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# CH and CD overtone decay times in partially deuterated benzenes

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A recently developed classical model for the simulation of overtone dynamics in  $C_6H_6$  and  $C_6D_6$ , is used to evaluate estimates for the decay times of CH and CD overtones in all deuterated benzenes for which experimental linewidths have been measured. The calculated and inferred decay times are compared for  $C_6H_6$ ,  $C_6H_5D$ ,  $p$ - $C_6H_4D_2$ ,  $C_6HD_5$ , and  $C_6D_6$ . Reasonable quantitative agreement between theory and experiment is reported and marked qualitative trends are reproduced.

## INTRODUCTION

The description of heavy atom-hydrogen vibrations in terms of local rather than normal modes has been well understood in recent years.<sup>1</sup> However, both extremes are necessarily approximations in real molecules. The measurement of rather broad overtone absorption line shapes in benzene and perdeuterobenzene<sup>2</sup> has suggested that local modes may provide an unexpectedly poor model of CH and CD stretching modes in those cases.

Sibert *et al.*<sup>3,4</sup> have performed both quantum and classical calculations which imply that a 2:1 Fermi resonance between these stretching modes and CCH(D) in-plane wagging modes, via the kinetic energy, is responsible for mixing the overtone states with several ring modes. In a time-dependent picture, an initially prepared CH(D) overtone state decays rapidly with intramolecular vibrational energy redistribution (IVR) into those ring modes which contain some contribution from the wag of the initially excited CH(D) bond.

Recently, we reported extensive classical simulations of this IVR in  $C_6H_6$  and  $C_6D_6$  using the best available potential energy surface<sup>3,6</sup> and the exact classical kinetic energy.<sup>5</sup> It was shown there that an accurate classical simulation gives a good semiquantitative description of the CH(D) overtone decay times. Moreover, the unexpected resonant interaction of para CH oscillators via 2:1 Fermi resonance with the ring modes was described in some detail.

In this short paper, the model<sup>5</sup> is used to estimate the CH(D) overtone decay times in  $C_6H_5D$ ,  $p$ - $C_6H_4D_2$ , and  $C_6HD_5$ . These calculations allow a complete comparison of the classical results with experimental data in all deuterated benzenes for which some data is available.<sup>2,7</sup> In discussing the results we draw attention to the role that the ring mode eigenvectors and frequencies play in determining the rate of IVR.

## THE METHOD

The model Hamiltonian and computational details have already been extensively described.<sup>5</sup> Briefly, a classical simulation, in Cartesian coordinates, of the *planar* vibrations of  $C_6H_nD_{6-n}$  is performed. The six CH(D) modes are treated as Morse oscillators. Five of the six Morse oscillators and the 15 ring modes are initially given near zero-point energy while one CH(D) local mode is given an energy appropriate

to a higher quantum number  $n$ ,  $n = 1, \dots, 8, 9$ . During the evolution of the trajectory, the energy of the initially excited oscillator and the remaining modes is monitored. The time-dependent classical energy of the initially excited Morse oscillator is allocated at short time intervals to a bin  $[E(n - \frac{1}{2}) < E(t) \leq E(n + \frac{1}{2})]$  labeled by the quantum number  $n$ . Repetition of this process for 200 trajectories, with random initial oscillator phases, provides a measure of the probability  $P(t)$  that the excited oscillator is still in its initial state at time  $t$ . A decay time  $\tau_D$  is defined by

$$\ln(P) = -t/\tau_D. \quad (1)$$

In practice a least-squares fit of  $\ln[P(t)]$  to a straight line is performed and the slope used to estimate  $\tau_D$ . In many cases,  $\ln[P(t)]$  is remarkably linear. However, in some cases, particularly where the decay rate is slow,  $\ln[P(t)]$  abruptly changes slope.<sup>8</sup> To show this effect,  $\tau_D$  is evaluated in the time interval before  $\ln[P(t)] < -2.5$  and over the longer interval before  $\ln[P(t)] < -3.5$ . The average of the two values is reported in the tables with a variation given by the difference. In virtually every case,  $\tau_D$  is shorter if measured over the shorter interval. A large variation in  $\tau_D$  implies very nonexponential decay. The statistical error in the calculated decay times was estimated by doubling the number of trajectories to 400 in a few cases. Where the decay was almost purely exponential the resultant change in decay time was less than 2–3 fs. The change was greater when the decay was nonexponential, but much less than the quoted variation with cutoff probability. It should be noted that markedly nonexponential decay implies that no simple relationship exists between the average decay time quoted and an observed absorption linewidth. The experimental decay times are evaluated in Refs. 2 and 7 from the observed absorption linewidths, though the lines are not necessarily Lorentzian.

