

Connecting Chemical Dynamics in Gases and Liquids

Christopher G. Elles and F. Fleming Crim, *Annu. Rev. Phys. Chem.* 57:273-302 (2006).



Schedule

- 11/22
 - Introduction
 - Theory
- 11/27
 - Energy transfer and Vibrational relaxation dynamics
- 11/29
 - Photodissociation reaction
 - Bimolecular reaction

Today

- 11/22
 - Introduction
 - Theory
- 11/27
 - Energy transfer and Vibrational relaxation dynamics
- 11/29
 - Photodissociation reaction
 - Bimolecular reaction

A decorative graphic on the left side of the slide, consisting of a light green vertical bar and a dark blue horizontal bar with rounded ends.

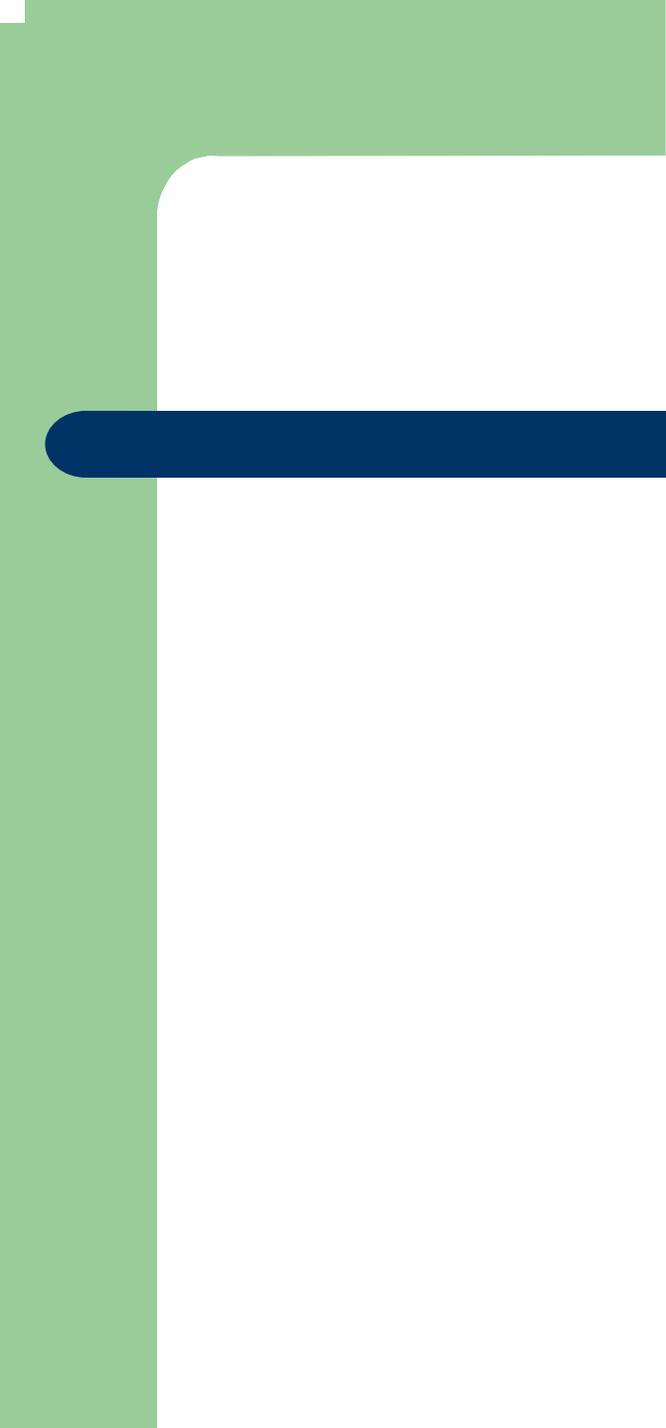
Introduction

Introduction

- Comparing chemical dynamics
 - Achieve information of more complex environments
- Effect of solvent
 - Minor limit : changing the energies slightly
 - Profound limit : intimate part of the chemistry

Introduction

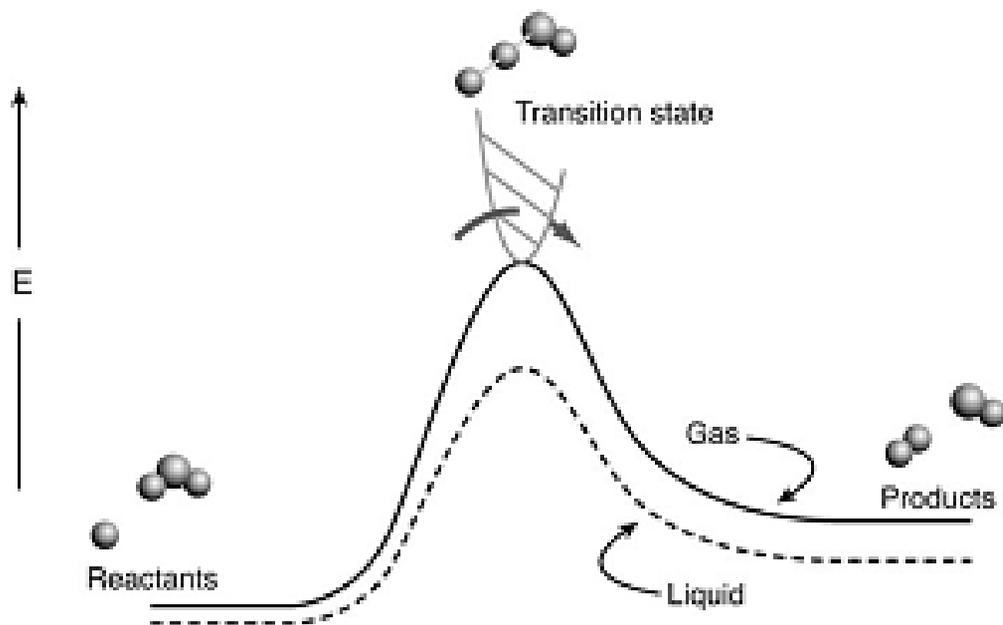
- Goal in this review
 - Examine recent progress
 - Look toward the prospect
- Examples
 - Energy transfer : extensively studied
 - Photodissociation
 - Bimolecular reaction : infancy

A decorative graphic on the left side of the slide, consisting of a light green vertical bar and a dark blue horizontal bar with rounded ends.

Theory

Transition state

- Unifying concept in chemistry
- Influence of the solvent



Transition state

- Statistical theory
 - Molecules explore all of the available configurations
- Convenient framework for discussing chemical dynamics

Simple comparison

	Gas	Liquid
Encounter	Translate freely between collisions	Controlled by diffusion
Limiting rate (for a bimolecular reaction)	Collision rate	Rate of diffusive encounter
Rate constant (for two reactant A and B)	$k_g(T) = \langle v_{AB} \sigma_{AB} \rangle$	$k_D(T) = 4\pi D_{AB}(R_A + R_B)$

- Both depends on the size of the reactants

Treating a liquid simply as a dense gas

- Means of estimating timescales
- Density of gas at 1 torr
 - Collide every 100ns
- Gas having the density of a liquid
 - Collide every 100fs
 - > interaction are not separated in time
- Limits
 - Leaves out important features

IBC model

- Treats the liquid as a lattice
- Relative motion of the lattice
 - Collision occurs every 300fs
- Surprisingly good estimates
- k of energy transfer : $k_{if}(T, \rho) = Z(T, \rho)P_{if}$
- $\langle v(t)v(0) \rangle$ provides an collision interval

IVR (intramolecular vibrational relaxation)

- Complete sampling of configuration
 - TS theory connects gases and liquids
- Energy flow among the available vibrational states within the molecule
- Gas : depends on the coupling within the molecule

IVR (intramolecular vibrational relaxation)

- Liquid : complications
 - Change the intramolecular coupling
 - Enable an otherwise unfavorable transition
 - Accepts or provides small amount of energy to bring the levels into resonance (counterpart of collision induced intramolecular energy flow)

IET (intermolecular energy transfer)

- Energy transfer from solute to solvent
- Vibration => vibration, collective mode
- Solute receives energy from the relaxing solute
- Counterpart of collisional energy transfer in the gases

Removal of Averaging

- Studying liquid recapitulates these of gas
- Removing of the averaging
 - First step of studying dynamics
- Preparing molecules in an excited state
 - Removes the averaging
- Knowing lifetime is important either in a liquid or a gas

Connecting Chemical Dynamics in Gases and Liquids

Christopher G. Elles and F. Fleming Crim, *Annu. Rev. Phys. Chem.* 57:273-302 (2006).

