Pressure Effects on the Relaxation of an Excited Hydrogen Peroxyl Radical in an Argon Bath
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Abstract

Molecular dynamics simulations were used to study the effect of pressure on the vibrational deactivation of HO₂ embedded in an Ar bath gas at 800 K and at pressures ranging from 10 atm to 400 atm. The time dependent decay of vibrational energy is found to be poly-exponential for all of the simulated pressures. Plots of the relaxation rate constants as a function of density show deviation from the expected linear dependence at ~250 atm. A combinatorial multi-bath-gas collisional model suggests this deviation is due to the breakdown in the isolated binary collision approximation. Comparisons to studies with similar findings and additional considerations for understanding this behavior are discussed.

Word Count:

Text (by Microsoft word)	3921
Equations	160
References	385
Tables (including captions)	182
Figures	<u>1140</u>
Total	5788

1. INTRODUCTION

Understanding intermolecular energy transfer for the chemically activated HO_2 peroxy radical is important in combustion because this pressure-dependent process influences the branching ratio of the $\text{H} + \text{O}_2$ reaction between chain branching to OH and O or stabilization to relatively inert thermalized HO_2 [1]. The pressure dependence of branching ratios are typically modeled by Master Equation methods that universally assume that inelastic collisions are binary events uninterrupted by collisions with other species. Since higher maximum pressures are becoming the norm in internal combustion engine design, [2] there is substantial interest in the pressures at which the isolated binary collision (IBC) assumption will break down. A substantial break down would make typical lower pressure measurements and standard Master Equation calculations unreliable at higher pressures in their modeling of the competition between stabilization and unimolecular addition-elimination reactions. This paper provides an initial theoretical answer to this question for the HO_2 system.

In a broad sense, theoretical energy transfer studies can be categorized by three types of methods. First, single collision methods simulate only isolated binary collisions in well-characterized initial states and account for the vast majority of studies.[3,4] Second, the successive collisions method of Schatz et al. [5] assumes only that the time between collisions is long enough for IVR to redistribute the energy under the constraint of conserved internal energy and angular momentum. This leads to a cascade of interconnected single collision calculations. Third, molecular dynamics (MD) methods explicitly follow both the molecule and atoms in a bath gas at a specific temperature and pressure. This method is free of the IBC assumption and any number of atoms as dictated by pressure can be involved in an inelastic collision with the molecule. There are only a recent few examples [6,7] of this approach in dense gases because of the computational expense of following bath gas collisions that largely serve only to maintain the thermal state of the bath. Only one of these examples, Rivera-Rivera et al. [7] (hereafter identified as RWST), explicitly considered IBC breakdown and concluded that for nitromethane in an Ar bath at 300K it occurs at ~ 100 atm, a pressure well within the operating range of engines.

The HO_2 system has had its potential energy surface, dynamics, and kinetics theoretically studied multiple times but never in the context of IBC breakdown. In a previous paper, [8] we compared two recent and one historic potential energy surfaces for their energetics, spectroscopy, IVR, isomerization, and unimolecular dissociation. We concluded that the XXZLG surface [9] was an efficient and reliable representation of the true HO_2 surface. The reaction kinetics of HO_2 has been studied in a variety of bath gases, including Argon. In RWST, pairwise potentials for Ar interacting with Ar, H, O, C, and N were developed, elements of which are applicable here.

The rest of this paper describes a classical trajectory MD study of the relaxation of vibrationally and rotationally excited HO_2 in an Argon gas over a range of pressures found in internal combustion engines. In Section II, we review the computational methods used. In Section III, we report both vibrational and rotational energy decay as a function of time for the various pressures and characterize that decay by functional forms whose parameters have a pressure dependence. From the pressure dependence we discuss at what pressure the IBC assumption begins to break down. In Section IV, we summarize our conclusions.

2. COMPUTATIONAL METHODS

In this section we describe the intermolecular potentials used, the home-grown MD simulation code, the process of preliminary calculations required to establishing the appropriate initial conditions, and the methods of analyzing MD simulations for the rotational and vibrational energy as a function of time.

