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## Competition between hydrogen and deuterium abstraction by methyl radicals in isotopomerically mixed methanol glasses

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Rate parameters are reported for hydrogen and deuterium abstraction of methyl radicals embedded in glassy mixtures of CH<sub>3</sub>OH and CD<sub>3</sub>OD. The mole fraction of CH<sub>3</sub>OH in these isotopomeric mixtures is 0, 0.05, 0.075, 0.10, 0.15, or 1. The nonexponential time dependence of the radical concentration is analyzed in terms of distributions of first-order rate constants. For the isotopomerically pure matrices, lognormal distributions describe the decay satisfactorily. The large difference between characteristic H and D transfer rate constants indicates tunneling. In the mixtures, there is competition between H and D abstraction processes which depends on the local structure about a radical, so that the corresponding rate parameters contain information about this structure. On the basis of earlier work [J. Chem. Phys. 86, 6622 (1987)], the analysis begins with the assumption that the structure about a radical resembles one of the crystalline phases of methanol. The entire set of decay curves is described by a (disordered)  $\beta$ -phase structure in which the radical replaces a methanol molecule and is located near the position associated with a methyl group. However, this static picture is inadequate because the radical can diffuse through the glass on the time scale of the kinetic measurements. Diffusion allows the radical to encounter more CH<sub>3</sub>OH molecules than would be expected for the static structure on a statistical basis-the effective mole fraction of CH<sub>3</sub>OH in the mixtures is higher than the analytical concentration. For the  $x_{\rm H} = 0.05$ mixture, we estimate that on the average the radical encounters approximately 26 methanol molecules before abstraction occurs. This corresponds to diffusion over roughly 1100 pm through the lattice.

#### I. INTRODUCTION

This paper is part of a series<sup>1-8</sup> dealing with methyl radicals trapped in glassy methanol. These radicals decay by abstraction of a hydrogen atom from the methyl group of one of the surrounding methanol molecules thereby turning into methane

$$CH_3 + CL_3OL \rightarrow CH_3L + CL_2OL, L = H \text{ or } D.$$

The reaction proceeds by quantum-mechanical tunneling, as indicated by the large deuterium isotope effect on the rate. It may be monitored via the electron-spin resonance (ESR) signals of the radicals. In an earlier paper,<sup>4</sup> hereafter referred to as D1, we investigated the kinetics of the tunneling reaction, which is complicated by the inhomogeneity of the glass. In a sequel,<sup>8</sup> hereafter referred to as D2, we studied the structure of the glass by means of satellite lines in the ESR spectrum which arise through dipolar coupling of the unpaired electron spin with the nuclear spins of the surrounding methanol molecules. In the present paper, we study the abstraction kinetics in mixtures of normal and perdeuterated methanol in order to use

the competition between hydrogen and deuterium abstraction to gain more insight into the structure of the glass in the vicinity of the radical.

Early interest<sup>9-19</sup> in the methyl-methanol system arose because it provides a simple example of a hydrogen transfer by tunneling. Although there are simpler tunneling reactions, in general, they can only be studied at high temperatures. The theoretical description of low-temperature tunneling poses a special challenge because the usual semiclassical approach becomes questionable in the lowtemperature limit. The methyl-methanol system offers a number of practical advantages, but one major complication—the reaction proceeds nonexponentially in time, i.e., the methyl radical concentration c(t) decays according to

$$c(t) = c(0) \exp[-k(t)t], \qquad (1)$$

where k(t) is not constant, but decreases monotonically as t increases. Such "stretched" exponentials are typical for disordered materials, including glasses, and are clearly related to the structural inhomogeneity of the material.<sup>7</sup> In D1, we showed that the observed decay curves allowed a simple interpretation in terms of a distribution of rate constants. In this picture, the time dependence f(t)=c(t)/c(0) is simply the Laplace transform of the distribution of rate constants F(k),

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$$f(t) = \int_0^\infty F(k) \exp(-kt) dk.$$
 (2)

F(k) may be represented by a lognormal distribution, i.e.,

$$\Phi(\ln k) = \pi^{-1/2} k^{-1} \gamma^{-1} \exp\{-[\ln(k/\bar{k})\gamma]^2\}, \qquad (3)$$

where  $\gamma$  is the Gaussian half-width for the distribution of ln k. For tunneling reactions, the rate constant is expected to vary exponentially with the tunneling distance q, at least for a short range of tunneling distances

$$k(q) = \bar{k} \exp[-\lambda(q - \bar{q})], \qquad (4)$$

where  $\bar{k}$  is the rate constant corresponding to the average transfer distance  $\bar{q}$  and  $\lambda$  measures the sensitivity of k to changes in q. Thus  $\Phi(\ln k)$  in Eq. (3) can be turned into a distribution of transfer distances  $\phi(q)$  by replacing  $\gamma$  by  $\Gamma = \gamma/\lambda$ , where  $\Gamma$  is the Gaussian half-width of the distribution of transfer distances. This may be taken to indicate that at each radical site, the methyl hydrogen nearest to the radical is abstracted and that the distance of these nearest hydrogens is distributed normally in the glass. The time dependence of the radical concentration is then given by

$$f(t) = \pi^{-1/2} \gamma^{-1} \int_{-\infty}^{+\infty} \exp(-y^2/\gamma^2 - \bar{k}te^y) dy, \qquad (5)$$

where  $y = \ln(k/\bar{k}) = -\lambda(q-\bar{q})$ . This equation provides an excellent fit to the time dependence of the methyl radical concentration in glasses made from pure CH<sub>3</sub>OH or pure  $CD_3OD$ .<sup>4,5,7</sup> It allows us to extract the rate constant  $\overline{k}$  as a true constant and to study its dependence on temperature and isotopic species (H or D). In D1, the results so obtained were analyzed in terms of a golden-rule description of the transfer process. However, the fitting by means of Eq. (5) does not allow us to factor  $\gamma = \lambda \Gamma$  into its components  $\lambda$  and  $\Gamma$ . In D1,  $\lambda$  was evaluated numerically on the basis of the theoretical model and found to be about 0.61  $pm^{-1}$ . For an experimental evaluation, it would be necessary to vary the transfer distance q. This is accomplished, in principle, through the present experiments in which the methyl group closest to the methyl radical often carries deuterium, giving nonnearest hydrogens a chance to compete.