2nd Day

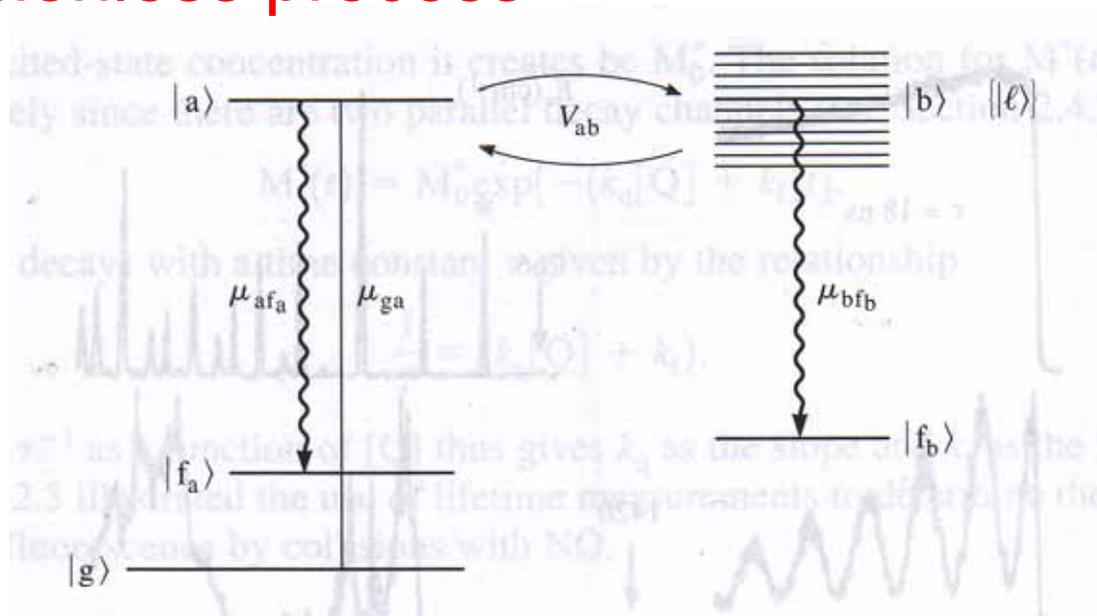


Today

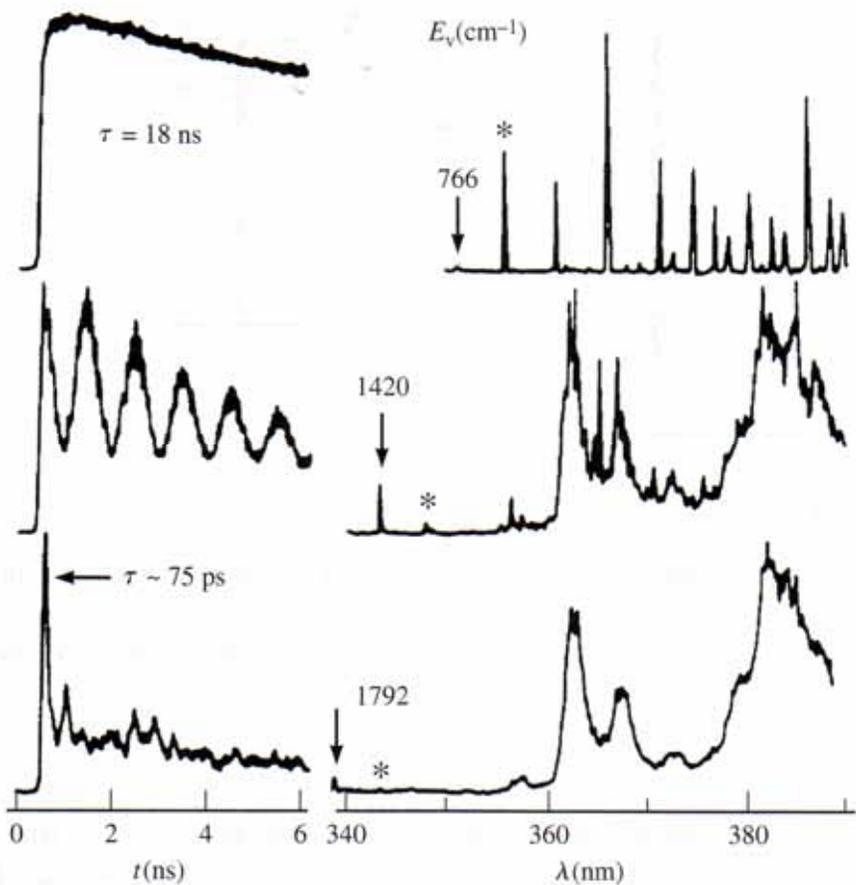
- 11/22
 - Introduction
 - Theory
- 11/27
 - Energy transfer and Vibrational relaxation dynamics
- 11/29
 - Photodissociation reaction
 - Bimolecular reaction

Intramolecular Vibrational Relaxation

- Coupling of different vibrational mode
 ➡ Energy redistribution over the collisionless process



Example



Fluorescence spectrum of anthracene

Rates of the IVR

- From Fermi's Golden Rule

$$k_{if} = (2\pi/h) |V_{if}|^2 \delta(E_i - E_f)$$

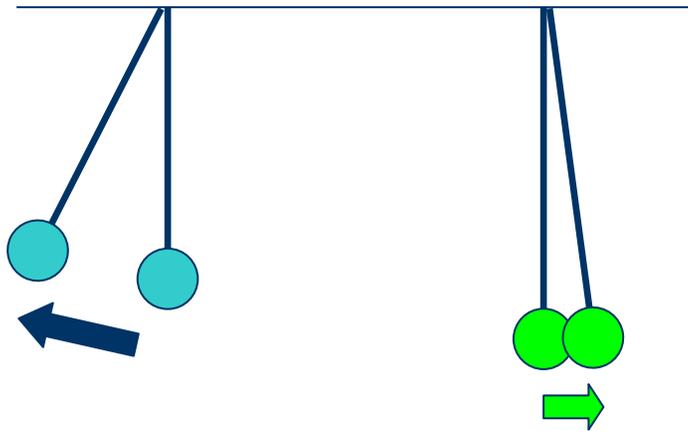
- For all final states,

$$k_i = (2\pi/h) |V|^2 \rho(E_i)$$

- Two key parameter :

density of states, coupling strength

Comparison with Pendulum



- Density of states
> Number of linked
Pendulums
- Coupling strength
> length

Landau - Teller Model

- Including the solvent effect
- Treating the solvent as a perturbation
- Solvent friction – relaxation rate
- Calculation of force correlation function – Information about relaxation rate

