

Mode to mode energy flow amongst the ring modes of benzene¹

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Abstract

How energy moves around the vibrational modes of a polyatomic molecule, such as benzene, is of considerable interest, both spectroscopically and theoretically. Much effort has been devoted to observing and understanding how energy is transferred out of initially excited overtone states involving the CH stretching modes. Significantly less study has been devoted to an understanding of how and on what timescale energy is transferred amongst the ring modes. Such low frequency modes dominate the vibrational state density and also play a role in the irreversible nature of the decay out of C–H modes.

The motivation for the present classical trajectory study, is to model the results of recent experimental observations regarding the extent and timescale of IVR involving the ring modes. The linewidths found experimentally were instrument limited at 1 cm^{-1} for a range of excited ring modes for excitations of between 1200 and 8200 cm^{-1} yielding an upper limit on the IVR rate of 0.094 ps^{-1} . This result is consistent with the results of our trajectory calculations which reveal an initially rapid decay followed by slow IVR at longer times.

Keywords: Benzene; Energy flow; Intramolecular vibrational energy redistribution; Overtone linewidths; Zero-point energy

1. Introduction

Benzene has been of considerable interest both spectroscopically [1–6] (based on the experimental estimate of the linewidth, the lifetimes and rate constants obtained in Ref. [6] are in error by a factor of two and have been corrected in the present paper) and theoretically [7–14]. Much effort has been devoted to observing and understanding how energy is transferred out of initially excited overtone states involving the C–H stretching modes. The energy transfer out of the C–H stretching modes is rapid, occurring on a subpicosecond timescale. Sibert et al. [7] explained

these results as a consequence of a cubic coupling involving the C–H stretch and levels containing two quanta of CCH wag. This sort of efficient 2:1 Fermi resonant stretch bend mechanism for C–H modes occurs in a wide range of other molecules.

Considerably less study has been devoted to an understanding of how and on what timescale energy is transferred amongst the ring modes. Such low frequency modes dominate the vibrational state density and play a role in the irreversible nature of the decay out of C–H modes.

Recent experimental evidence obtained by Nicholson and Lawrance [6] has indicated that IVR amongst the ring modes is relatively slow. Indeed, analysis of high-resolution dispersed fluorescence spectra suggests that IVR amongst the ring modes in S_0 benzene up to 8200 cm^{-1} is much slower than that involving

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the excited C–H overtones. The instrument limited linewidths of 1.0–1.3 cm^{-1} were consistent with an IVR contribution of 0.5 cm^{-1} and indicate that the IVR rate has an upper limit of 0.094 ps^{-1} (IVR lifetime > 11 ps) [6].

The aim of the present study is to determine whether this experimental behaviour can be modelled by classical trajectory methods. The computational methods employed are briefly outlined in the next section, typical results are presented in Section 3 and conclusions are summarised in Section 4.

2. Computational methods

2.1. Potential energy surface

Many of the previous theoretical studies [7–14] have focussed on accounting for the interaction of the vibrational modes in planar models of benzene. This is apparently a good approximation when modelling the rapid IVR out of the C–H overtones [9]. In the present study the focus is on modelling IVR amongst the ring modes which occurs on a much

longer timescale [6]. Thus, in addition to the in-plane modes, we also consider the effect of out of plane modes. At the first level of approximation we assume Morse terms for the C–H stretches and a quadratic force-field for the remaining internal modes. The quadratic part of the force-field is largely based on the ab initio calculations of Pulay et al. [15]. A recent study by Handy et al. [16,17] reported some information on the potential energy surface of benzene up to quartic terms but they noted that most such potential coupling terms are small: ‘... the dominant potential coupling is C–H \leftrightarrow C–H potential coupling which includes diagonal anharmonicity and also anharmonic coupling between the C–H stretch normal modes to produce C–H stretch local modes. This accounts for over 80% of the potential coupling’.

Thus, such additional higher order potential couplings are likely to be small and are unlikely to play a significant role in the nature of the IVR involving the ring modes. This assumption will be tested in future studies.

The normal mode frequencies for the present model are compared with those of ab initio calculations, experiment and an earlier planar model in Table 1.