In order to use such kinetic information effectively, structural information will be needed. In D2, we concluded that the structure of the glass is locally similar to the structure of the crystalline  $\beta$  phase, which is itself orientationally disordered. Within this structure, the methyl radical was found to occupy on the average a position close to that of the methyl group of the methanol molecule it replaces. This picture allows us to calculate the average tunneling distance  $\bar{q}_j$  for the *j*th methyl hydrogen in the solvent shell closest to the radical. In principle, we can thus compute the transfer rate constant for each of these hydrogens and evaluate the resulting overall rate constant for each methyl radical site.

The purpose of the present paper is to probe the contributions of nonnearest neighboring hydrogens to the depletion of the radicals and to test the relevance of the proposed structure of the glass. To this end, we mix the methanol isotopomers CH<sub>3</sub>OH and CD<sub>3</sub>OD in such proportions that nonnearest hydrogens will be in competition with the nearest deuteriums. Again we follow the time dependence of the methyl radical signal f(t), but instead of considering a single distribution of rate constants F(k), we consider distributions associated with all hydrogens in the nearest solvent shell. A similar albeit less elaborate approach was taken previously in support of a  $t^{1/2}$  law for stretched exponential decay.<sup>20</sup>

## II. DISPERSIVE KINETICS IN A MIXTURE OF ISOTOPOMERS

If the local structure of the glass is uniform, every methyl radical is surrounded by N potentially reactive methanol molecules. The introduction of dispersion in the number of molecules was considered but rejected because it conflicts with the assumed local structure. Each molecule can be characterized by its distance from the radical, which is taken to be the  $C \cdots C$  internuclear separation. If the glass is made from a pure methanol isotopomer, either  $CH_3OH$  or  $CD_3OD$ , all N positions must be occupied by this isotopomer. However, if the glass is made from a mixture of isotopomers with mole fractions  $x_{\rm H}$  of CH<sub>3</sub>OH and  $x_{\rm D} = 1 - x_{\rm H}$  of CD<sub>3</sub>OD, some positions, say *n*, will be occupied by CH<sub>3</sub>OH, while the other N-n are occupied by  $CD_3OD$ . The probability that a cage comprised of N molecules contains  $n \, \text{CH}_3\text{OH}$  molecules is given by the binomial distribution

$$\alpha(n) = \binom{N}{n} x_{\rm H}^n (1 - x_{\rm H})^{N - n}, \tag{6}$$

where  $\binom{N}{n} = N!/n!(N-n)!$ , the binomial coefficient. The time decay of the methyl radical concentration is an average over all possible sites, which may be written as

$$f(t) = \sum_{n=0}^{N} \alpha(n) \widetilde{f}_n(t), \tag{7}$$

where  $\tilde{f}_n(t)$  is a decay function which describes all of the radicals that are surrounded by  $n \text{ CH}_3\text{OH}$  molecules and  $N-n \text{ CD}_3\text{OD}$  molecules.

To describe the N+1 functions  $\tilde{f}_n(t)$ , we note that there is a decay function associated with each of the Npositions about the radical. Each of the n CH<sub>3</sub>OH molecules may occupy any one of these positions, which yields  $\binom{N}{n}$  distinct occupation schemes for the solvent cage. To each of these spatial arrangements, there corresponds an overall rate constant that represents competition between the possible abstraction reactions

$$\cdot$$
 CH<sub>3</sub>+CH<sub>3</sub>OH  $\rightarrow$  CH<sub>4</sub>+  $\cdot$  CH<sub>2</sub>OH

and

$$\cdot$$
 CH<sub>3</sub>+CD<sub>3</sub>OD  $\rightarrow$  CH<sub>3</sub>D+  $\cdot$  CD<sub>2</sub>OD.

The maximum number of reactions possible is 3N, i.e., one for each methyl hydrogen of N molecules. Although exchange of the hydroxyl hydrogen is facile in the liquid, its abstraction is not important according to the experimental evidence<sup>4</sup> and is indeed less favorable thermodynamically.<sup>21–23</sup> If only two reactions were in competition, the overall rate constant would be the sum of the individual rate constants  $k_1+k_2$ . Dispersion in the transfer distance creates a distribution of rate constants for each reaction and the analog of the sum of discrete rate constants is the convolution of the distributions  $F_1(k)$  and  $F_2(k)$ , namely,

$$\widetilde{F}(k) = \int_0^k F_1(k-\kappa)F_2(\kappa)d\kappa = F_1 * F_2.$$
(8)

In the case of two discrete rate constants,  $k \approx k_1$  if  $k_1 \gg k_2$ . Similarly,  $\widetilde{F}(k) \approx F_1(k)$  if the rate constant distribution  $F_2$  corresponds to processes much slower than those described by  $F_1$  or, more precisely, if  $F_1(k-\kappa) \approx F_1(k)$  for all  $\kappa \leqslant k$ , i.e., all  $\kappa$  that contribute to the integral in Eq. (8).