Landau - Teller Model

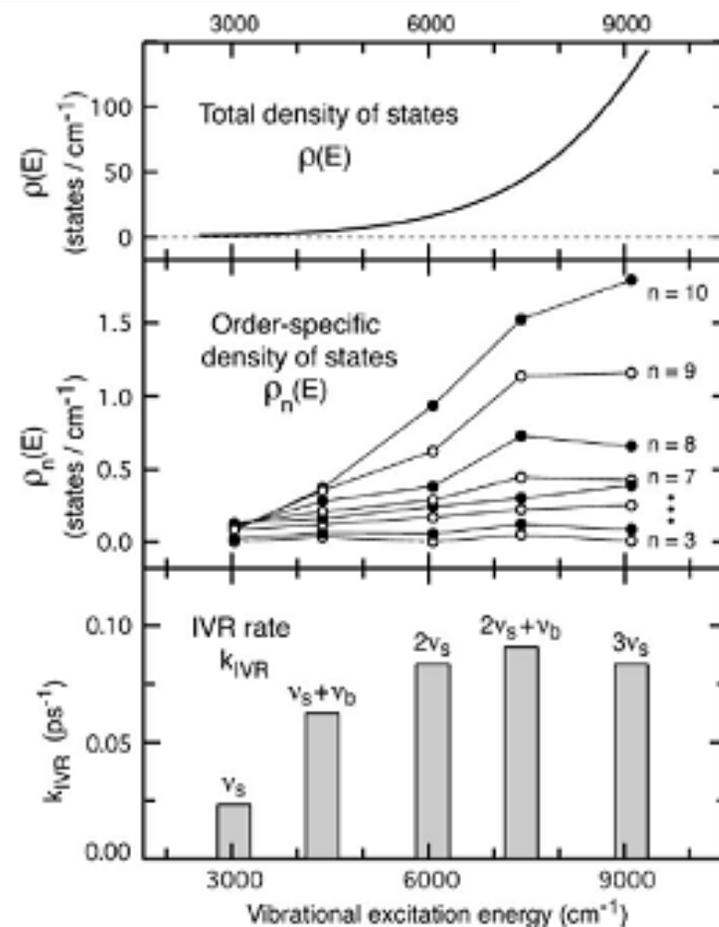
- Two limits
 - Solvent dose not matter
 - Solvent-driven dynamics dominates
- Many molecule are in intermediate regime

IVR in Gases and Liquids

- Ways to controlling aspects of vibrational energy flow
 - : changing the state structure, changing the strength of its interaction with the solvent

Example 1 – CH₂I₂

- C-H stretch and stretch-bend combination mode
- Not all available states participate in the energy flow
- Changing the solvent affects fundamental C-H stretch then the first overtone
- Stronger influence on the slow dynamics



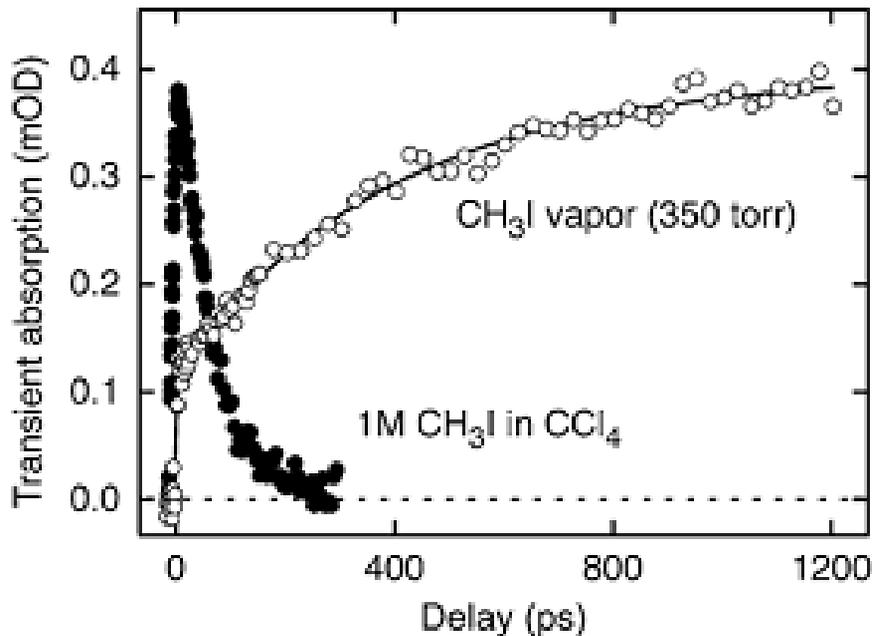
Example 2 – C-H stretch of benzene

- Two characteristic timescale : fast(<0.5ps) and slow(50ps)
- fast : from strongly coupled states, not affected by solvation
- slow : from weakly coupled states, greatly affected by solvation (4ps)

Example 3 – Supercritical fluids

- Changing its density from that of a gas to that of a liquid
- fast one : dose not change
- slow one : continuously change (Fits with Landau - Teller model)

Example 4 – Competes with IET



- Time evolution of the population of the low-frequency C-I stretch mode of CH₃I
- In solution, IET to the solvent drains the molecule of its energy before the second stage of IVR occurs

Example 5 – Terminal acetylene

- Most comprehensive comparison
- Solvent accelerates the relaxation
- Same extent of acceleration for all of the acetylenic molecule -> intrinsic IVR and solvent-driven IVR occurs independently
- $k_{IVR} = k_{intrinsic} + k_{solvent}$

Connecting Chemical Dynamics in Gases and Liquids

Christopher G. Elles and F. Fleming Crim, *Annu. Rev. Phys. Chem.* 57:273-302 (2006).

3rd Day



Today

- 11/22
 - Introduction
 - Theory
- 11/27
 - Energy transfer and Vibrational relaxation dynamics
- 11/29
 - Photodissociation reaction
 - Bimolecular reaction

Photodissociation Reaction

- $AB + h\nu \longrightarrow A + B$
- Unique window into chemical dynamics
- Presence of solvent
 - altering energy disposal
 - changing the relative energies
 - limiting the separation

> Substantial effect
- Same principles apply to other unimolecular reactions

Examples

- PES of isolated molecule
: starting point for describing photodissociation reactions in solution
- Solvent does not change the shape of the surface in the Franck-Condon region
- Gas-phase potential contains information about the initial dynamics in solution

Example 1 : iodialkane

- Resonance Raman spectra
- Little effect on the initial dynamics
- early photo dissociation dynamics are not greatly altered by solvation

Resonance Raman lines of CH₃I

Transition	Vapor [8,11]		Solution phase (this work)			Calculated	
	freq. (cm ⁻¹)	rel. int. ^{a)}	freq. (cm ⁻¹) ^{b)}	rel. int. ^{c)}	width (cm ⁻¹) ^{d)}	freq. (cm ⁻¹)	rel. int.
3 ₁	528	1.00	531	1.00	9	528	1.00
3 ₂	1050	0.90	1053	0.98	14	1050	0.75
2 ₁	1254	0.10	1242	0.14	<6	1242	0.02
3 ₃	1567	0.56	1565	0.83	22	1565	0.60
2 ₁ 3 ₁	(1780)	<0.02	1759	0.03	<6	1770	0.03
3 ₄	2082	0.50	2076	0.64	36	2074	0.51
				(13.2 × 10 ⁻¹¹) ^{e)}			(7.9 × 10 ⁻¹⁰) ^{e)}
2 ₁ 3 ₂	(2297)	<0.02	2288	0.06	27	2292	0.03
3 ₅	2587	0.39	2579	0.60	49	2576	0.44
2 ₁ 3 ₃	2797	0.02	–	–	–	2807	0.03
3 ₆	3092	0.42	3070	0.84 ^{f)}	76 ^{f)}	3072	0.39
2 ₁ 3 ₄	3307	0.08	–	–	–	3316	0.04
3 ₇	3588	0.40	3558	0.41	68	3562	0.35
2 ₁ 3 ₅	3799	0.08	3787	0.03	31	3818	0.04
3 ₈	4073	0.36	4045	0.41	74	4046	0.32
2 ₁ 3 ₆	(4304)	<0.07	4276	0.12	70	4314	0.04
3 ₉	4562	0.26	4518	0.28	88	4523	0.29
2 ₁ 3 ₇	4781	–	4766	0.02	24	4804	0.03
3 ₁₀	5044	–	4995	0.45	114	4994	0.27
2 ₁ 3 ₈	5277	–	5234	0.06	(48)	5288	0.03
3 ₁₁	5516	–	5450	0.40	104	5458	0.25
3 ₁₂	5982	–	5906	0.43	98	5916	0.23
3 ₁₃	6446	–	6366	0.34	110	6368	0.22
3 ₁₄	6896	–	6813	–	–	6813	0.20
3 ₁₅	7347	–	7244	–	–	7253	0.19

Example 2 : CH₂I₂

- Solvent induced symmetry breaking
 - : changes the short time dynamics
- In gas phase
 - moves along symmetric I-C-I stretch
 - selection occur outside of Franck-Condon region.
- In solution phase
 - one bond to stretch more than the other
 - selection occurs inside of Franck-Condon region.