Table 1

Normal mode frequencies of benzene from ab initio studies of Pulay et al. (PFB) [15], experiment [15] and an earlier planar model of Clarke et al. [8] compared with the current model

Symmetry	Mode	PFB Set I	PFB Set II	Experiment	Clarke et al.	This work
e_{2u} (op,d)	16	402		398		401.1
e_{2g} (d)	6	607	607	606	606	606.1
a_{2u} (op)	11	667		673		662.7
b_{2g} (op)	4	701		707		699.9
e_{1g} (op,d)	10	843		846		838.5
e_{2u} (op,d)	17	969		967		963.5
b_{2g} (op)	5	996		990		990.1
a_{1g}	1	983	993	993	993	993.5
b_{1u}	12	997	1010	1010	1009	1009.1
e_{1u} (d)	18	1036	1036	1037	1033	1033.5
b_{2u}	15	1162	1145	1146	1140	1139.9
e_{2g} (d)	9	1183	1185	1178	1179	1179.1
b_{2u}	14	1297	1307	1309	1305	1305.5
a_{2g}	3	1365	1358	1350	1479	1350.5
e_{1u}	19	1482	1485	1482	1479	1479.3
e_{2g}	8	1607	1604	1599	1602	1602.2
b_{1u}	13	3051	3052	3057	3135	3135.9
e_{2g} (d)	7	3061	3061	3056	3145	3145.6
e_{1u} (d)	20	3080	3080	3064	3163	3164.4
a_{1g}	2	3095	3096	3073	3178	3179.2

Frequencies in cm^{-1} . op = out of plane modes, d = degenerate modes.

The overall agreement is reasonable, with some over-prediction of the C–H stretching frequencies but the ring mode frequencies, which are the primary focus of the present study, are well reproduced.

2.2. Classical trajectory analysis

Ensembles of 1000 classical trajectories are generated by integrating the equations of motion using a vectorised version of the “velocity Verlet” integrator [18]. Initial states are specified by excitations corresponding to local C–H modes or normal ring modes. Zero-point energy was allocated to all the other vibrational normal modes. The rate of IVR is monitored by investigating the ensemble averaged local and normal mode energies as a function of time. From comparison of ensembles of 1000 and 500 trajectories, these ensemble averaged energies are typically converged to better than 30 cm^{-1} .

3. Results and discussion

3.1. C–H overtone decays

Though the focus of the current study is on IVR involving the ring modes it is of interest to examine the behaviour of the present model on excitation of the C–H overtones. As in previous theoretical studies [7–14], the initial IVR involving the highly excited C–H overtones is found to be rapid as can be seen in Fig. 1

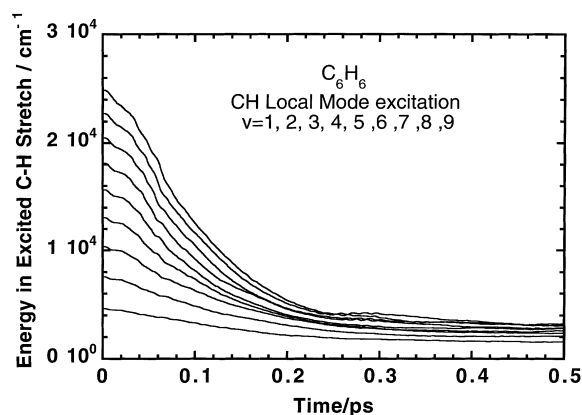


Fig. 1. Decay of the excitation energy in the initially excited C–H local mode of benzene for excitations of (in ascending order) $v = 1$ –9 quanta.

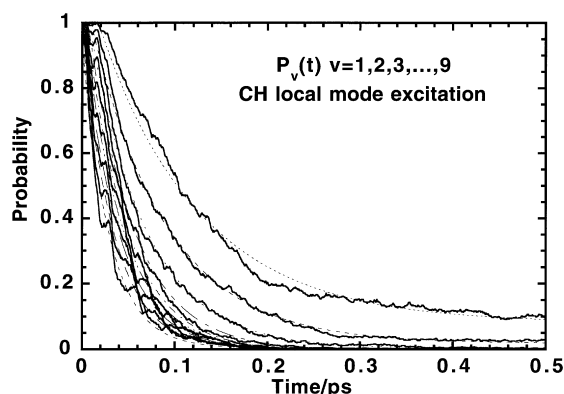


Fig. 2. Time dependent probability of remaining in the initially excited C–H local mode quantum state of benzene for excitations of (in descending order) $v = 1$ –9 quanta.

which depicts the decay of the excitation energy in the initially excited C–H local mode. By examining the time-dependent probability shown in Fig. 2 of remaining in a particular C–H local mode quantum state, overtone lifetimes can be determined to be in the range 30–144 fs. This is comparable with similar calculations [11] which show lifetimes in the range of 71–106 fs and with experimental results [1] which yield (deconvoluted) overtone lifetimes of the order of 48–123 fs.