It would seem that very many distributions, namely 3N, must be convolved even if the hydroxyl hydrogens are excluded, but this is unnecessary. Because the abstraction rate constant is a sensitive function of the transfer distance, the more distant hydrogens will not be reactive and can be excluded from consideration. If only M of the 3N hydrogens compete to react with the trapped radical, the overall rate constant distribution is a convolution of the M individual distributions. Furthermore, it is possible that some of the M hydrogens may belong to the same methanol molecule, in which case their isotopic nature is fixed once the identity of any one is known. The number of unique combinations of isotopomers remains unaffected because it is determined by the numbers of CH<sub>3</sub>OH and CD<sub>3</sub>OD molecules.

For sites composed of  $n \operatorname{CH}_3\operatorname{OH}$  molecules and  $N-n \operatorname{CD}_3\operatorname{OD}$  molecules, the overall rate constant distribution is a simple average of the distributions for all possible combinations of isotopomers, each of which is equally probable. This average is given by

$$\widetilde{F}_{n}(k) = \binom{N}{n}^{-1} \sum_{i=1}^{\binom{N}{n}} \mathscr{P}_{i}(F_{1} * F_{2} * F_{3} * \cdots * F_{M}), \qquad (9)$$

where  $\mathcal{P}_i$  is the *i*th unique permutation of *n* CH<sub>3</sub>OH molecules among *N* positions and  $F_j$  is the rate constant distribution for the *j*th position. Clearly  $F_j(k)$  depends on whether the *j*th position is occupied by CH<sub>3</sub>OH or CD<sub>3</sub>OD. To determine the decay function  $f_n(t)$ , we take the Laplace transform of  $\tilde{F}_n(k)$ , as in Eq. (2). According to the convolution theorem for Laplace transforms,<sup>24</sup> the transform of a convolution of functions is equal to the product of their Laplace transforms. Therefore, we may write

$$\widetilde{f}_{n}(t) = \binom{N}{n}^{-1} \sum_{i=1}^{\binom{N}{n}} \mathscr{P}_{i}[f_{1}(t)f_{2}(t)f_{3}(t)\cdots f_{M}(t)],$$
(10)

where

$$f_j(t) = \int_0^\infty F_j(k) \exp(-kt) dk.$$
(11)

If there is a normal distribution of transfer distances, each of the 2M functions  $f_i(t)$  can be evaluated by Eq. (5).

Clearly, the functions  $f_j(t)$  depend on the precise location of the methyl radical in the lattice. The model in-

cludes a rattling motion of the radical, corresponding to variation of the CC distance between the radical and each of the methyl groups. Presumably, this would be adequate if the radical were confined to a single lattice position, e.g., that corresponding to the methyl group of the methanol molecule it replaces. Appropriate equilibrium positions and corresponding transfer distances  $\bar{q}_j$  have been explored in D2. With this input, the time dependence of the radical concentration in an isotopomerically mixed glass depends on five parameters— $\bar{k}_{\rm H}$  the rate constant for H abstraction from the methyl group nearest to the methyl radical;  $\bar{k}_{\rm D}$  the corresponding rate constant for D abstraction; the sensitivity parameters  $\lambda_{\rm H}$  and  $\lambda_{\rm D}$ ; and the Gaussian half-width of the distribution of transfer distances  $\Gamma$ .

However, it seems likely that the radical can move between different positions in its cage on the time scale of the kinetics experiment, on the order of  $10^2$  h. If slow diffusion of the radical within the solvent cage brings methyl hydrogens closer to the radical than they would be in the static structure, the radical will decay more rapidly than expected. The best way to study this diffusion is probably to simulate the dynamics of the system, but such calculations would be extremely time consuming and do not lend themselves to the approach taken here.

#### **III. EXPERIMENT**

Methanol mixtures were prepared so as to contain mole fractions of 0.05, 0.075, 0.10, or 0.15 methanol- $h_4$ (Aldrich, 99.9%, dried over barium oxide) in methanol- $d_4$ (MSD Isotopes, 99.6 at. % D). Rapid exchange of the labile hydrogen scrambles the isotopes among the hydroxyl groups of the two isotopomers, but this is inconsequential because the hydroxyl hydrogen is not abstracted in these experiments and because any secondary kinetic isotope effect is negligible. Measurements were performed on samples in 4 mm o.d. quartz electron-spin resonance (ESR) tubes. Solutions containing about 2 mol % chloromethane and a trace of diphenylamine in the solvent methanol were degased, sealed under vacuum, and cooled rapidly to 77 K by immersion in liquid nitrogen. Samples were irradiated at 77 K in the cavity of a Varian E-4 ESR spectrometer with light from a 1 KW xenon-mercury lamp for several seconds. At this temperature, the radicals were generated instantaneously on the ESR time scale. Depletion of the radical concentration was observed by monitoring the high-field line of the methyl quartet, which exhibits the least overlap with the multiplet due to the hydroxycarbinyl product. Multiple trials were performed so that the reproducibility of the data could be judged. The error in the intensity measurements is about 5% of the peak height at the initial radical concentration.

Nonlinear least-squares fitting was performed with the Marquardt modification of the Gauss–Newton–Raphson method.<sup>25,26</sup> Although this is not a statistically robust method, it is appropriate to the data under consideration, where no serious outliers are present and the distribution of errors is at least Poisson-like. Data sets containing the time dependence of the signal intensity for the pure  $CD_3OD$  glass; mole fractions of 0.05, 0.075, and 0.10

 TABLE I. Parameter values from nonlinear least-squares fitting of Eq.