## RESULTS AND DISCUSSION

The calculated decay times and corresponding experimental values are shown in Tables I–IV. Tables I and III show the CH and CD local mode decay times, respectively, in four compounds. Where three inequivalent bonds occur, CH bonds on  $C_6H_5D$  and CD bonds in  $C_6HD_5$ , a weighted average decay time is given. The separate decay times for local bond modes ortho, meta, and para to the isotopic impurity are reported in Tables II and IV for CH and CD modes,

TABLE I. Comparison of CH overtone decay times.<sup>a</sup>

Quantum number	C <sub>6</sub> H <sub>6</sub>		C <sub>6</sub> H <sub>5</sub> D		<i>p</i> -C <sub>6</sub> H <sub>2</sub> D <sub>4</sub>		C <sub>6</sub> HD <sub>5</sub>	
	Theory <sup>b</sup>	Expt. <sup>c</sup>	Theory	Expt. <sup>c</sup>	Theory	Expt. <sup>d</sup>	Theory	Expt. <sup>c</sup>
1	122		132	177	230	177	274 <sup>e</sup>	
2	65	230	77		92		83 ± 1	
3	56 ± 1	230	48 ± 1		47 ± 2		48 ± 2	180
4	44	74	40		40 ± 2		44 ± 2	> 47
5	38 ± 1	> 51	38	54	33	51	34 ± 1	69
6	36 ± 1	62	33 ± 1	59	33 ± 2	63	28 ± 2	> 46
7	35	66	31		27		29	55
8	33	58	29 ± 1		23 ± 1		26	49
9	43	130	32		32 ± 2		29 ± 2	

<sup>a</sup> Decay times in fs.<sup>b</sup> The range of theoretical values is discussed in the text.<sup>c</sup> Reference 2.<sup>d</sup> Reference 7.<sup>e</sup> Nonexponential for  $\ln(P) > -1$ .

respectively. Though previously reported,<sup>5</sup> the results for C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub> are included for comparison.

In discussing the mechanism for the overtone decay, it is useful to consider the wagging modes which are available to interact with the excited stretch via 2:1 Fermi resonance. Table V shows the frequencies of those normal modes which involve CCH or CCD in-plane wagging in the molecules considered here. A particular normal mode can extract energy from an excited CH(D) stretch if two conditions are satisfied. First, the normal coordinate must involve substantial in-plane wagging of the CCH(D) angle at the excited CH(D) bond. The anharmonicity of the kinetic energy operator in internal coordinates provides the coupling between wag and stretch: principally because the moment of inertia of the wagging CH(D) "pendulum" depends on the CH(D) bond length.<sup>3</sup> Second, the frequency of the wagging motion must be half that of the stretch or the frequencies of two modes, which both satisfy the first condition, must sum to the stretching frequency. The local stretching mode is described by a Morse oscillator, so that its frequency decreases with increasing energy. As energy flows out of an initially highly excited CH(D) bond stretch, its frequency increases.

TABLE II. Comparison of CH overtone decay times in C<sub>6</sub>H<sub>5</sub>D<sup>a</sup>.

Quantum number	Theory <sup>b</sup>			Expt. <sup>c</sup>
	<i>o</i> -H	<i>m</i> -H	<i>p</i> -H	
1	145	122	126	177
2	80	73	80	
3	50	50 ± 4	44	
4	39	41	39	
5	40 ± 1	38	38	54
6	28	38	34	59
7	27	38 ± 2	27 ± 3	
8	27	30 ± 1	31	
9	30	30 ± 2	41 ± 1	

<sup>a</sup> Decay time in fs.<sup>b</sup> The range of theoretical values is discussed in the text.<sup>c</sup> Reference 7.

Hence for energy to flow smoothly throughout the decay, a number of wagging modes must be involved whose spread in frequency is sufficient to allow the resonance condition to be satisfied over a wide range of stretching frequencies. This concept of overlapping nonlinear resonances has been described in some detail.<sup>4</sup> We note that the energy gap between the Morse oscillator energy levels decreases from 3047 to 2130 cm<sup>-1</sup> for 0 → 1 and 8 → 9 in C<sub>6</sub>H<sub>6</sub> and from 2290 to 1853 cm<sup>-1</sup> for 0 → 1 and 7 → 8 in C<sub>6</sub>D<sub>6</sub>.