3.2. Ring mode decay

The experimental study of Nicholson and Lawrance [6] probed a series of ring mode states involving

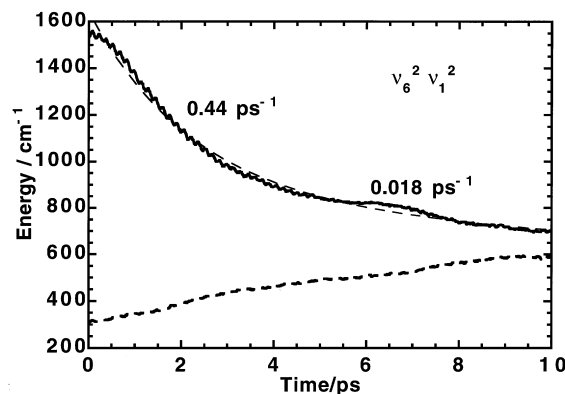


Fig. 3. Decay of the excitation energy in mode 6 for the initially excited $\nu_6^2\nu_1^2$ ring mode state of benzene. Both the initially excited and unexcited degenerate modes are shown.

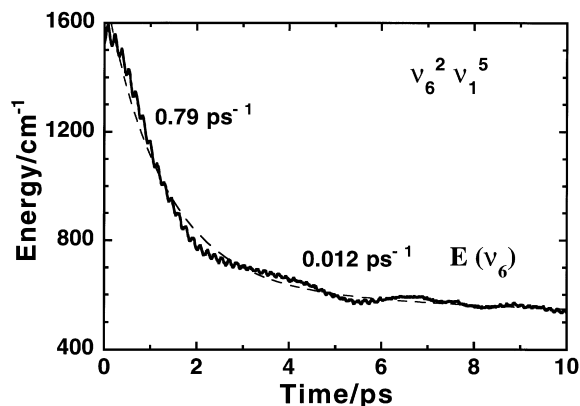


Fig. 4. Decay of the excitation energy in mode 6 for the initially excited $\nu_6^2\nu_1^5$ ring mode state of benzene.

several quanta of excitation in mode 1, the ring breathing mode (993 cm^{-1}), and two quanta of excitation in mode 6 (608 cm^{-1}). To compare with the experimental results, classical trajectory calculations were performed and the IVR out of these modes is shown for the initial states $\nu_6^2\nu_1^2$, $\nu_6^2\nu_1^5$ and $\nu_6^2\nu_1^7$ in Fig. 3, Fig. 4 and Fig. 5, respectively.

In Fig. 3 and Fig. 4, a rapid initial (subpicosecond up to picosecond) decay of energy out of the normal mode corresponding to mode 6 is followed by a much slower decay (on the timescale of many picoseconds). The primary source of the initial fast decay is shown in Fig. 5. There is an accidental Fermi resonance of mode 1 and mode 6 with mode 8 (1602 cm^{-1}). As energy drains from the initially excited mode 1 and mode 6 it enters mode 8 on a timescale of about a

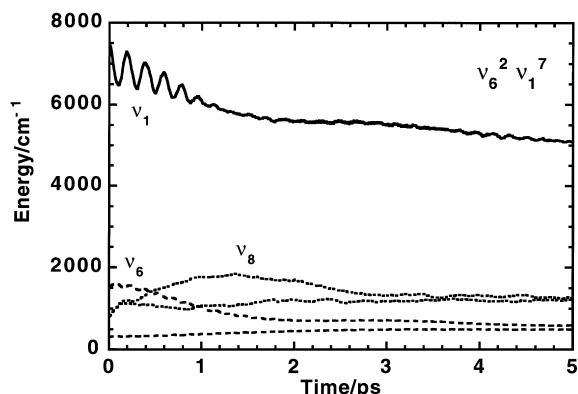


Fig. 5. Decay of the excitation energy in modes 1, 6 and 8 for the initially excited $\nu_6^2\nu_1^7$ ring mode state of benzene. Both of the degenerate 6 (dashed) and degenerate 8 (dotted) modes are shown.

Table 2

Timescale for the decay of energy out of the initially excited ring mode state. The decay times are obtained from a biexponential fit of the trajectory data

Excitation	Fast decay	Slow decay
$\nu_6^2\nu_1^2$	0.44 (2.3)	0.018 (57)
$\nu_6^2\nu_1^5$	0.79 (1.3)	0.012 (82)
$\nu_6^2\nu_1^7$	1.09 (0.9)	0.028 (36)
$\nu_6^2\nu_1^{10}$	1.43 (0.7)	0.029 (34)

Based on $E(\nu_6)$ for $\nu_6^2\nu_1^n$ excitations, $n = 2, 5, 7, 10$. Rates in ps^{-1} , lifetimes in ps in parentheses.

picosecond and then is transferred to other modes. On a much longer timescale, some of the remaining energy in mode 1 and mode 6 is transferred to other much more weakly coupled modes.