 (5) to the radical depletion data.

x <sub>H</sub>	$\log \bar{k}(s^{-1})$	γ	rms	
0	- 5.646	2.99	0.025	
0.05	4.551	3.60	0.006	
0.075	-4.622	3.47	0.008	
0.10	-4.541	3.50	0.009	
0.15	4.098	3.56	0.007	
1	-2.356	1.84	0.005	

CH<sub>3</sub>OH in CD<sub>3</sub>OD; and pure CH<sub>3</sub>OH glass were given equal weight, irrespective of the relative numbers of data points, to ensure that the fit was not biased in favor of any particular decay curve. All data points within the data set were given equal weight because all measurements were judged to be equally precise. In order to balance the dependence of the calculated curves on the parameters, we have used ln  $\bar{k}$  rather than  $\bar{k}$  as an adjustable parameter in Eq. (5). Convergence on the parameter values was the convergence criterion for each fit.

### IV. RESULTS FOR THE DISORDERED $\beta$ -PHASE LATTICE

Because the decay curves for the pure glasses could be fitted well by Eq. (5), we performed fits to Eq. (5) for each mole fraction  $x_{\rm H}$ . We do not display the calculated curves, but the fits are excellent in every case and the rms deviations are usually less than 1% of the initial signal height. Values for the characteristic rate constant  $\overline{k}$  and the halfwidth  $\gamma$  appear in Table I. These independent fits correspond to a single, Gaussian distribution of transfer distances. There is no input information concerning the composition or the structure of the glass. Each fit requires two adjustable parameters, namely, k and  $\gamma$ , for a total of 12 independent parameters. The parameter values vary somewhat erratically with the mole fraction of CH<sub>3</sub>OH, which suggests that this fitting procedure lacks physical significance for the mixed glasses. Even for the pure glasses, methyl hydrogens other than the nearest may compete with the nearest hydrogen to react with the radical, although abstraction of the nearest hydrogen is most probable by far. When hydrogen and deuterium abstractions compete, a single Gaussian distribution is expectedly inadequate. We therefore turn to the more appropriate formulation developed in Sec. II.

To minimize the number of variable parameters, we begin with an assumed structure and introduce the dispersion characteristics of the glasses through the single adjustable parameter  $\Gamma$ . There are four more adjustable parameters— $\overline{k}_{\rm H}$  the abstraction rate constant for the hydrogen nearest to the radical, and  $\lambda_{\rm H}$  the sensitivity of this rate constant to changes in the transfer distance, together with the corresponding parameters  $\overline{k}_{\rm D}$  and  $\lambda_{\rm D}$  for deuterium abstraction. For a given structure of the solvent shell, these parameters may be determined by simultaneous fitting to the decay data for a series of mixtures with different  $x_{\rm H}$  values by a nonlinear least-squares procedure.

FIG. 1. A schematic representation of the disordered  $\beta(11.2;30)$  structure of methanol projected on the *bc* plane. Hydrogen bonds, denoted  $\cdots$ , link the methanol chains in the *c* direction. Adjacent layers are displaced by one-half unit-cell dimension (3215 pm) in the *a* direction (perpendicular to the page). The radical is represented by a single sphere at the position of the methyl group of the methanol molecule that it replaces.

As before, the molecular geometry of methanol is that found from millimeter-wave spectroscopy,<sup>27</sup> excluding the slight tilt of the methyl group. The lattice structure to be probed is that found relevant in D2. It corresponds to the  $\beta$ -phase crystal structure of methanol<sup>28</sup> with one molecule replaced by a methyl radical. The true  $\beta$ -phase is probably orientationally disordered such that the methyl groups are located randomly above and below the plane defined by the hydrogen-bonded oxygen atoms.<sup>29</sup> In our model structure for the disordered  $\beta$  phase, the methyl groups alternate regularly above and below this plane at a relatively arbitrary angle of 30°; this structure, referred to as  $\beta(11.2;30)$ , is described in detail in D2. It appears schematically in Fig. 1.

In D2, we found that the best overall fit results when the radical replaces the methyl group of a methanol molecule. The satellite intensity measurements were performed immediately after generation of the methyl radicals and on a time scale that was short relative to the abstraction rate. The calculated intensity ratios did not involve a distribution of distances for each nucleus, but subsequent calculations have shown that the occurrence of such distributions (with  $\Gamma$  on the order of a few picometers) would have no observable effect. Therefore, the conclusions of D2 hold even if the radial coordinates of the nuclei are not sharp, but distributed normally. In principle, the intensity measurements could have been made again after some decay had occurred and, for an otherwise static structure, this later measurement would have reflected the depletion of the methyl hydrogens nearest to the radical.

In Figs. 2 and 3, we display the scaled ESR signal intensity as a function of time for methyl radicals in pure CH<sub>3</sub>OH and pure CD<sub>3</sub>OD. The solid decay curves represent fits of the model described in Sec. II. In the analysis of these data, we have chosen to fix the ratio  $\lambda_D/\lambda_H = \sqrt{2}$  because the sensitivity of the transfer rate to distance is expected to scale as the square root of the mass. After some initial trials, the half-width of the Gaussian distribution of transfer distances  $\Gamma$  was fixed at 2 pm. This value is consistent with earlier estimates of about 3 pm.<sup>4,8</sup> The param-





 TABLE II. Parameter values from nonlinear least-squares fitting of Eq.