Beginning with Table I, we see that both experimental and theoretical CH decay times are short for 4 ≤ *n* ≤ 8. The classical times are on average 61% of the experimental, in this range of *n*. In this energy regime, there are many combinations of ring modes whose pairwise added frequencies lie close to the CH stretch frequency. For *n* = 9, fewer modes can satisfy the 2:1 resonance requirement initially, hence the calculations for all four molecules show a rise in the decay time. The experimental data (for C<sub>6</sub>H<sub>6</sub>) shows a similar but much more pronounced rise. Calculations show a steady increase in decay time as *n* decreases below four. The limited data suggests the theoretical times are much too low at *n* = 2, 3 but reasonable at *n* = 1. At *n* = 1 few ring modes can satisfy the 2:1 resonance condition and the (otherwise) pure exponential decay of CH stretching modes can be lost. The theory shows a tendency for  $\tau_D$  to be smaller in heavily deuterated compounds. Here, the ring mode eigenvectors are such that the relative amplitude of the few CCH wags is larger for many modes than it is in C<sub>6</sub>H<sub>6</sub>. Hence, the kinetic energy coupling<sup>3,5</sup> between wag and stretch is stronger for the lighter atoms in these deuterated compounds. Moreover, the lower symmetry of the partially deuterated molecules leads to a splitting of wagging modes degenerate in C<sub>6</sub>H<sub>6</sub>. Thus a much greater spread of wagging frequencies is available, particularly in C<sub>6</sub>H<sub>5</sub>D and *p*-C<sub>6</sub>H<sub>2</sub>D<sub>4</sub>, and the resonance condition is more readily satisfied, leading to faster overtone decay.

Table II compares the available data with the decay times for CH modes ortho, meta, and para to the deuterium in C<sub>6</sub>H<sub>5</sub>D. The same Morse potential<sup>3,5</sup> has been used for CH bonds in all positions (and all compounds reported).

TABLE III. Comparison of CD overtone decay times<sup>a</sup>

Quantum number	C <sub>6</sub> D <sub>6</sub>		C <sub>6</sub> HD <sub>5</sub>		p-C <sub>6</sub> H <sub>2</sub> D <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> D
	Theory <sup>b</sup>	Expt. <sup>c</sup>	Theory	Expt. <sup>c</sup>	Theory	Theory
2	209 <sup>d</sup>		161 ± 6		138 ± 7	220 <sup>d</sup>
3	121 ± 48	480	94 ± 2	91	108 ± 2	113 ± 33
4	74 ± 4	100	80	120	71 ± 3	78 ± 3
5	76 ± 3	160	78 ± 7	160	71	82
6	87 ± 2	410	81 ± 6	100	67 ± 2	105 ± 2
7	145 ± 37	560	77 ± 1	68	67 ± 5	111 ± 21
8	102 ± 29	100	81 ± 1		102	124 ± 43

<sup>a</sup> Decay times in fs.<sup>b</sup> The range of theoretical values is discussed in the text.<sup>c</sup> Reference 2.<sup>d</sup> Nonexponential for  $\ln(P) > -2.5$ .

However, it should be noted that the absorption maximum for a particular overtone varies in frequency between partially deuterated benzenes, by as much as 10–20 cm<sup>-1</sup>.<sup>2,7</sup> Hence, the Morse potential describing a CH stretch may vary with position in C<sub>6</sub>H<sub>5</sub>D with individual local mode overtones differing by several cm<sup>-1</sup>. The available experimental data does not resolve distinct local mode transitions.

It is clear that the dynamics of excited ortho, meta, and para CH bonds are sufficiently different to produce measurable differences in their decay times. While Table V shows that all 15 in-plane “ring” modes have some component of CCH wagging motion, the magnitude of this component varies between symmetry distinct CH bonds. All modes contain a mixture of ortho and meta CCH wagging, in different proportions, while wagging of the para CCH bond contributes to only eight modes. However, the amplitude of the para CCH wag is larger here than in related modes of C<sub>6</sub>H<sub>6</sub>. The light atom wag at the para position apparently “steals” amplitude from the CCD wag. This amplitude effect compensates for the symmetry effect whereby the para wag contributes to fewer modes than do the ortho and meta CCH wags. Overall many modes are involved in a very complex wagging motion at each position so that, given the large amplitude of these light atom motions, the overtone decay is rapid with only slight differences in rate.

