentrated sample. This suggests that the 1900-cm^{-1} band in the tetraalkylammonium hydrogen difluorides might arise from moderately intense combination modes and that the absorption in the 1300-cm^{-1} region represents both ν_3 and ν_2. If this were true, ν_3 has shifted to lower frequency and ν_3 to higher frequency in the tetraalkylammonium ion salt relative to the potassium salt, which would indicate that the F–H–F hydrogen bonds in the latter are stronger.

The absorptions shown by the hydrogen difluoride ion in tetramethylammonium hydrogen difluoride do not resolve or sharpen significantly at 10 K. Salthouse and Waddington[15] observed similar behavior in potassium hydrogen difluoride and have shown that the width of these absorptions arises from oscillator coupling in the crystalline solid. This suggested that greater resolution could be effected by observing the spectrum of tetramethylammonium hydrogen difluoride isolated in a matrix of tetramethylammonium hydrogen-*d* difluoride. This was realized; the spectrum of the isotopically diluted material (Figure 3, B and C) shows ν_3 at 1376 cm^{-1} and ν_2 as a narrowly cleaved doublet at 1264–1255 cm^{-1} and also shows resolution of the combination bands. Spectral assignments for tetrapropylammonium, tetramethylammonium, and potassium hydrogen difluorides are listed in Table II. The resolved infrared spectrum of the hydrogen difluoride anion in tetramethylammonium hydrogen difluoride is entirely consonant with $D_{\infty h}$ symmetry. The hydrogen bond in the ion in tetramethylammonium hydrogen difluoride appears to be somewhat stronger than that in potassium hydrogen difluoride; this is not unreasonable. In the potassium salt each fluorine is backed up by four close potassium ion neighbors; Coulombic interactions between the fluorines and the larger tetramethylammonium ions in tetramethylammonium hydrogen difluoride would be expected to be less, which would result in a greater F–H–F interaction.

Hydrogen-Bond Energy in Tetramethylammonium Hydrogen Difluoride. The observation that the hydrogen bond in tetramethylammonium hydrogen difluoride is similar to and probably stronger than the hydrogen bond in potassium hydrogen difluoride conflicts with published thermochemical data. Waddington[16] has used a Born–Haber cycle to calculate a value of 243 kJ mol^{-1} for the hydrogen bond in potassium hydrogen difluoride, and numerous other calculations[1,17] are in reasonable agreement with the magnitude of this figure. On the other hand, the experimental value of 155 kJ mol^{-1} found by Harrell and McDaniel[7] for the hydrogen bond in tetramethylammonium hydrogen difluoride is significantly less.

The following Born–Haber cycle can be written for the formation of a complex between a fluoride salt and a hydrogen fluoride molecule:

$$\begin{tikzcd}
A^+(g) + F^-(g) + HF(g) \arrow[r, shift left, "\Delta H^\circ_1"] \arrow[d, shift left, "\Delta H^\circ_2"] & A^+(g) + FHF^-(g) \arrow[l, shift left, "\Delta H^\circ_{-1}"] \arrow[d, shift left, "\Delta H^\circ_3"] \\
(A^+F^-)(s) + HF(g) \arrow[r, shift left, "\Delta H^\circ_4"] \arrow[u, shift left, "\Delta H^\circ_{-2}"] & (A^+FHF^-)(s) \arrow[l, shift left, "\Delta H^\circ_{-4}"] \arrow[u, shift left, "\Delta H^\circ_{-3}"]
\end{tikzcd}$$

We have previously[18] defined the differential lattice enthalpy, ΔH°_L, by the equation

$$\Delta H^\circ_4 = (\Delta H^\circ_3 - \Delta H^\circ_2) + \Delta H^\circ_1 = \Delta H^\circ_L + \Delta H^\circ_1 \qquad (1)$$

In their pressure studies Harrell and McDaniel assumed that ΔH°_L for the formation of solid tetramethylammonium hydrogen difluoride from solid tetramethylammonium fluoride and hydrogen fluoride gas was zero, and thus assumed that ΔH°_1, the hydrogen-bond energy of the hydrogen difluoride anion, was equal to ΔH°_4, the experimentally measured enthalpy change. We now know that this cannot be correct. For a metal fluoride, ΔH°_L is simply $U^\circ_{MF} - U^\circ_{MHF_2}$. However, for the formation of tetramethylammonium hydrogen difluoride, ΔH°_L consists of two terms, ΔU°, the Coulombic energy change from lattice expansion, and $\Delta H^\circ_{H\text{-bond}}$, the change in cation-to-anion hydrogen bonding. Thus, for the reaction

$$(CH_3)_4NF(s) + HF(g) = (CH_3)_4NHF_2(s)$$

we would write

$$\Delta H^\circ_4 = \Delta U^\circ + \Delta H^\circ_{H\text{-bond}} + \Delta H^\circ_1 \qquad (2)$$

In a comprehensive study of crystal structure–infrared spectral correlations,[8] we have shown that the cations are as close together as possible in tetramethylammonium bromide. The methyl groups are "dovetailed", and with the smaller chloride ion, and presumably with fluoride ion, the distance between cation centers does not diminish. However, with anions larger than bromide (r = 195 pm), such as iodide (r = 216 pm), perchlorate (r = 236 pm), or hexafluorosilicate (r = 306 pm), the cations move progressively farther apart. Since the hydrogen difluoride ion has a longitudinal radius of 249 pm, lattice expansion must occur for formation of the hydrogen difluoride from the fluoride, and ΔU° will be positive for this process.