 (7) to the radical depletion data in Figs. 2-6.

x	Pure glasses	Pure and mixed glasses	Moving distant methyls radially
$\log \bar{k}_{\rm H}({\rm s}^{-1})$	-3.57	-3.58	-3.63
$\log \overline{k}_{\rm D}({\rm s}^{-1})$		-6.78	-6.92
$\lambda_{\rm H}/{\rm pm}^{-1}$	1.556	1.556	1.556
$\lambda_{\rm D}/{\rm pm}^{-1}$	2.201	2.200	2.200
total rms	0.022	0.054	0.047
rms CH <sub>3</sub> OH1	0.014	0.016	0.014
rms CH <sub>3</sub> OH2	0.026	0.024	0.021
rms CD <sub>3</sub> OD1	0.022	0.080	0.062
rms CD <sub>3</sub> OD2	0.026	0.106	0.094
rms CD <sub>3</sub> OD3	0.024	- 0.067	0.059
rms $x_{\rm H} = 0.05$	•••	0.061	0.060
rms $x_{\rm H} = 0.075$		0.042	0.034
$rms x_H = 0.10$		0.038	0.026

FIG. 2. Observed decay of the methyl radical concentration in glassy  $CH_3OH$  at 77 K. Open and solid symbols represent two separate runs. The solid curve represents the best fit of Eq. (7) if only the pure solvent data are used. Corresponding parameter values are given in the first column of Table II. The computed curve is essentially identical if the mixed glasses are included in the fit.

eter values appear in the first column of Table II. Both log  $\bar{k}$  values are smaller than the corresponding numbers in Table I, which is expected because the radical can now abstract one of several hydrogens on the neighboring molecules. Log  $\bar{k}_{\rm H}$  is only slightly smaller than log  $k_0(11/11)$ = -3.05 determined in D1 for the pure glass under the assumption that each radical has 11 nearest neighbor methanol molecules. The  $\lambda$  values are somewhat higher than, but not inconsistent with, our previous estimates, e.g.,  $\lambda_{\rm H}$ =0.61 pm<sup>-1</sup> from D1 and  $\lambda_{\rm H}$ = $\gamma_{\rm H}/\Gamma$ =1.84/2 =0.92 pm<sup>-1</sup> from Table I.

From the log  $\overline{k}$  values, hydrogen transfer is about 4000 times faster than deuterium transfer at 77 K. Therefore, methyl decay in the mixed glasses is likely to be very sensitive to the structure of the glass in the vicinity of the radical. In order to investigate this structure, we first calculated decay curves for the mixtures based on the parameter values from the pure glasses that appear in the first column of Table II without fitting to the mixtures' data. These are represented by the solid lines in Figs. 4-7. Clearly, these fits leave room for improvement. This is to be expected because radicals in the pure glass most probably react with the nearest methyl group. Therefore, the fit to these data contains relatively little information about the structure of the solvent cage. Only the competition between proximate deuteriums and distant hydrogens provides insights on the surrounding structure.



FIG. 3. Observed decay of the methyl radical concentration in glassy CD<sub>3</sub>OD at 77 K. Open, solid, and half-solid symbols represent three separate runs. The solid curve represents the best fit of Eq. (7) if only the pure solvent data are used. Corresponding parameter values are given in the first column of Table II. The dashed curve represents the best fit of Eq. (7) when the data for the  $x_{\rm H}$ =0.05, 0.075, and 0.10 mixtures are included. Parameter values are given in the second column of Table II.

FIG. 4. Symbols represent the observed decay of the methyl radical concentration in a glassy mixture of CH<sub>3</sub>OH in CD<sub>3</sub>OD at 77 K. The mole fraction of CH<sub>3</sub>OH is 0.05. The solid curve was calculated with Eq. (7) and the parameter values for the pure glasses, which are given in the first column of Table II. The dashed curve represents the best fit with Eq. (7), which yielded the numbers in the second column of Table II. The dotteddashed curve was computed with the parameter values from the pure glass and an effective mole fraction  $x_{\rm H}$ =0.20.



FIG. 5. Symbols represent the observed decay of the methyl radical concentration in a glassy mixture of CH<sub>3</sub>OH in CD<sub>3</sub>OD at 77 K. The mole fraction of CH<sub>3</sub>OH is 0.075. The solid curve was calculated with Eq. (7) and the parameter values for the pure glasses, which are given in the first column of Table II. The dashed curve represents the best fit with Eq. (7), which yielded the numbers in the second column of Table II. The dotteddashed curve was computed with the parameter values from the pure glass and an effective mole fraction  $x_{\rm H}$ =0.17.

To explore this structure, we next fitted the model to the data for the pure glasses and the  $x_{\rm H}$ =0.05, 0.075, and 0.10 mixtures simultaneously with the local structure fixed at that of the  $\beta$ (11.2;30) model. The plot for pure CH<sub>3</sub>OH is indistinguishable from Fig. 2, as expected. A plot for pure CD<sub>3</sub>OD appears as the dashed curve in Fig. 3 and plots for the mixtures appear in Figs. 4–6. The computed concentration of radicals in pure CD<sub>3</sub>OD decays more quickly than the observed concentration. Simultaneously, the computed curves continue to overestimate the radical



FIG. 6. Symbols represent the observed decay of the methyl radical concentration in a glassy mixture of CH<sub>3</sub>OH in CD<sub>3</sub>OD at 77 K. The mole fraction of CH<sub>3</sub>OH is 0.10. The solid curve was calculated with Eq. (7) and the parameter values for the pure glasses, which are given in the first column of Table II. The dashed curve represents the best fit with Eq. (7), which yielded the numbers in the second column of Table II. The dotted– dashed curve was computed with the parameter values from the pure glass and an effective mole fraction  $x_{\rm H}$ =0.19.