2.1. Intermolecular Potentials

The potential energy for the system is given by

$$V = V_{HO_2} + V_{Inter}, \quad (1)$$

where V_{HO_2} is represented by the XXZLG potential [9] and V_{Inter} is the intermolecular potential between HO_2 -Ar and Ar-Ar, which is described using the pairwise additive Buckingham potential (Exp-6)

$$V_{ij} = \sum_i \sum_{j>i} A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (2)$$

The heteroatomic parameters of A_{ij} , B_{ij} , and C_{ij} used in Eq. (2) were the same as those used in RWST. The computational cost of evaluating V_{inter} was reduced by smoothly turning off the potential at a distance of 10 angstroms and using a neighbor-list [10] to exclude any pairwise interactions outside a cutoff distance of 12 angstrom. The neighbor-list was automatically updated when any atom in the simulation move a distance of 1 Å or greater.

Although a smaller part of the cost of the total potential, V_{HO_2} is a three dimensional spline which can be more rapidly evaluated than typical implementations of multidimensional splines [11]. V_{HO_2} uses three coordinates: R_{OO} (O-O distance), R_{OH} (O-H distance), and ϑ (H-O-O angle). While convenient to do the splines in three directions sequentially, this requires determining spline coefficients (the expensive part) in two dimensions and then evaluating the splines at the desired coordinate value with the coefficients (the inexpensive part). The more efficient approach [12] is to generate and archive once and for all the 64 coefficients in each hypercube that describe the cubic fit in three dimensions. The potential evaluation then involves trivial arithmetic to identify the relevant hypercube, construction of the cubic product basis set from the three coordinate values, and appropriate dot products of the basis times the recalled coefficients. There are two issues in applying this strategy to the XXZLG potential. First, for each of the 589 nodes in the (R_{OH}, ϑ) two dimensional grid there is a customized R_{OO} grid, resulting in altogether 295 unique R_{OO} values. To apply the strategy, the XXZLG value for all 295 unique R_{OO} values must be determined for each (R_{OH}, ϑ) grid point, resulting in $295 \times 589 = 173755$ hypercubes whose 64 coefficients must be stored. Second, round off error is reduced if the coefficients are with respect normalized coordinates, e.g., $(x - x_{lo}) / (x_{hi} - x_{lo})$ where $x_{lo}(x_{hi})$ are the lowest(highest) value of the coordinate for the selected hypercube. This form of the XXZLG potential is more than 50 times faster than the conventional form.

2.2. MD Simulation Code

All of the simulations were performed using the classical trajectory code GENDYN [13] modified for the dense gas simulations. The simulations of HO₂, embedded in a bath across a series of pressures (10, 50, 100, 150, and 400 atm) consisted of 1000 Ar atoms with a single HO₂ radical in a simulation box under standard periodic boundary conditions [14]. The bath temperature was 800 K and each ensemble consisted of 1,000 trajectories. The velocity Verlet integrator was used for integrating the equations of motion. The integration step size was 0.1 fs and the maximum integration time needed to relax HO₂ was determined from preliminary simulation results. Phase space points of the system were recorded every 3 fs for analysis.

2.3. Initial Conditions

As in RWST, the initial conditions were done in three sequential steps: (1) Populate the simulation box with the desired number of bath gas atoms, followed by adjustment of the box volume to obtain the desired pressure (done once for each pressure); (2) select the initial conditions of the HO₂; and (3) thermalize the bath gas. After the third step an NVE trajectory was integrated to near thermalization times determined by test simulations at each pressure.