Also, the cation in tetramethylammonium fluoride is very strongly hydrogen bonded to fluoride ion with what are apparently the strongest C–H···X hydrogen bonds yet

---

(15) J. A. Salthouse and T. C. Waddington, *J. Chem. Phys.*, **48**, 5274 (1968).

(16) T. C. Waddington, *Trans. Faraday Soc.*, **54**, 25 (1958).

(17) H. D. B. Jenkins and K. F. Pratt, *J. Chem. Soc., Faraday Trans. 2*, **73**, 812 (1977).

(18) K. M. Harmon, S. D. Alderman, K. E. Benker, D. J. Diestler, and P. A. Gebauer, *J. Am. Chem. Soc.*, **87**, 1700 (1965).

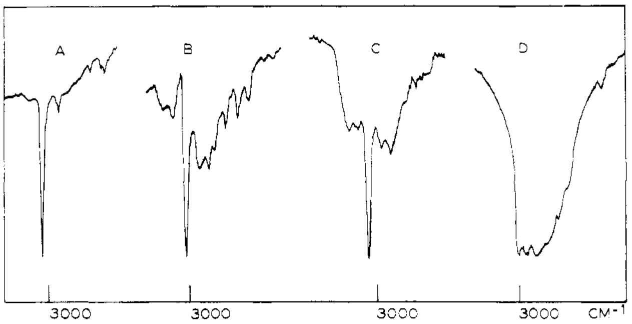

Figure 4. C–H stretching absorptions of non-hydrogen-bonded (A = $SnBr_6^{2-}$), weakly hydrogen-bonded (B = Br^-, C = HF_2^-), and very strongly hydrogen-bonded (D = F^-) tetramethylammonium ion salts (Fluorolube mulls on NaCl (A, B, D) and AgCl (C) plates).

observed.[8] The cation in tetramethylammonium hydrogen difluoride, however, is much more weakly hydrogen bonded to anion than in the fluoride (Figure 4); the cation-to-anion hydrogen bonding in the hydrogen difluoride is about the same as that in the bromide or perchlorate salts. The large loss of cation-to-anion hydrogen bonding will make $\Delta H^\circ_{\text{H-bond}}$ positive for the formation of tetramethylammonium hydrogen difluoride.

Since, in eq 2, both ΔU° and $\Delta H^\circ_{\text{H-bond}}$ are positive, ΔH°_1, the actual hydrogen-bond energy, must be negative and larger than -155 kJ mol^{-1}, the experimentally determined value of ΔH°_4.

It is not possible to quantify the exact value of ΔH°_1 for tetramethylammonium hydrogen difluoride at this time. Nevertheless, our observation of a very strong hydrogen bond in tetramethylammonium hydrogen difluoride is not obviated by the measurements of Harrell and McDaniel.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work, and to the Oakland University Research Committee, for additional support.

Comparison of Semiempirical Formulas for the Electric Field Dependence of Geminate Recombination Fluorescence[†]

J. K. Baird,[‡]

Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

J. Bullot, P. Cordier,*

Laboratoire de Chimie Physique des Matériaux Amorphes, Université de Paris Sud, Centre d'Orsay, 91405 Orsay, France

and M. Gauthier

ERA 718, Université de Paris-Sud, Centre d'Orsay, 91405 Orsay, France (Received: July 31, 1981)

The probability of recombination of geminate ions produced in photochemistry or radiation chemistry follows the predictions of the Onsager theory. According to the theory, an isolated pair starts from an initial separation r and subsequently executes a Brownian motion which leads either to recombination or to escape. To evaluate the recombination probability for an ensemble of pairs, as occurs in experiment, the Onsager recombination probability is averaged over a distribution function $\sigma(r)$. As the form of this function is not known a priori, various representations for it have been assumed in order to calculate the average. In this paper, we show that a more direct method is to assume an a priori functional dependence of the recombination probability $Q(0,E)$ on the magnitude E of an externally applied electric field. Forms for $Q(0,E)$ are more easily surmised from experimental data than are forms for $\sigma(r)$. Given a representation for $Q(0,E)$, we work backward to obtain expressions for the first k-moments of the function $4\pi r^2\sigma(r)\exp(-r_c/r)$. Here $r_c = e^2/\epsilon k_BT$ is the Onsager length, e is the electron charge, k_B is Boltzmann's constant, and ϵ and T are, respectively, the dielectric constant and absolute temperature of the fluid. As an example of our procedure, we analyze recent experimental data on geminate ion recombination fluorescence using two semiempirically derived representations for $Q(0,E)$. We determine the primary process quantum yield, the dissociation probability of the pair, and the first nine moments of the function written above. We compare our results with those obtained from two popular representations for $\sigma(r)$.

Introduction

The fate of electron–ion pairs produced by photolysis or radiolysis of solutions is determined by two effects: (i) diffusion and (ii) drift of the species under their mutual interaction and/or interaction with externally applied fields. Recent experiments on the electric field quenching of recombination fluorescence in photoionized doped nonpolar solutions have been explained within this framework.[1-5]

[†] Research sponsored by the office of Health and Environment Research, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation.

[‡] General Electric Company, Knolls Atomic Power Laboratory, Schenectady, NY 12301.

(1) J. Bullot, P. Cordier, and M. Gauthier, *Chem. Phys. Lett.*, **54**, 77 (1978).

(2) J. Bullot, P. Cordier, and M. Gauthier, *J. Chem. Phys.*, **69**, 1374 (1978).

0022-3654/82/2086-0903$01.25/0