TABLE VI. Most probable internal coordinate displacements of diiodomethane at $t=15$ fs assuming the C-I bond becomes longer.

Internal coordinate	Gas phase 15 fs ^a	Solution phase (in methanol solvent)	
		15 fs with $\Delta_2=+1.3^\circ$	15 fs with $\Delta_2=-1.3^\circ$
C-H bonds	-0.008 Å (-0.009 Å)	-0.004 Å (-0.006 Å)	-0.004 Å (-0.006 Å)
C-I bond, atoms 1 and 4	+0.146 Å (+0.142 Å)	+0.169 Å (+0.162 Å)	+0.010 Å (+0.004 Å)
C-I bond, atoms 1 and 5	+0.146 Å (+0.142 Å)	+0.010 Å (+0.004 Å)	+0.169 Å (+0.162 Å)
H-C-H angle, atoms 2, 1, and 3	-2.4° (-2.5°)	-1.5° (-1.4°)	-1.5° (-1.4°)
H-C-I angle, atoms 2, 1, and 4	+2.8° (+3.2°)	-0.4° (+0.1°)	+3.5° (+4.0°)
H-C-I angle, atoms 3, 1, and 5	+2.8° (+3.2°)	+3.5° (+4.0°)	-0.4° (+0.1°)
H-C-I angle, atoms 2, 1, and 5	+2.9° (+3.3°)	+3.5° (+4.0°)	-0.2° (+0.3°)
H-C-I angle, atoms 3, 1, and 4	+2.9° (+3.3°)	-0.2° (+0.3°)	+3.5° (+4.0°)
I-C-I angle, atoms 4, 1, and 5	-8.9° (-11°)	-4.9° (-7.0°)	-4.9° (-7.0°)

Example 3 : OCIO

- More dramatic example
- Difference in the Franck-Condon region
- Solvation initially preserves the C_{2v} symmetry of the dissociating molecule
- Solvation makes Cl+O₂ channel more important

Example 4 : triatomic molecule(HgI_2 , I_3^-)

- Solvent changes distribution of excess energy
 - > affects to the dynamics
- Excess energy >> rotation and vibration of the diatomic fragment
- Gas
 - fragment(HgI , I_2^-) has higher excitation level
- Solution
 - relaxes the vibration within 2 or 3 ps
 - high time resolution needed
- Prediction on CN fits well to the following experiment

Example 5 : HOCl (1)

- Inhibiting the separation of the fragments
 - > trap the nascent pair within a solvent cage
- Excess energy goes into the relative translational energy of the atomic fragments
 - > measure the stopping power of the solvent
- Germinate recombination

Example 5 : HOCl (2)

- r_0 determines the probability that they will recombine

- $$P(t) = 1 - \frac{(R_A + R_B)}{r_0} \cdot \operatorname{erfc}\left[\frac{r_0 - (R_A + R_B)}{\sqrt{4D_{AB}t}}\right]$$

- r_0 increased linearly with the excess energy

Example 6 : CH_2I_2

- Recombination can cause isomer and it can play an important role in secondary reaction
- $\text{CH}_2\text{I-I}$ isomer formed within 1ps
- Several polyhalomethane can also form that kind of isomer

Bimolecular Reactions

- Generating reactants with well-defined initial internal energy is hard in solution
 - > hard to achieve good state resolution
- There are no examples of state-to-state studies

Bimolecular Reactions

- Photodissociation is an effective means of producing reactive radicals in solution
- Interaction rapidly dissipate the excess kinetic energy
 - > little excess energy for reactions occurring beyond the first solvent shell
- Vibrational excitation can survive for up to hundreds of picoseconds

Examples

- Few examples of generating reactive species which have sufficient time resolution and state selectivity
- Some pioneering experiments
 - Absorptions of the solvent and products lie in separate spectral regions
 - Cl, CN can be prepared with selected vibrational states and survive long enough for a reactive encounter

Example 1 : Cl + C₆H₁₂

- $Cl_2 + h\nu \rightarrow 2Cl$
- $Cl + C_6H_{12} \rightarrow HCl + C_6H_{11}$
- Using transient infrared absorption, detects HCl product
- Determine the rate constant

Example 2 : CN + CHCl₃

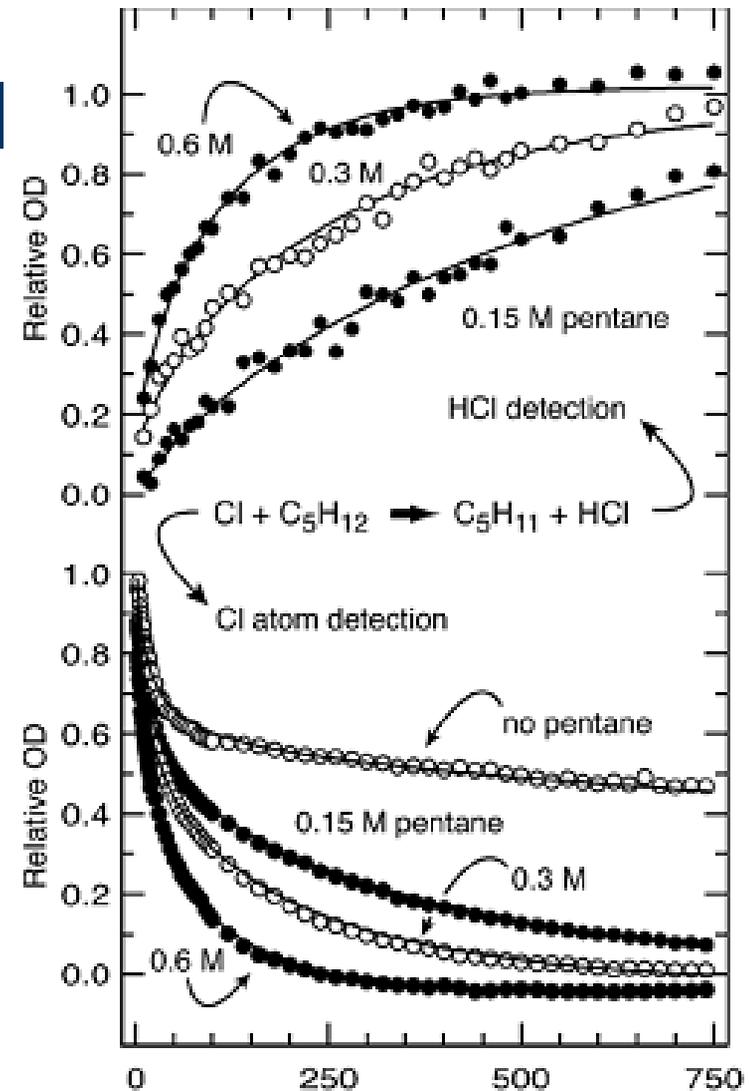
- $ICN + h\nu \rightarrow CN + I$
- Competition between two reaction channels
- HCN or ClCN

Example 3 : Cl in CH₂Cl₂

- Photolysis of Cl₂ in CH₂Cl₂
- Hydrogen abstraction reaction
- Addition of n-pentane
 - Provides other abstraction channel
 - Accelerates the reaction