2.3.1. Pressure

The initial volume of the simulation box was calculated using the ideal gas law for the desired temperature and pressure. HO₂ was centered in the box. Ar atoms were randomly inserted in the simulation box using a simple acceptance/rejection scheme. A trial placement of a bath gas atom was done by randomly selecting a previously placed atom, adding a random displacement to its three Cartesian coordinates, and inserting a test atom at the resulting position. The displacement of the test atom was randomly selected from a range of zero to half of the current simulation box length. The new placement was accepted if the total potential energy with the test atom remained less than zero; if rejected a new trial placement was generated. This process was repeated until all of the bath gas atoms were placed in the simulation box. A larger number of insertion rejections happened in the setup of the higher pressure simulations since positive potential energies due to strongly repulsive configurations occurred more frequently. A simple solution to prevent large rejection rates was to start with a larger estimated ideal gas volume and correct for the overestimated volume in the pressure adjustment trajectory. The lowest acceptance rate for the box population procedure was $\approx 20\%$.

After the placement of all of the bath gas atoms, Cartesian velocities were assigned to the bath atoms from Maxwell velocity distributions for the desired temperature. The trajectory was integrated for 25 ps with a 0.1 fs step size and the temperature and pressure for the system were calculated at each integration step and were smoothed by using a rolling average [15] with a 200 fs window (2,000 integration steps). After every 1000 integration steps (100 fs), the rolling average temperature of the bath was compared to the desired temperature and if the absolute difference was greater than 10 K the momenta were scaled using

$$P_N = P_O \sqrt{\frac{T}{T_{roll}}}, \quad (3)$$

where P_N and P_O are the new and old momenta, respectively, and T is the desired temperature. After the temperature was tested the rolling-average pressure was compared to the desired pressure. If the absolute difference was greater than 5% of the desired pressure then the volume

of the simulation box was resized to give the desired pressure and Cartesian positions of the bath gas were linearly scaled to reflect the change in the size of the simulation (with the HO₂ held stationary at the center of the box). The simulation box lengths were retained and smoothed with a 50 point rolling average.. The last rolling averaged box-length was determined for each pressure and used for all of the trajectories in each respective ensemble.

2.3.2. Solute Initial Conditions

The initial conditions of the radical were selected using *efficient microcanonical sampling* [16] with a total internal energy of 45 kcal/mol and no restriction on the angular momentum of the radical. The bath atoms were held fixed at the positions reached at the end of step (1) and only the reactant was changed during the Markov walk. The intermolecular potential was ignored, so the surrounding bath gas had no effect on the selection of the internal state of the reactant. Any possible interatomic overlaps between HO₂ and Ar were dealt with in step (3) below. A warm-up walk of 250,000 steps in Cartesian coordinates was started from the equilibrium geometry in which all three atoms of HO₂ were allowed to move with random displacements. The maximum possible displacement of a single atom was 0.2 Å. At the end of the walk a set of momenta were sampled and scaled to obtain the desired energy. The final coordinates of HO₂ at the end of the Markov walk were used as the starting configuration for selecting the initial conditions of the next trajectory in the simulation. Subsequent walk lengths consisted of 100,000 steps that were taken between trajectories. The length of subsequent walks was selected based on the convergence of the coordinates and potential energy as a function of the number of steps in the Markov walk. The number of accepted moves of each walk was between 0.4 and 0.6. After assigning the initial conditions for the vibrational and rotational degrees of freedom a set of translational velocities were selected and assigned to the center of mass of HO₂. The result is a radical that is vibrationally and rotationally hot, but translationally thermal with respect to the bath gas.

2.3.3. Final Thermalization

The previous step can result in highly repulsive interatomic overlaps between the HO₂ and Ar atoms. To correct for this possibility, the bath gas atoms were re-thermalized with a new set of velocities. The reactant was again held fixed, as described in step (1) but retained the phase space point selected in step (2). A thermal trajectory was integrated for 25 ps with the temperature controlled in the same manner as in step (1). The final Cartesian coordinates of the bath-gas atoms were stored at the end of each thermalization trajectory, and used as the starting configuration for subsequent thermalization trajectories in the respective ensemble.