FIG. 7. Symbols represent the observed decay of the methyl radical concentration in a glassy mixture of CH<sub>3</sub>OH in CD<sub>3</sub>OD at 77 K. The mole fraction of CH<sub>3</sub>OH is 0.15. The solid curve was calculated with Eq. (7) and the parameter values for the pure glasses, which are given in the first column of Table II. The decay curve computed with Eq. (7) and the parameter values from the second column of Table II is shown by the dashed line. The  $x_{\rm H}$ =0.15 data were not included in the fitting procedure.

concentration in the mixed glasses. The corresponding parameter values appear in the second column of Table II. Two significant differences should be noted between this fit and that for the pure glasses alone (solid curves). First, the deuterium transfer rate constant increases if the mixtures are included, although there is no corresponding increase in log  $\bar{k}_{\rm H}$ . Second, the rms deviation is larger for this run than for the pure glasses. This increase arises from the larger rms deviations for the mixture data sets individually and from the increased rms deviations for the pure CD<sub>3</sub>OD data is obviously a consequence of the increase in log  $\bar{k}_{\rm D}$ . A simple interpretation of this increase is that the methyl radicals in the mixed glasses decay more rapidly than expected on the basis of the mole fraction of CH<sub>3</sub>OH present.

In support of our procedure, we compare the computed decay curve for the  $x_{\rm H}$ =0.15 mixture with the experimental data in Fig. 7. The dashed curve was calculated using the parameter values in the second column of Table II without fitting to the  $x_{\rm H}$ =0.15 data. The quality of the fit is similar to that for the other mixtures. The rms deviation is 0.061, which is consistent with the other deviations in the second column of Table II.

As mentioned above, radicals in pure CH<sub>3</sub>OH will readily abstract hydrogen from a nearby molecule, but in the mixtures there will be competition between proximate deuteriums and more distant hydrogens. Because the rate constant is very sensitive to transfer distance, this competition is strongly influenced by the separation of the radical and the abstractable hydrogen. In the  $\beta(11.2;30)$  structure, nine hydrogen atoms are sufficiently close and have an orientation such that they may react. Five of these are proximate and four are distant. In order to see what improvement might be gained, we performed a fit in which the two distant methanol molecules bearing these four hydrogens were allowed to move radially. In this run, the CC separation decreased from 6 to 1.7 pm. Parameter values appear in the third column of Table II. Although  $\log \bar{k}_D$  decreases somewhat, it fails to attain the value from pure CD<sub>3</sub>OD (first column of Table II) and the fit to the pure CD<sub>3</sub>OD data is not greatly improved over that of the dashed curve in Fig. 3.

Another structural possibility is that the radical does not occupy the position of a methyl group in the lattice but is displaced. We investigated this idea in D4 and concluded that the methyl carbon position was most likely. As in D4, we have performed fits with the radical displaced from this position by  $\pm 50$  pm along the unit cell axes. The resulting rms deviations appear in Table III. It is apparent that the radical at C, the carbon position, provides the best fit overall. Notice particularly that the fits to the mixtures do not improve for these displacements. This suggests that a static distribution of radical positions within the solvent cage is not likely to improve the agreement between computed and observed decay curves.

We have also performed fits in which the restriction  $\lambda_{\rm D}/\lambda_{\rm H} = \sqrt{2}$  was removed, i.e.,  $\lambda_{\rm H}$  and  $\lambda_{\rm D}$  were adjusted independently, while  $\Gamma$  was kept at 2 pm. The results were similar to those in the second column of Table II except that  $\lambda_{\rm H}$  dropped to from 1.55 to 0.48 pm<sup>-1</sup>, although the confidence limits are rather larger also. Parenthetically, this number is quite close to our theoretical estimate 0.61  $pm^{-1}$  in D1. This decrease may be an indication that the half-width of the distribution of transfer distances  $\Gamma$  is effectively larger for deuterium than for hydrogen. Of course, for a static structure  $\Gamma$  is expected to be isotope independent because it is determined by the lattice modes of the glass. However, if in fact  $\lambda_D / \lambda_H = \sqrt{2}$ , the numbers in Table II suggest that  $\Gamma_{\rm D} = \gamma_{\rm D} / \lambda_{\rm D} = \lambda_{\rm D} \Gamma / \lambda_{\rm H} \sqrt{2} = 2.20(2) / 2$  $0.48\sqrt{2}=6.5$  pm rather than 2 pm. A large value for  $\Gamma_{\rm D}$ could be associated with motion of the radical through the CD<sub>3</sub>OD cage in addition to the usual lattice vibrations.

These results reinforce the conclusions that (1) distant hydrogens do compete with proximate deuteriums and (2) the effective mole fraction of CH<sub>3</sub>OH molecules in the mixed glasses is greater than the analytical concentration. One illustration of this second point is obtained by fitting the data for a mixed glass with the pure glass parameters from the *first column* of Table II by varying the effective mole fraction of CH<sub>3</sub>OH within the calculation. The decay curves computed in this way for  $x_{\rm H} = 0.05, 0.075, \text{ and } 0.10$ appear as dotted-dashed curves in Figs. 4-6. The effective mole fractions are 0.20 = 0.05 + 0.15,  $0.17 \approx 0.075 + 0.10$ , and 0.19=0.10+0.09, respectively. The fits are clearly superior to the solid curves obtained for the analytical concentrations, although not in perfect agreement with observation. Notice also that the difference between the effective and analytical concentration of CH<sub>3</sub>OH decreases as  $x_{\rm H}$ increases, as expected if diffusion becomes less important as the analytical concentration of CH<sub>2</sub>OH rises.