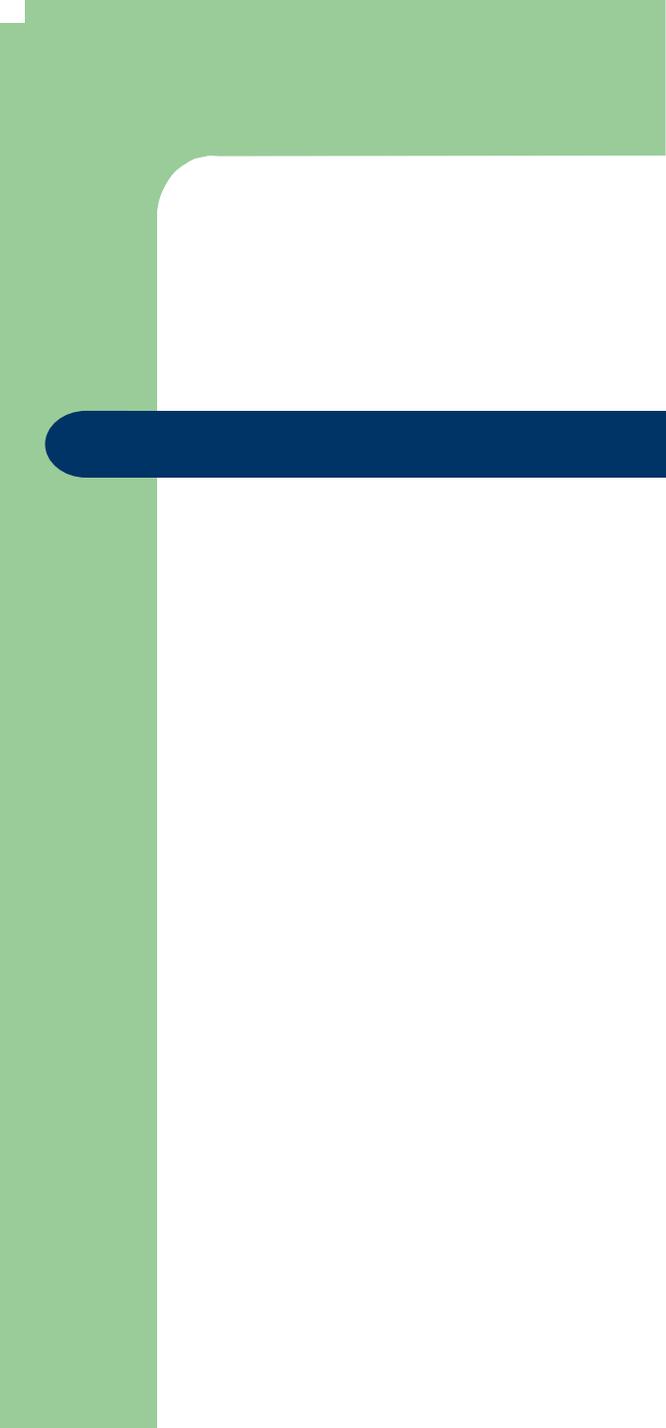
Example 3 : Cl in CH₂Cl₂

- Cl detection
 - Determines rate constant between pentane and Cl
- Product detection
 - Same information
 - Additional information
 - Branching between products
 - Vibrational energy contents



Conclusion

- Emphasized essential connections between chemical dynamics in gases and liquids
- Described recent progress in liquids
- It is hard and complex to study dynamics of the liquids but it is challenging and promising



Connecting Chemical Dynamics in Gases and Liquids

- Christopher G. Elles and F. Fleming Crim, *Annu. Rev. Phys. Chem.* 57:273-302 (2006). -

(Class 1 : Introduction & theory)

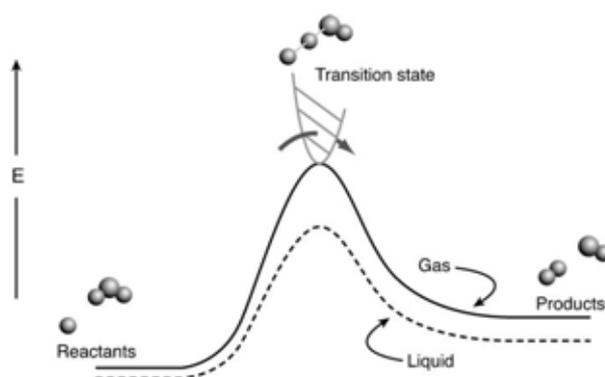
I. Introduction

- Comparing chemical dynamics in gases with their solution-phase counterparts is useful : Information of more complex environments
- Effect of solvent can range from minor to profound.
 - Minor limit : changing the energies slightly
 - Profound limit : intimate part of the chemistry
- Goal in this review
 - to examine recent progress in translating experimental studies of chemical dynamics in gases to liquids
 - look toward the prospect of making more extensive comparison
- Examples
 - Energy transfer : have yielded most dynamical information in liquid
 - Photodissociation
 - Bimolecular reaction : infancy

II. Theory

1) Transition state

- Unifying concept in chemistry
- The rate of passage through the transition state determines the rate of the reaction



- Solvent can influence the reaction rate by changing the relative energies
- Statistical theory
 - : molecules explore all of the available configurations and momenta accessible at a particular energy.
- Convenient framework for discussing chemical dynamics in gases and in solution.

2) Simple comparison

	Gas	Liquid
Encounter	Translate freely between collisions	Controlled by diffusion
Limiting rate (for a bimolecular reaction)	Collision rate	Rate of diffusive encounter
Rate constant (for two reactant A and B)	$k_g(T) = \langle v_{AB}\sigma_{AB} \rangle$	$k_D(T) = 4\pi D_{AB}(R_A + R_B)$

- Both depend on the size of the reactants.

3) Treating a liquid simply as a dense gas

- Convenient means of estimating timescales
- Density of gas at 1 torr : collide approximately every 100ns
- Gas having the density of a liquid : collide approximately every 100fs
 - : interaction are not separated in time
- Limit : leaves out important features
 - Many-body interaction
 - Hydrogen-bonded structures and etc.

4) IBC (isolated binary collision) model

- Treats the liquid as a lattice
- Accounts for the relative motion of the lattice to yield the result that a molecule has a collision as a typical liquid (every 300fs)
- Surprisingly good estimates of rates
- For the energy transfer between states i and f, $k_{if}(T, \rho) = Z(T, \rho)P_{if}$
 - (product of that probability and density dependent collision rate constant)
- Decay of the velocity correlation function $\langle v(t)v(0) \rangle$ provides an collision interval.

5) IVR (intramolecular vibrational relaxation)

- The complete sampling of configurations and momenta : an aspect of transition state theory connects reactions in gases and liquids.
- The energy flow among the available vibrational states within the isolated molecule depends on the coupling within the molecule.
- There are several complication in a liquid

Interaction of the solvent with the solute can change the intramolecular coupling -> change the rate of vibrational energy flow

Making up small differences in the energy of two states enabling an otherwise unfavorable transition

Solvent either accepts or provides small amounts of energy to bring the levels into resonance. (counterpart of collision induced intramolecular energy flow)

6) IET (intermolecular energy transfer)

- Energy transfer from the vibrations of the solute to vibrations of the solvent molecules and to the collective modes of the solvent.
- Receive energy from the relaxing solute.
- Similar to collisional vibration-to-vibration energy transfer in gases : The flow of vibrational energy into translations and rotations in gases.

7) Removal of Averaging

- Developments of studying dynamics in liquid recapitulates these of gases.
- Removing of the averaging was one of the first step of studying reaction dynamics.
- Preparing molecules in an excited vibrational state removes the averaging over the thermal distribution of initial states.
- Knowing lifetime of the initially prepared state is important in order to study its chemistry either in a liquid or a gas.

Connecting Chemical Dynamics in Gases and Liquids

- Christopher G. Elles and F. Fleming Crim, Annu. Rev. Phys. Chem. 57:273-302 (2006).