2.4. Internal Molecular Energy Analysis

Analysis of the energy transfer between the hydrogen peroxy radical and the bath was done by decomposing the Hamiltonian of the radical into the translational, rotational, and vibrational components. The separation of linear momenta of the radical is exact. After removing the translational component a zeroth-order separation of rotational and vibrational energy was assumed

$$H_{RV} = H_R + H_V, \quad (4)$$

where H_R was calculated using

$$H_R = \frac{1}{2} L \cdot I^{-1} \cdot L. \quad (5)$$

L is the whole-body rotational angular momentum

$$L = r \times p, \quad (6)$$

and I is the instantaneous moment of inertia. This allows the vibrational energy to be defined as

$$H_V = H_{RV} - H_R. \quad (7)$$

Frederick et al. [17] described several different ways of approximately separating the vibrational and rotational degrees of freedom in molecular systems and recommended using Eq. (5) because the definition is independent of the coordinate system.

The vibrational or rotational energy was calculated using Eqns. (4)-(7) as a function of time and the asymptotic thermal energy $E(\infty)$ ($3\kappa T$ for vibration and $1.5\kappa T$ for rotation where κ is the Boltzmann constant) was subtracted to obtain a quantity designated “excess vibrational (or rotational) energy.” The energy loss from the radical will cause the bath to heat to a new asymptotic temperature. With full thermalization of the initial molecular excitation of 45 kcal/mol over 1000 Ar atoms, the temperature increase is ~ 13 K. Consequently, ensemble average temperature T of the bath gas is time-dependent and was saved during the simulation.

3. RESULTS

We have calculated trajectories to determine the relaxation of HO_2 , with initial internal energy 45.0 kcal/mol above the classical ground state, in Ar at 800 K and at pressures of 10, 50, 100, 150, and 400 atm. The initial energy is low enough below the dissociation threshold so that none of the 1000 trajectories in the ensemble dissociate. In part 3.1 of this section, the ensemble-averaged energy in HO_2 as a function of time is presented for all five pressures. In part 3.2, analytic fits to the decay curves are presented and discussed.

3.1. Decay curves

The ensemble-averaged rotational (blue curve), vibrational (red curve), and translational (green curve) energies over 1000 ps are shown in Fig. 1 for 100 atm. The results clearly show the equilibration of the rotational and translational energy to values approaching $1.5 \kappa T$ (~ 2.4 kcal/mol for $T = 800$ K). The inset in Fig. 1 shows that translation equilibrates within ~ 100 ps, while the full plot shows that the rotational energy takes more than twice as long while vibrational energy is only half way to equilibrium (~ 4.8 kcal/mol) by 1000 ps. These equilibration times vary with pressure in expected ways but the order-of-magnitude difference in equilibration times for rotation and vibration stays the same. As the green curve in the inset in Fig. 1 shows, the translational energy of the molecule increases significantly from its initial equilibrium value for the first few picoseconds. This is likely an artifact of initial condition preparation where molecule-bath interactions are ignored during assignment of the molecular center-of-mass kinetic energy. The internal energy relaxation times are significantly slower than

RWST found for CH_3NO_2 , a consequence of the relatively few vibrational modes in HO_2 and

FIG. 1. Ensemble averaged vibrational, rotational, and translational energies versus time at 100 atm. The inset is a zoom-in of the lower left-hand corner of the plot.

their stiff nature.

In Fig. 2, the normalized ensemble-averaged *excess* vibrational energy $Enrm-vib(t)$ is plotted as a function of time for all five pressures in the main panel for $t \leq 1000$ ps and for $P = 10$ and 50 atm in the inset for up to $t = 5000$ ps. Since Fig. 2 is on a log scale, a single-exponential decay would be a straight line. The results show curvature at all pressures indicating multiple decay rates govern the relaxation to vibrational equilibrium. The results also show the expected increase in decay rates with pressure.

In Fig. 3, $Enrm-rot(t)$ for rotational relaxation is displayed in a manner similar to Fig. 2 only for a shorter time scale. As expected Fig. 3 shows rotational relaxation increases monotonically with pressure. However, the most striking feature of the results in Fig. 3 is that ~5% of the initial excess rotational energy (~0.1 kcal/mol) remains

FIG. 2. $Enrm-vib$ versus time. Solid curves are the trajectory results; dashed curves are fits. The inset expands the 10 and 50 atm results to up to 5000 ps.