Alternatively, these numbers may indicate that all three mixtures behave in the same way, namely, as if the mole faction of  $CH_3OH$  were about 0.20, irrespective of analytical concentration. Comparison of the decay curves shows that this interpretation is incorrect. In reality, radicals disappear more quickly in mixtures having a higher mole fraction of  $CH_3OH$ . The fits are superior in that they distribute the residuals more evenly over the curve, but the agreement with observation is not good enough to justify a literal interpretation of the effective mole fractions.

As noted in Sec. III, the "pure" CD<sub>3</sub>OD used in these experiments actually contains 0.4 at. % D, which implies that the solvent is only 98.4 mol % CD<sub>3</sub>OD and that 1.6 mol % of the solvent molecules carry a single hydrogen. In Sec. II, it was assumed that the isotopic nature of the methyl groups was either CH<sub>3</sub> or CD<sub>3</sub>. This assumption is still reasonable if we assume that a radical will react with a CHD<sub>2</sub> group as readily as with a CH<sub>3</sub> group in the dilute mixtures. If the pure CD<sub>3</sub>OD data is then treated as representative of a 1.6 mol % mixture of CH<sub>3</sub>OH in CD<sub>3</sub>OD and only the pure solvent data are included in the run,  $\log \bar{k}_D$  decreases from -7.17 to -7.22, while  $\log \bar{k}_H$ ,  $\lambda_H$ ,  $\lambda_{\rm D}$ , and the rms deviations are unchanged from the values in the first column of Table II. If the pure solvents and the  $x_{\rm H} = 0.05$  and 0.075 mixtures are fitted simultaneously (with  $x_{\rm H}$  increased by the residual hydrogen in the CD<sub>3</sub>OD solvent), log  $\bar{k}_D$  decreases form -6.78 to -6.89, while log  $\bar{k}_{\rm H}$ ,  $\lambda_{\rm H}$ , and  $\lambda_{\rm D}$  are unchanged from the values in the second column of Table II. In this run, the rms deviations for the mixed solvent data are essentially unchanged, but those for the pure CD<sub>3</sub>OD glasses decrease by about 0.012. These observations suggest that residual CHD<sub>2</sub>OD does contribute to radical decay in the pure CD<sub>3</sub>OD glass, especially at long times. However, the present model is rather insensitive to small changes in  $x_{\rm H}$ in the mixed glasses.

All of these observations draw us to the conclusion that the structure in the vicinity of the methyl radical is not static, but evolves in such a way that the radical has a higher probability of encountering a CH<sub>3</sub>OH molecule. It seems clear that this is accomplished as the radical diffuses through the glass structure during the course of the kinetic measurements. Presumably, the radical moves through channels between and along the hydrogen-bonded chains because, as Tauer and Lipscomb have indicated,<sup>28</sup> the methanol lattice is not entirely well packed and permits some large-amplitude motion. Signs of large-amplitude motion also appear in the dielectric properties of the  $\beta$ phase.<sup>30,31</sup> Davidson has suggested that the dominant dispersion arises from the existence of anisotropic crystallites oriented in different directions.<sup>31</sup> Because proximate hydrogens react quickly, diffusion has little influence on the pure CH<sub>3</sub>OH data. The effect is pronounced in the mixed glasses and it follows that similar effects may be present in the pure CD<sub>3</sub>OD data. Some information on the diffusion process may be available from the study of the time evolution of ESR satellite intensities from mixed glasses. The experiments in D2 were performed for pure glasses shortly after irradiation and so provide information about the environment of the nascent radicals. By monitoring the satellite intensities as a function of time since irradiation, it may be possible to detect diffusion of the radical towards CH<sub>3</sub>OH molecules.

TABLE III. Root-mean-square (rms) deviations from fits of Eq. (7) with various placements of the radical within the  $\beta(11.2;30)$  unit cell.<sup>a</sup>

rms	Radical position								
	C	C+0.078a	C-0.078a	C+0.069b	C-0.069b	C+0.107c	C-0.107c		
Total CH3OH	0.048	0.062	0.063	0.056	0.052	0.063	0.062		
Run #1	0.047	0.016	0.017	0.017	0.029	0.016	0.016		
Run #2	0.047	0.013	0.013	0.013	0.028	0.013	0.013		
CD3OD									
Run #1	0.054	0.113	0.111	0.094	0.087	0.111	0.113		
Run #2	0.082	0.118	0.123	0.109	0.095	0.123	0.118		
Run #3	0.046	0.070	0.076	0.065	0.053	0.076	0.070		
Mixture									
$x_{\rm H} = 0.05$	0.059	0.059	0.059	0.059	0.057	0.059	0.059		
$x_{\rm H} = 0.075$	0.033	0.049	0.048	0.044	0.040	0.049	0.049		
$x_{\rm H} = 0.10$	0.032	0.052	0.052	0.043	. 0.036	0.052	0.052		

<sup>a</sup>Displacements of 50 pm relative to the carbon position given in terms of unit-cell dimensions.