(Class 2 : Energy transfer and Vibrational relaxation)

I. Intramolecular Vibrational Relaxation

- Diatomic molecule : collisions are required to redistribute vibration energy
- In large system
 - coupling of different vibrational modes by small perturbations (usually neglected in the Hamiltonian)
 - => Energy can be redistributed in a collisionless process

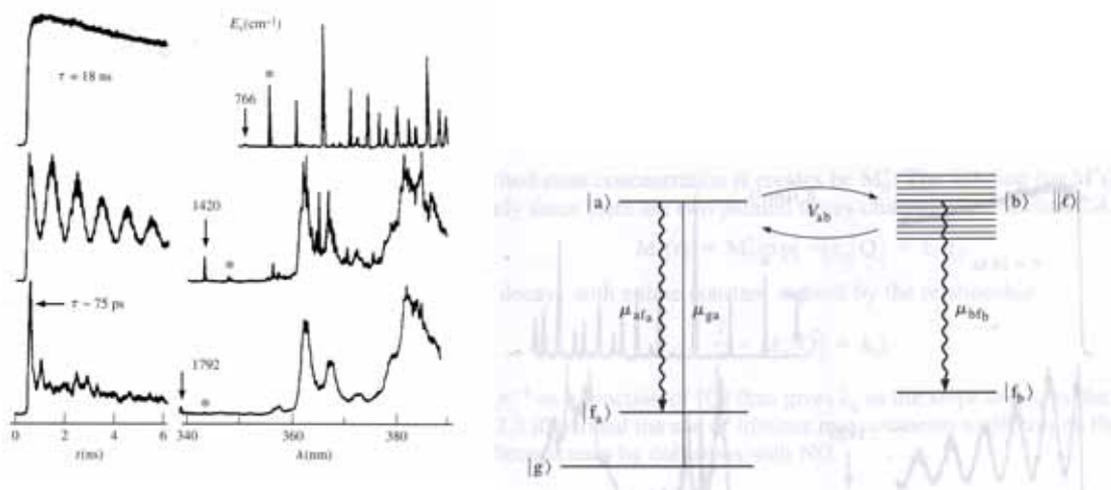


Fig. Fluorescence spectrum of Anthracene

- Rate of IVR

$$k_{if} = (2\pi/\hbar) |V_{if}|^2 \delta(E_i - E_f)$$

$$k_i = (2\pi/\hbar) |V|^2 \rho(E_i)$$

- Two key parameter : density of states and coupling strength

II. The Landau-Teller Model

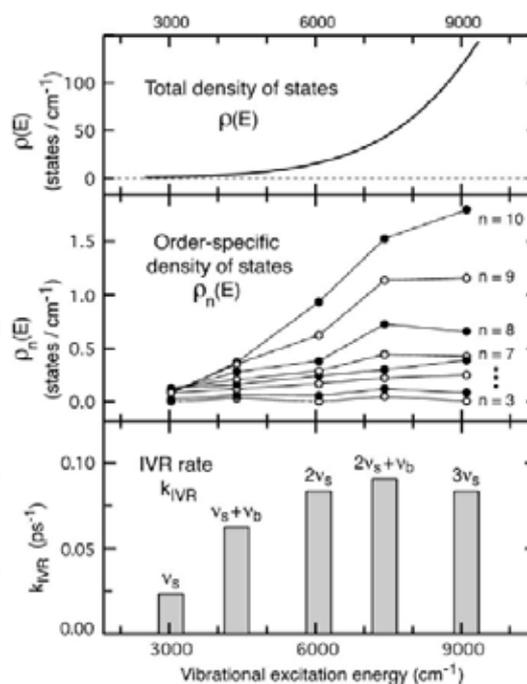
- Method for including the solvent in vibrational relaxation
- Treating the solvent as a perturbation that couples the vibrational levels of a molecule
- The inclusion of states of the solvent allows it to make up the difference in energy as well as provide the fluctuating force that drives the transition
- Relates solvent friction (macroscopic property) to the relaxation rate by force correlate function
- Calculation of force correlate function -> Information about relaxation rate (MD etc.)
- Two limits
 - One** : Solvent dose not matter (Solvent interacts weakly or the density of states in the most strongly coupled tiers is so large)
 - The other** : Solvent-driven dynamics dominates (intramolecular coupling is weak or there are too few states available)
- Many molecules are in some intermediate regime where solvent driven IVR and intrinsic IVR both contribute.

III. IVR in Gases and Liquids

- Ways to controlling aspects of vibrational energy flow
 - : changing the state structure,
 - changing the strength of its interaction with the solvent

* **Example 1** : *C-H* stretch and stretch-bend combination mode in CH_2I_2

- Not all of the available states participate in the energy flow.
- Changing the solvent affects fundamental C-H stretch then the first overtone
- Stronger influence on the slow dynamics



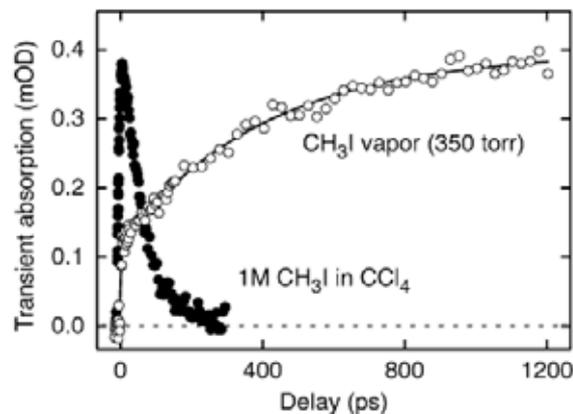
* **Example 2** : C-H stretch overtone of benzene

- Two characteristic timescale : fast(<0.5ps) and slow(50ps)
- fast : from strongly coupled states, not affected by solvation
- slow : from weakly coupled states, greatly affected by solvation (4ps)

* **Example 3** : supercritical fluids

- changing its density from that of a gas to that of a liquid
- fast one : dose not change
- slow one : continuously change (Fits with Landau-Teller model)

* **Example 4** : Competes with IET



- Time evolution of the population of the low-frequency C-I stretch mode of CH_3I
- In solution, IET to the solvent drains the molecule of its energy before the second stage of IVR occurs

* **Example 5** : Terminal acetylene

- most comprehensive comparison
- high-resolution spectroscopy of the cold molecule in a molecular beam & infrared pump-probe spectroscopy of the room temperature molecule
- solvent accelerates the relaxation
- same extent of acceleration for all of the acetylenic molecule -> intrinsic IVR and solvent-driven IVR occurs independently
- $k_{IVR} = k_{intrinsic} + k_{solvent}$
- Studies on the supercritical fluids supports this

Connecting Chemical Dynamics in Gases and Liquids

- Christopher G. Elles and F. Fleming Crim, Annu. Rev. Phys. Chem. 57:273-302 (2006).

-

(Class 3 : Photodissociation & Bimolecular reaction)

I. Photodissociation Reactions

1. Photodissociation Reaction

- $AB + h\nu \rightarrow A + B$
- Provides unique window into chemical dynamics
 - : detailed information about potential energy surfaces
- Presence of solvent
 - : altering energy disposal, changing the relative energies, limiting the separation
 - > Substantial effect
- Many of the same principles apply to other unimolecular reactions (ex. excited-state photoisomerization)

2. Examples

- PES of isolated molecule : starting point for describing photodissociation reactions in solution when the coupling is weak.
- Solvent generally does not change the shape of the surface in the Franck-Condon region
 - > Gas-phase potential contains some information about the initial dynamics in solution

* Example 1 : iodoalkanes

- Resonance Raman spectra of isolated and solvated iodoalkanes
- Solvation has little effect on the initial dynamics.
- The relative intensities of the C-I overtones in CH_3I are similar in vapor and solution phases, indicating that the early photodissociation dynamics are not greatly altered by solvation.