FIG. 3. $Enrm-rot$ versus time analogous to Fig. 2 only for a maximum time of 500 ps (1500 ps for the inset).

in the molecule for very long times. We suspect this is due to the fact vibrational and rotational energy are not strictly separable, leading to the residual coupling seen in the figure whose size is consistent with studies [18] on other triatomic molecules.

3.2. Analytic fits to decay curves

The presence of curvature in Fig. 2 for the excess vibrational energy requires a representation more flexible than a single exponential. As in RWST, the Lendvay and Schatz [19] (LS) form is used:

$$E_{nrm}(t) = [1 - (1 - m)k_i t]^{1/(1-m)} \quad (8)$$

This form has only *two* parameters: k_i which is the initial rate of decay and m which determines departure of the decay curve from a straight-line single-exponential behavior on a semi-log plot ($m > 1$ implies $E_{nrm}(t)$ curves up). The LS fit for $E_{nrm-vib}$ are the dashed curves in Fig. 2 with optimized parameter values in Table I.

Inspection of Fig. 2 shows the fit is reasonably good though at 400 atm and at later times, the computed $E_{nrm-vib}(t)$ becomes small and the finite sampling error introduces raggedness in the data. However as shown in Fig. 4, at times less than 100 ps, the LS fit systematically underestimates the rate of decay at higher pressures (see dashed black lines in the figure). Figure 4 also shows that the data has significant noise on the scale of the figure due to finite sampling. This means that the k_i value in the LS fit is not fully reliable as an estimation of the *initial* rate which in turn cannot be known to great precision without running a larger number of trajectories. The dashed colored lines in the figure are LS fits *only* over 100 ps. These fits are much improved over only 100 ps and their k_i values, designated k_i^{100} , are also listed in Table I.

Table I. Parameter values m , k_i , and k_i^{100} versus pressure or density for fits to $E_{nrm-vib}(t)$.

Pressure(Density)	m	k_i	k_i^{100}
(atm) ($\times 10^3 \text{ \AA}^{-3}$)		($\times 10^3$)	(ps $^{-1}$)
10 (0.0912)	3.21	0.171	0.507
50 (0.452)	3.57	0.641	0.645
100 (0.891)	3.62	1.23	2.06
150 (1.33)	2.74	1.27	1.93
400 (3.29)	2.14	2.56	4.23

Plots of the parameter values m and k_i^{100} as functions of density are shown in Figs. 5 along with error bars determined by bootstrap methods [20] using 2000 random realizations of the 1000 trajectories. The m parameter values fall between ~ 2.5 to ~ 3.5 . The persistence of this curvature over such a wide variation of conditions suggests that the *intra*-molecular dynamics of HO₂ primarily controls the curvature. The C₆F₆/N₂ study of Paul et al. [6] and the RWST CH₃NO₂/Ar study show noticeable curvature (though not at all at such a high level), indicating a common behavior of polyatomic energy decay. The solid red curve in Fig. 5 is a fit of m to a convenient form $a + b\rho e^{-c\rho}$ used in RWST where ρ is the density in $1/\text{\AA}^3$ and the optimized values of (a, b, c) are (2.251, 9873 $\text{\AA}^3$, 2321 $\text{\AA}^3$).

Figure 5 shows that the k_i^{100} parameter values increase monotonically with the density but not in direct proportion to density. Given the large error bars, at a density of $\sim 0.002 \text{ \AA}^{-3}$ corresponding to ~ 250 atm, k_i^{100} begins to drop below direct proportionality, indicating a departure from the IBC model where rates directly scale with density. (RWST observed a similar density for CH₃NO₂.) The loss of direct proportionality indicates the molecular/bath-gas interaction changes

with density. The rise of interfering collisions of multiple bath gas atoms with the molecule is an example of such a change. In RWST, a model was developed that estimated the probability of molecular/bath-gas collision events involving N bath-gas atoms. This model discretizes space into cells one Ar atom in size. The molecule centered in this space occupies the cells required by its size (2.0 Å radius based on its equilibrium geometry and pairwise interactions with Ar). Combinatorial arithmetic determines for a given density the probability of N cells bordering HO₂ being occupied by an Ar atom, i.e., N Ar atoms in a collision event. By optimization to k_i^{100} values, a relaxation rate for a single collision (2.0 ps⁻¹) and a rate per atom for multiple collision (0.74 ps⁻¹) lead to the solid blue line in Fig. 5. The parameter values roughly suggest that while