As mentioned above with reference to Table III, it is unlikely that a static distribution of radical positions within the solvent cage would provide an appropriate description of this dynamical phenomenon. For example, a radical situated in a solvent cage composed entirely of  $CD_3OD$  molecules at time t=0 may, in the time interval  $\tau$ , either react by abstracting a deuterium or migrate to a new environment that happens to contain a CH<sub>3</sub>OH molecule from which it abstracts a hydrogen. Clearly, this time evolution is different from that of a radical in a cage containing a CH<sub>3</sub>OH molecule at t=0.

In the absence of information on the rate of diffusion in such a case, it may be possible on the basis of the effective mole fractions above to estimate the number of methanol molecules that the radical encounters before reacting. In the static  $\beta(11.2;30)$  structure with the radical at C, there are six methanol molecules with which the radical is likely to react. Because hydrogen abstraction is much faster than deuterium abstraction, the effect of changing N is more important in Eq. (6) than in Eq. (10). Given that the  $x_{\rm H} = 0.05$  mixture has an effective mole fraction of 0.20, Eq. (6) indicates that the effective probabilities of a solvent cage containing zero, one or two CH<sub>3</sub>OH molecules are  $\alpha(0) = 0.262, \alpha(1) = 0.393$ , and  $\alpha(2) = 0.246$ , respectively. By setting  $x_{\rm H} = 0.05$  in Eq. (6) and varying N, we can approximate these coefficients as 0.264, 0.361, and 0.237, respectively, with  $N_{\text{effective}} = 26$ . Roughly speaking, the radical must encounter about 26 methanol molecules before the effective mole fraction of CH<sub>3</sub>OH rises to 0.20. From the crystallographic analysis,<sup>28</sup> this corresponds to six-anda-half unit cells or to a radius of about 1100 pm. For the  $x_{\rm H} = 0.075$  mixture,  $N_{\rm effective} = 14$  and, for  $x_{\rm H} = 0.10$ ,  $N_{\text{effective}} = 11$ , i.e., at twice the analytical concentration of CH<sub>3</sub>OH, the radical encounters roughly half as many solvent molecules before it reacts. In fact,  $N_{\text{effective}}$  is quite close to the number ratio of CD<sub>3</sub>OD to CH<sub>3</sub>OH molecules, which is given by  $x_{\rm H}^{-1} - 1 = 19$  for  $x_{\rm H} = 0.05$ , 12 for  $x_{\rm H}$ =0.075, and 9 for  $x_{\rm H}$ =0.10. By extrapolation, we estimate that before decaying, a methyl radical in pure CD<sub>3</sub>OD will

encounter about 60 methanol molecules, corresponding to a radius of about 1500 pm.

If we take 1500 pm as the rms displacement of the radical,  $\langle \Delta x^2 \rangle^{1/2}$ , after  $\tau = 10^6$  s, the diffusion coefficient at 77 K is on the order of  $\langle \Delta x^2 \rangle / 6\tau = \sim 10^{-25} \text{ m}^2 \text{ s}^{-1}$ . Admittedly, this estimate is quite crude, but not inconsistent with other values for diffusion through solids. For hard spheres having a radius of 200 pm (the van der Waals radius of a methyl group) and the same number density as the  $\beta$  phase of methanol, the coefficient of self-diffusion<sup>32</sup> is about  $10^{-11} \text{ m}^2 \text{ s}^{-1}$  at 77 K, which is well above our estimate for methyl radicals. If the diffusion coefficient at the melting point of methanol is on the order of  $10^{-13} \text{ m}^2 \text{ s}^{-1}$ , a typical value for self-diffusion, and if diffusion is an activated process with activation energy  $E_a = 2\Delta H_{\text{sublimation}} = ~75 \text{ KJ mol}^{-1,33}$  the diffusion coefficient D is about  $10^{-42} \text{ m}^2 \text{ s}^{-1}$  at 77 K.<sup>34</sup> In this context, the estimate derived from the effective mole fractions is not unreasonable.

#### **V. CONCLUSIONS**

On the basis of a statistical model for the decay of methyl radicals in glassy methanol at 77 K, we have determined characteristic rate constants for hydrogen and deuterium abstraction. Fits to the experimental data for pure CH<sub>3</sub>OH and pure CD<sub>3</sub>OD are good, as expected from earlier work. Competition between hydrogen and deuterium abstraction has been used to investigate the structure of the solvent cage about the radical. The results are consistent with the  $\beta(11.2;30)$  structure described in D2, but fits to the data for glassy mixtures of CH<sub>3</sub>OH in CD<sub>3</sub>OD are not as good as those for the pure solvents. A number of indicators suggest that this is a consequence of diffusion of the radical through the glass during the course of the experimental measurements. These include an increase in  $\log \overline{k}_{\rm D}$  when the mixtures are included in the fitting, a preference to move distant methyl groups toward the radical, a large variation in the transfer distance for deuterium relative to hydrogen, and an increase in the effective mole

fraction of CH<sub>3</sub>OH in the mixed glasses. All of these actions have the effect of increasing the rate of decay of radicals in the mixed glasses. We conclude that radicals in the dilute mixtures can diffuse through the disordered structure, often until a CH<sub>3</sub>OH molecule is encountered and hydrogen abstraction occurs. Thus, quite distant hydrogens compete with a large number of deuteriums as the radical migrates. If the reaction products were analyzed, the fraction of methyl groups that decay by hydrogen abstraction would be larger than expected on a statistical basis. Methyl radicals in CD<sub>3</sub>OD may diffuse over sufficiently large distances as to encounter other radicals and decay by combination to form ethane. Detection of this ethane could provide a means to determine the rate of diffusion.

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