Table III compares the calculated decay times for CD stretching states in C<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>HD<sub>5</sub>, p-C<sub>6</sub>H<sub>2</sub>D<sub>4</sub>, and C<sub>6</sub>H<sub>5</sub>D with the available experimental data for C<sub>6</sub>D<sub>6</sub> and C<sub>6</sub>HD<sub>5</sub>. The effect of changes in the ring mode eigenvectors with isotopic substitution is most marked in these CD overtone decay times.

For C<sub>6</sub>D<sub>6</sub> the overtone decay is exponential only for  $n = 4, 5, 6$ . Here the calculated decay times are approximately twice the corresponding CH decay times in C<sub>6</sub>H<sub>6</sub>: the time scale determined by the stretching frequency is longer by a factor of  $\sqrt{2}$  and the kinetic energy coupling of wag and stretch is smaller by a factor of  $\sqrt{2}$ . The decay is highly non-exponential for all other  $n$  values and the decay times are higher as fewer ring modes can achieve 2:1 resonance for  $n < 4$  or  $n > 6$ . The quantitative correlation with experiment is much worse for C<sub>6</sub>D<sub>6</sub> than for C<sub>6</sub>H<sub>6</sub>, though the overall trends are similar. On average, the calculated decay times for CD overtones in C<sub>6</sub>D<sub>6</sub> and C<sub>6</sub>HD<sub>5</sub> are 64% of the experimental values.

When a hydrogen is introduced to give C<sub>6</sub>HD<sub>5</sub>, the degeneracy of the CCD(H) wagging modes is broken. There is now a much greater spread of wagging mode frequencies than in C<sub>6</sub>D<sub>6</sub> and several modes can participate in 2:1 resonance with CD stretching states. Hence the decay times for  $n < 4$  and  $n > 6$  fall dramatically and the decay is quite exponential in many cases. This calculated dramatic fall in decay times from C<sub>6</sub>D<sub>6</sub> to C<sub>6</sub>HD<sub>5</sub> is in good agreement with the experimental data.

The CD decay times for C<sub>6</sub>HD<sub>5</sub> in Table III are obtained from a weighted average of symmetry distinct CD bonds. Table IV presents the individual ortho, meta, and para CD decay times. The variation of decay time with position is quite striking. The para CD decay is significantly non-exponential for  $n = 5, 6$  and the decay times are higher than those at either ortho or meta positions when  $n = 4-6$ , in particular. Table V indicates those modes which contain some component of wag at the para position. As one might expect on symmetry grounds, fewer modes involve wagging at the para position than at the ortho or meta positions. The same amplitude stealing process occurs here as in C<sub>6</sub>H<sub>5</sub>D, so that the para CCD wag generally has lower amplitude than would be expected by comparison with related modes in

TABLE IV. Comparison of CD overtone decay times in C<sub>6</sub>HD<sub>5</sub>.<sup>a</sup>

Quantum number	Theory <sup>b</sup>			Expt. <sup>c</sup>
	o-D	m-D	p-D	
2	148 ± 7	189	132 ± 13	
3	86 ± 7	100 ± 3	98 ± 1	91
4	78 ± 2	76 ± 1	89	120
5	66	71	117 ± 30	160
6	77 ± 2	76	100 ± 36	100
7	78 ± 4	73 ± 2	83 ± 5	68
8	85 ± 3	77 ± 2	83 ± 5	

<sup>a</sup> Decay times in fs.<sup>b</sup> The range of theoretical values is discussed in the text.<sup>c</sup> Reference 2.

TABLE V. CCH(D) in-plane wagging frequencies ( $\text{cm}^{-1}$ ).