Resonance Raman lines of CH₃I

Transition	Vapor [8,11]		Solution phase (this work)			Calculated	
	freq. (cm ⁻¹)	rel. int. ^{a)}	freq. (cm ⁻¹) ^{b)}	rel. int. ^{a)}	width (cm ⁻¹) ^{a)}	freq. (cm ⁻¹)	rel. int.
3 ₁	528	1.00	531	1.00	9	528	1.00
3 ₂	1050	0.90	1053	0.98	14	1050	0.75
2 ₁	1254	0.10	1242	0.14	<6	1242	0.02
3 ₃	1567	0.56	1565	0.83	22	1565	0.60
2 ₁ 3 ₁	(1780)	<0.02	1759	0.03	<6	1770	0.03
3 ₄	2082	0.50	2076	0.64	36	2074	0.51
				(13.2×10 ⁻¹¹) ^{a)}			(7.9×10 ⁻¹¹) ^{a)}
2 ₁ 3 ₂	(2297)	<0.02	2288	0.06	27	2292	0.03
3 ₅	2587	0.39	2579	0.60	49	2576	0.44
2 ₁ 3 ₃	2797	0.02	-	-	-	2807	0.03
3 ₄	3092	0.42	3070	0.84 ^{c)}	76 ^{d)}	3072	0.39
2 ₁ 3 ₄	3307	0.08	-	-	-	3316	0.04
3 ₇	3588	0.40	3558	0.41	68	3562	0.35
2 ₁ 3 ₅	3799	0.08	3787	0.03	31	3818	0.04
3 ₄	4073	0.36	4045	0.41	74	4046	0.32
2 ₁ 3 ₆	(4304)	<0.07	4276	0.12	70	4314	0.04
3 ₉	4562	0.26	4518	0.28	88	4523	0.29
2 ₁ 3 ₇	4781	-	4766	0.02	24	4804	0.03
3 ₁₀	5044	-	4995	0.45	114	4994	0.27
2 ₁ 3 ₈	5277	-	5234	0.06	(48)	5288	0.03
3 ₁₁	5516	-	5450	0.40	104	5458	0.25
3 ₁₂	5982	-	5906	0.43	98	5916	0.23
3 ₁₃	6446	-	6366	0.34	110	6368	0.22
3 ₁₄	6896	-	6813	-	-	6813	0.20
3 ₁₅	7347	-	7244	-	-	7253	0.19

* **Example 2 : photodissociation of CH₂I₂ (exception)**

- Solvent induced symmetry breaking
-> changes the short time dynamics
- In gas phase : initially moves along the symmetric I-C-I stretch coordinates, selection of breaking bond occurs outside of the Franck-Condon region.
- In solution phase : one bond to stretch more than the other at early time, selection of breaking bond occurs inside of the Franck-Condon region.

TABLE VI. Most probable internal coordinate displacements of diiodomethane at $t=15$ fs assuming the C-I bond becomes longer.

Internal coordinate	Gas phase	Solution phase (in methanol solvent)	
	15 fs ^a	15 fs with $\Delta_p=+1.3^b$	15 fs with $\Delta_p=-1.3^c$
C-H bonds	-0.008 Å (-0.009 Å)	-0.004 Å (-0.006 Å)	-0.004 Å (-0.006 Å)
C-I bond, atoms 1 and 4	+0.146 Å (+0.142 Å)	+0.169 Å (+0.162 Å)	+0.010 Å (+0.004 Å)
C-I bond, atoms 1 and 5	+0.146 Å (+0.142 Å)	+0.010 Å (+0.004 Å)	+0.169 Å (+0.162 Å)
H-C-H angle, atoms 2, 1, and 3	-2.4° (-2.5°)	-1.5° (-1.4°)	-1.5° (-1.4°)
H-C-I angle, atoms 2, 1, and 4	+2.8° (+3.2°)	-0.4° (+0.1°)	+3.5° (+4.0°)
H-C-I angle, atoms 3, 1, and 5	+2.8° (+3.2°)	+3.5° (+4.0°)	-0.4° (+0.1°)
H-C-I angle, atoms 2, 1, and 5	+2.9° (+3.3°)	+3.5° (+4.0°)	-0.2° (+0.3°)
H-C-I angle, atoms 3, 1, and 4	+2.9° (+3.3°)	-0.2° (+0.3°)	+3.5° (+4.0°)
I-C-I angle, atoms 4, 1, and 5	-8.9° (-11°)	-4.9° (-7.0°)	-4.9° (-7.0°)

* **Example 3 : photodissociation of OCIO**

- More dramatic example

- difference in the Franck-Condon region of the excited state changes the dissociation dynamics
- Solvation initially preserves the C_{2v} symmetry of the dissociating molecule
- Solvation makes $Cl + O_2$ channel more important

*** Example 4 : Triatomic molecule (HgI_2 , I_3^-)**

- Solvation changes the distribution of excess energy -> affects to the dynamics
- Excess energy can go into rotation and vibration of the diatomic fragment
- In gas phase, fragment(HgI , I_2^-) has higher excitation level
- In solution phase, energy transfer to the solvent relaxes the vibration within 2 or 3 ps => high time resolution
- Prediction on the CN fragment from the photodissociation of ICN well matched with the measurement

*** Example 5 : photodissociation of $HOCl$**

- Inhibiting the separation of the fragments
- > trap the nascent pair within a solvent cage
- Excess energy goes into the relative translational energy of the atomic fragments => measure the stopping power of the solvent
- Direct recombination (geminate recombination) of the fragments is possible
- Geminate recombination kinetics provide information about the kinetic energy release in the dissociation and the dissipation of that energy by the solvent
- Geminate recombination is unique property of condensed-phase reaction
- $$P(t) = 1 - \frac{(R_A + R_B)}{r_0} \cdot \operatorname{erfc}\left[\frac{r_0 - (R_A + R_B)}{\sqrt{4D_{AB}t}}\right]$$
, r_0 determines the probability that they will recombine
- r_0 increased linearly with the excess energy

*** Example 6 : photodissociation of CH_2I_2**

- Recombination can cause isomer and it can play an important role in secondary reaction
- CH_2I_2 forms CH_2I-I isomer within 1 ps : resonance Raman spectrum

measured I-I stretching

- Several polyhalomethane can also form that kind of isomer

II. Bimolecular Reactions

1. Bimolecular Reaction study

- Generating reactants with well-defined initial internal energy is impossible in solution -> hard to achieve good state resolution
- There are no examples of state-to-state studies
- Photodissociation is an effective means of producing reactive radicals in solution
- Interaction rapidly dissipate the excess kinetic energy -> little excess energy for reactions occurring beyond the first solvent shell
- Vibrational excitation can survive for up to hundreds of picoseconds, corresponding to thousands of collisions with solvent
- Relatively few examples of generating reactive species which have sufficient time resolution and state selectivity to reveal the fine details of bimolecular reaction.

2. Examples

- Some pioneering experiments
- carefully chosen systems where the absorptions of the solvent and products lie in separate spectral regions.
- Cl, CN can be prepared with selected vibrational states and survive long enough for a reactive encounter

* Example 1 : Hydrogen abstraction reaction

- $Cl_2 + hv \rightarrow 2Cl$
- $Cl + C_6H_{12} \rightarrow HCl + C_6H_{11}$
- using transient infrared absorption, detects HCl product

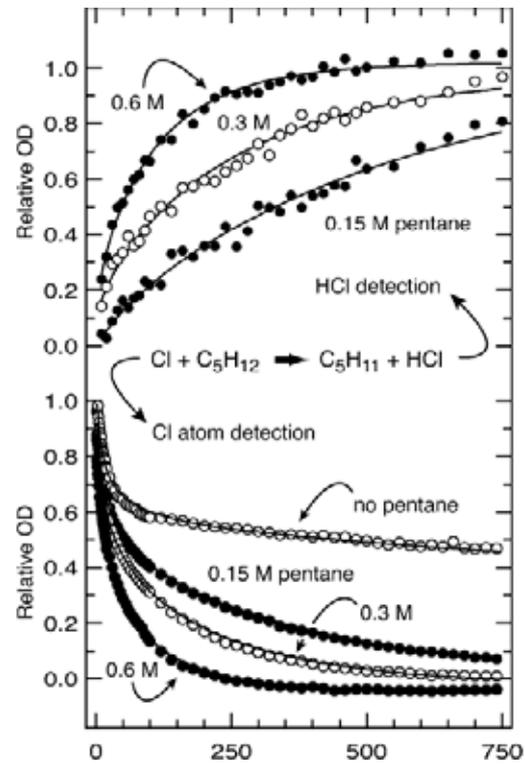
* Example 2 : $CN + CHCl_3$

- $ICN + hv \rightarrow CN + I$
- There is competition between two reaction channels
- HCN or ICN

* Example 3 : photolysis of Cl_2 in methylene chloride

- Cl detection

- : Additional pentane provides other abstraction channel -> determines rate constants between pentane and Cl.
- Product detection (HCl)
- : same information of Cl detection, additional information (vibrational energy content, branching between different reaction channels)



III. Conclusion

- Emphasized essential connections between chemical dynamics in gases and liquids
- Described recent progress in liquids
- It is hard and complex to study dynamics of the liquids but it is challenging and promising.