The timescale for the decay of energy out of the initially excited ring mode state is given in Table 2. For excitations in mode 1 of 2 up to 10 quanta, the initially rapid decay associated with the accidental Fermi resonance occurs on a timescale ranging from 2 ps down to 0.7 ps. The subsequent decay out of mode 6 (or mode 1), is much slower and occurs on a timescale ranging from 34 to 57 ps. This prediction of slow IVR is consistent with the results of the experimental study [6] which yield an upper bound on the irreversible IVR rate constant of 0.094 ps^{-1} (or a decay time of greater than 11 ps).

The current observations that IVR involving the ring modes of benzene is much slower than IVR out of the C–H overtones are consistent with a previous theoretical study [10] on the relaxation of excited normal modes of benzene. It concluded that the relaxation of the excited modes was incomplete on a timescale of 1 ps. Our findings are also consistent with the idea of that IVR occurs on a sequence of different timescales [1,7,11], reflecting the hierarchy from strong through to weaker mode-mode couplings present in benzene and in many other polyatomic systems. The fact that IVR may not be globally rapid throughout the energetically accessible phase space of a polyatomic reactant molecule has important ramifications for the validity of statistical theories of unimolecular reaction [19–21].

3.3. Influence of zero-point energy

The important question of how to deal with zero-point energy in a classical trajectory has been

considered previously via a large number of different approaches (see Refs. [7,11,12,22–29] and references therein). As noted by Hase [26], an example of good agreement between classical and quantum studies of IVR was demonstrated by Sibert, Reinhardt and Hynes [7,29] for the decay of excited CH overtones in benzene. The same is true of recent studies of IVR in a model of CH_3OOCH_3 [27,28] where excellent agreement was found between classical and quantum calculations. In both studies, the classical trajectories were performed by including all of the zero-point energy in the usual way [7,27–29].

It has been argued [12] that zero-point energy should be left out of the other modes to get accurate agreement with the experimental overtone linewidth for IVR in benzene. However, using this approach the agreement between corresponding classical and quantum simulations (e.g. for CH_3OOCH_3 in [27,28]) would be extremely poor as the classical IVR would be much too slow (since important coupling terms would be inactive or much less effective). Nevertheless it is possible that the nonconservation of zero-point energy can lead to some problems with classical simulations causing disagreement with quantum studies [7].

In the present study, the only modes suffering from a nonconservation of zero-point energy were the six high frequency C–H stretching modes which were initialised with just their zero-point energy. On a timescale of about 0.1 ps, about 250 cm^{-1} of zero-point energy was lost per C–H stretching mode. On a longer timescale of about 10 ps a further 250 cm^{-1} of zero-point energy was lost, leading to an overall loss of about 1/3 of the C–H stretching mode zero-point energy. To test whether this leakage of zero-point energy into the other modes could be avoided, further trajectory calculations were performed with zero energy in each of the C–H stretching modes and the same ring mode excitations described above. As a result, energy was drained from modes coupled to the C–H stretches (e.g. mode 8) leading to further zero-point energy violations. While the loss of energy from the excited ring modes was only slightly slowed, significantly less energy flowed to some of the other vibrational modes. Thus, leaving out zero-point energy for the C–H stretching modes leads to much less efficient IVR than in the calculations presented above which include all of the zero-point energy.

For the present study, the focus is on IVR in ring

modes of benzene and our results show that IVR is extremely slow (on the timescale of many picoseconds) compared with IVR out of the C–H overtones, consistent semi-quantitatively with experimental results [6]. Leaving out the zero-point energy assigned to the other normal modes would most likely slow the IVR further. The trajectories would still be consistent with the experiments [6] which yield an upper bound on the IVR rate (the linewidths are instrument limited). However, the author feels that leaving out the zero-point energy entirely is a worse approximation than including all of it. A more sophisticated approach would be to adopt one of the zero-point energy constraint procedures [22,23] but they have been known to lead to unphysical behaviour in certain cases [24]. The zero-point energy problem, fortunately, does not directly impact the aim of the present study which is to show that a simple model can indeed demonstrate slow IVR amongst the ring modes on a timescale consistent with the experimental results.

4. Conclusions

Classical trajectory calculations on a full-dimensional model of benzene, indicate that, whereas IVR out of excited C–H overtones is on a subpicosecond timescale, IVR involving the ring modes is on a considerably slower timescale, involving many picoseconds (more than 34 ps).

These results are consistent with lifetimes extracted from high-resolution dispersed fluorescence spectra obtained in recent experimental investigations [6] of IVR in the ring modes of benzene. These experiments suggest a lower limit on the IVR lifetime of 11 ps.

Further calculations are proposed on a more sophisticated model incorporating higher order potential couplings to determine their effect on the IVR lifetimes. What the effect will be is unclear at this stage, as the high order potential couplings are both small and numerous [17] and potential coupling can either reinforce or oppose the existing largely kinematic coupling.

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