$\text{C}_6\text{H}_6$	$\text{C}_6\text{H}_5\text{D}$		$p\text{-C}_6\text{H}_2\text{D}_4$		$\text{C}_6\text{HD}_5$		$\text{C}_6\text{D}_6$
	H	D	H	D	H	D	
	599						
606	603 <sup>b</sup>	603	585	585	582	582 <sup>b</sup>	579
1033	854 <sup>b</sup>	854		590		584	809
1140	982 <sup>a</sup>			813		811	820
	1005 <sup>a</sup>						
1179	1030		815 <sup>a</sup>	815	815 <sup>a</sup>	815 <sup>b</sup>	860
1305	1078 <sup>b</sup>	1078		861	838	838 <sup>b</sup>	1051
						861	
1350	1154 <sup>b</sup>	1154	963	963		952 <sup>a</sup>	1284
						978 <sup>a</sup>	
1479	1179			982 <sup>a</sup>	980	980 <sup>b</sup>	1326
1602	1295 <sup>b</sup>	1295	1051	1051	1166	1166 <sup>b</sup>	1559
	1327 <sup>b</sup>	1327	1259	1259	1285	1285 <sup>b</sup>	
	1450 <sup>b</sup>	1450	1285	1285		1335	
	1474			1344	1392	1392 <sup>b</sup>	
	1595 <sup>b</sup>	1595	1431	1431		1565	
	1597			1571	1570	1570 <sup>b</sup>	
			1578	1578			

<sup>a</sup> Only weakly involves wagging.<sup>b</sup> Involves significant wagging at the para position.

$\text{C}_6\text{D}_6$ . For both these reasons, we expect the para CD overtone decay to be slower than that at the ortho and meta positions. Examination of the time dependent energy of all ring modes during CD overtone decays, shows that only six modes participate in para CD overtone decay compared to eight or nine modes for ortho and meta CD overtone decay, and the para CD overtone decay is often slower and markedly nonexponential. It is interesting that the para CD decay times are in better agreement with experiment than those at the other positions. This is probably fortuitous. However, a general point is worth mentioning in this context. The broad overtone absorptions are due to transitions to many molecular eigenstates which contain some CD overtone character. Assuming that the absorption by any one eigenstate is proportional to the percentage of CD stretching involved in that state, the “purest” overtone states will dominate the absorption profile.<sup>1</sup> The slower decay of the para CD stretch implies that eigenstates involving large quanta of these modes are more nearly local mode states than is the case for states involving overtones of the ortho and meta bonds. Thus, the absorption intensity associated with excitation of symmetry distinct “local” CD bonds need not be equal. It is not possible to determine from the current analysis whether the expected higher transition probability to para CD overtone states is sufficient to dominate the spectrum.

When two hydrogens are present as in  $p\text{-C}_6\text{H}_2\text{D}_4$ , an examination of the ring mode eigenvectors shows that as many as 14 modes contain some CCD wag character. Not surprisingly, the simulations show that CD decay times are generally shorter in this compound, and that the energy of ten ring modes increases significantly during the CD overtone decay. The major exception to the trend is seen to be the decay of the  $n = 8$  stretching state where a relatively high decay time is calculated. Unfortunately, no experimental

data is available for comparison.

When five hydrogens are present, in  $\text{C}_6\text{H}_5\text{D}$ , the trend in decay times from  $\text{C}_6\text{D}_6$  to  $\text{C}_6\text{HD}_5$  to  $p\text{-C}_6\text{H}_2\text{D}_4$  is reversed. Now, the ring modes involving in-plane bond wagging are dominated by the higher frequency CCH wag motion. Only one mode (at  $854\text{ cm}^{-1}$ ) involves a very large amplitude CCD wag, though a number of other modes show a small degree of CCD wagging (see Table V). Consequently, the CD stretching decay times are long and the decay is nonexponential at large  $n$ , where the lack of low frequency wagging modes is most important. No data is currently available for the CD overtone absorptions in this molecule.

## SUMMARY

An accurate classical simulation of the in-plane vibrational dynamics of five deuterated benzenes has shown significant differences in the decay rates of CH and CD local mode overtones between molecules and between symmetry distinct bonds within molecules. The observed trends in decay rates can be qualitatively understood in terms of a 2:1 Fermi resonance mechanism whereby IVR takes place between the excited local mode and ring modes which involve wagging of that bond. The number, frequency, and character of these wagging modes appear to determine the calculated decay times.

The quantitative agreement between calculated decay times and experimental values is good in view of the fact that the total molecular density of states spans several orders of magnitude over the range of overtone states studied. Marked trends, including the fall in CD decay times from  $\text{C}_6\text{D}_6$  to  $\text{C}_6\text{HD}_5$  and the rise of decay times at low and high quantum states are reproduced. Additionally, strong variations of CD

overtone decay times across the series  $C_6HD_5$ ,  $p-C_6H_2D_4$ , and  $C_6H_5D$  are predicted.

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<sup>8</sup>Figure 3 of Ref. 5.