Connecting Chemical Dynamics in Gases and Liquids

- Christopher G. Elles and F. Fleming Crim, Annu. Rev. Phys. Chem. 57:273-302 (2006).

1.

$$Z = 4 \frac{N}{V} d^2 \sqrt{\frac{\pi RT}{M}}$$

1 torr

state-to-state resolution

가

가?

(300K, $3 \times 10^{-10} m$ 가)

:

$$\frac{N}{V} = \frac{P}{RT} N_A = 3.22 \times 10^{22} m^{-3}$$

$$\sqrt{\frac{\pi RT}{M}} = 6.6 \times 10^2 m/s$$

$$Z = 7.7 \times 10^6 s^{-1}$$

$$\therefore \frac{1}{Z} = \frac{1}{7.7 \times 10^6} s = 130 ns, 130 ns$$

130ns

disturb

time-resolved

experiment

state-to-state resolution

2. Condensed phase dense gas 가

1g/mL

$$Z = 4 \frac{N}{V} d^2 \sqrt{\frac{\pi RT}{M}} \quad)$$

condensed phase

state-to-state resolution

(300K)

:

$$\frac{N}{V} = \frac{6.022 \times 10^{23} / 18}{10^{-6} m^3} = 3.34 \times 10^{28} m^{-3}$$

$$\sqrt{\frac{\pi RT}{M}} = 6.6 \times 10^2 m/s$$

$$Z = 7.9 \times 10^{12} s^{-1}$$

$$\therefore \frac{1}{Z} = \frac{1}{7.9 \times 10^{12}} s = 126 fs, 126 ns$$

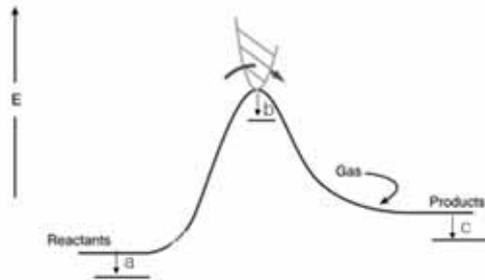
solution

100fs

disturb

state-to-state resolution 가 .

3. solvation 가 .



a = 10, b = 5, c = 10
 a = 5, b = 10, c = 5
 a = 10, b = 0, c = 30

a = 10, b = 10, c = 5
 a = 5, b = 10, c = 0

: ,

4. Bimolecular reaction , condensed phase

가 gas phase .

가 .

:

gas phase

. gas phase

, solution cage

cage

가

5. Fermi Golden rule

Intramolecular vibrational relaxation

. IVR

가

parameter ,

symbol

$$k_i = (2\pi/\hbar)|V|^2\rho(E_i)$$

:

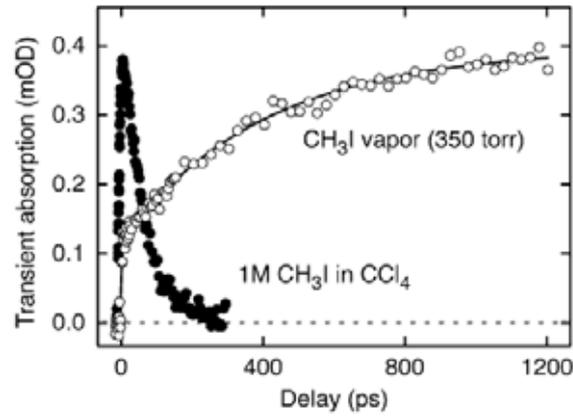
V : coupling strength

$\rho(E_i)$: density of state

6. IVR time constant solvent , supercritical fluid 가 가?

: supercritical fluid gas liquid 가 , density 가 . , gas phase liquid phase dynamics가 가 .

7. gas phase solution CH_3I IVR . CH_3I IVR solvent 가? CH_3I 가 .



: , 가 (stiff) 가 solution . (signal) solvent IVR IVR .

8. CH_3I photodissociation reaction 15fs time delay resonance Raman spectrum data . Vapor solution C-I overtone 가 가?

Resonance Raman lines of CH₃I

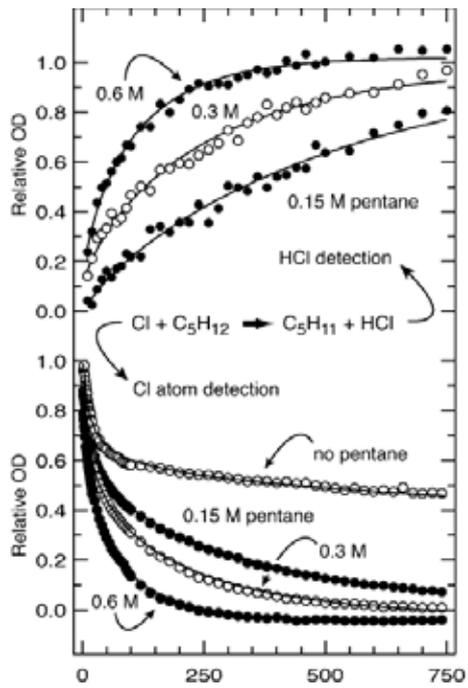
Transition	Vapor [8,11]		Solution phase (this work)			Calculated	
	freq. (cm ⁻¹)	rel. int. ^{a)}	freq. (cm ⁻¹) ^{b)}	rel. int. ^{c)}	width (cm ⁻¹) ^{d)}	freq. (cm ⁻¹)	rel. int.
3 ₁	528	1.00	531	1.00	9	528	1.00
3 ₂	1050	0.90	1053	0.98	14	1050	0.75
2 ₁	1234	0.10	1242	0.14	<6	1242	0.02
3 ₃	1567	0.56	1565	0.83	22	1565	0.60
2 _{1,2}	(1780)	<0.02	1759	0.03	<6	1770	0.03
3 ₄	2082	0.50	2076	0.64	36	2074	0.51
				(13.2×10 ⁻¹¹) ^{e)}			(7.9×10 ⁻¹¹) ^{e)}
2 _{1,2}	(2297)	<0.02	2288	0.06	27	2292	0.03
3 ₁	2587	0.39	2579	0.60	49	2576	0.44
2 _{1,3}	2797	0.02	-	-	-	2807	0.03
3 ₄	3092	0.42	3070	0.84 ^{f)}	76 ^{f)}	3072	0.39
2 _{1,4}	3307	0.08	-	-	-	3316	0.04
3 ₇	3588	0.40	3558	0.41	68	3562	0.35
2 _{1,3}	3799	0.08	3787	0.03	31	3818	0.04
3 ₄	4073	0.36	4045	0.41	74	4046	0.32
2 _{1,3}	(4304)	<0.07	4276	0.12	70	4314	0.04
3 ₆	4562	0.26	4518	0.28	88	4523	0.29
2 _{1,3}	4781	-	4766	0.02	24	4804	0.03
3 ₁₀	5044	-	4995	0.45	114	4994	0.27
2 _{1,3}	5277	-	5234	0.06	(48)	5288	0.03
3 ₁₁	5516	-	5450	0.40	104	5438	0.25
3 ₁₂	5982	-	5906	0.43	98	5916	0.23
3 ₁₃	6446	-	6366	0.34	110	6368	0.22
3 ₁₄	6896	-	6813	-	-	6813	0.20
3 ₁₅	7347	-	7244	-	-	7253	0.19

15fs early dynamics (Franck-Condon region) dissociation
 C-I bond vibration early dynamics
 solvent

9. Solution Bimolecular reaction dynamics

Time resolved study, bimolecular
 reaction activation
 solution solvent activation 가
 relaxation

10. CH₂I₂, Cl radical hydrogen abstraction
 Pentane 가 가 가
 Cl radical pentane



:
 Pentane CH_2I_2 hydrogen pentane
 가 channel (pentane hydrogen abstraction) 가
 .
 가 Cl radical pentane bimolecular reaction
 rate constant .