FIG. 4. As in Fig. 2, only for data and fit restricted to first 100 ps. The black lines reproduce the dashed lines in Fig. 2.

FIG. 5. From Table I, m and k_i^{100} values for vibrational relaxation versus density. The solid lines are fits to m and k_i^{100} (see text).

N -collisions rates are generally more effective than single collision rates, they are not N times more effective. At higher densities, N -collisions begin to replace N single collisions, leading to rates no longer proportional to density. Because this model depends on density, as the temperature increases the pressure corresponding to critical densities will also increase, e.g., ~100 atm at 300 K in RWST and ~250 atm at 800 K here.

The LS fits for $E_{nrm-rot}$ are the dashed curves in Fig. 3. However, the presence of the slowly decaying residual energy complicates the fitting process. As in RWST, the maximum time over which the LS fit is applied is limited to that time for which the LS fit falls within the error of the mean 85% of the time. RWST found 85% limit is sufficient to capture the rotational decay while excluding the slow residual

Table II. Parameter values m and k_i versus pressure or density for fits to $E_{nrm-rot}(t)$.

Pressure(Density)		m	k_i
(atm)	($\times 10^3 \text{ Å}^{-3}$)		
10	(0.0912)	1.23	0.021
50	(0.452)	1.28	0.114
100	(0.891)	1.27	0.217
150	(1.33)	1.44	0.373
400	(3.29)	1.40	0.943

energy that persists at long times. The figure shows the LS fit is quite reasonable at all pressures when the residual energy is excluded. Table II lists the optimal LS parameter values.

As in CH_3NO_2 the m parameter values in Table II are in a narrow range somewhat above unity. The narrow time window for the LS fit accentuates single-exponential decay and corresponding low values of m . Unlike the vibrational k_i in Fig. 5, k_i in Table II is nearly directly proportional to density as also seen in CH_3NO_2 . Higher pressures affect vibrational and rotational energies differently. Not unexpectedly, k_i is ~ 100 times larger than its vibrational analogue, although it is ~ 10 times slower than its counterpart in CH_3NO_2 .

4. CONCLUSIONS

The relaxation of highly vibrationally and rotationally excited HO_2 in an Ar bath gas at 800 K was simulated by molecular dynamics techniques over a range of pressures from 10 atm to 400 atm. The decay of vibrational energy was not well represented by a single exponential function and in particular the vibrational relaxation rate slowed down as the energy content of the molecule dropped. This was also true for rotational relaxation but is much less prominent. All decay rates are fit reasonably well by the Lendvay-Schatz [19] form that conveniently represents poly-exponential decay behavior. This behavior suggests that the intramolecular dynamics plays an active role in energy transfer to the bath gas atoms. The initial vibrational decay rate begins to show a non-linear dependence on densities higher than $\sim 0.002 \text{ \AA}^{-3}$ corresponding to ~ 250 atm at 800 K. This deviation implies the breakdown of the isolated binary collision model. The density dependence can be reasonably well represented by a combinatorial collision model proposed Rivera-Rivera et al.⁷ that represents the effect of interfering collisions of multiple bath gas atoms with the molecule. Rotational relaxation rates remain proportional to density over the full range of pressures studied. All of these results are qualitatively similar to results of $\text{CH}_3\text{NO}_2/\text{Ar}$ at 300 K found by Rivera et al. and are related to results of $\text{C}_6\text{F}_6/\text{N}_2$ found by Paul et al.[6]

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