INTERACTION OF PICOSECOND INFRARED PULSES WITH ISOLATED MOLECULES

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May, 1988

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1973: A REVOLUTION IN CHEMISTRY?

CO_2 Laser-Induced Dissociation of SiF_4 Molecules into Electronically Excited Fragments[1]

N. R. ISENOR, V. MERCHANT ,[2] AND R. S. HALLSWORTH [2]
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Division of Physics, National Research Council of Canada, Ottawa, Canada
Received February 8, 1973

Observation of the visible fluorescence of the SiF radical in SiF_4 gas irradiated by the pulsed output of a CO_2 laser leads to the conclusion that the molecules are dissociated into electronically excited fragments by the action of the intense laser field. A clear distinction is observed between the fluorescence produced through this process and that associated with thermalization of the incident energy.

L'observation de la fluorescence visible du radical SiF dans le gaz SiF_4 irradié par le faisceau pulsé d
laser au CO_2 conduit à la conclusion que les molécules sont dissociées en fragments électroniquement
cités par l'action du champ laser intense. Une nette distincion est observée entre la fluorescence produi
selon ce procédé et celle qui est associée avec la thermalisation de l'énergie absorbée.

[Traduit par le jou

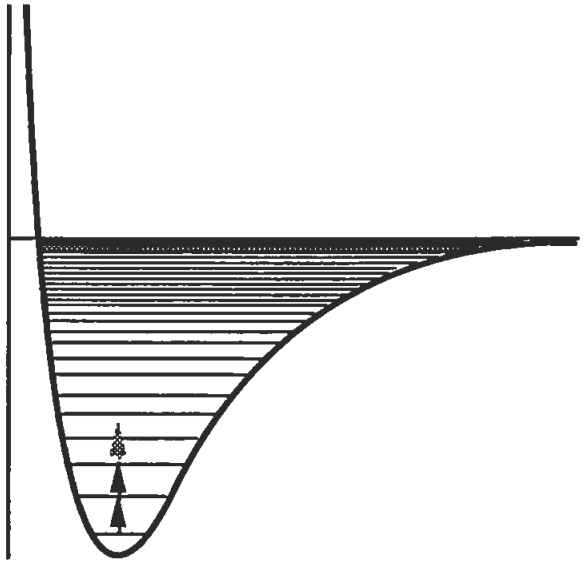
Can. J. Phys., 51, 281 (1973)

$SiF_4 + n\ h\nu \rightarrow SiF^* + \ldots$

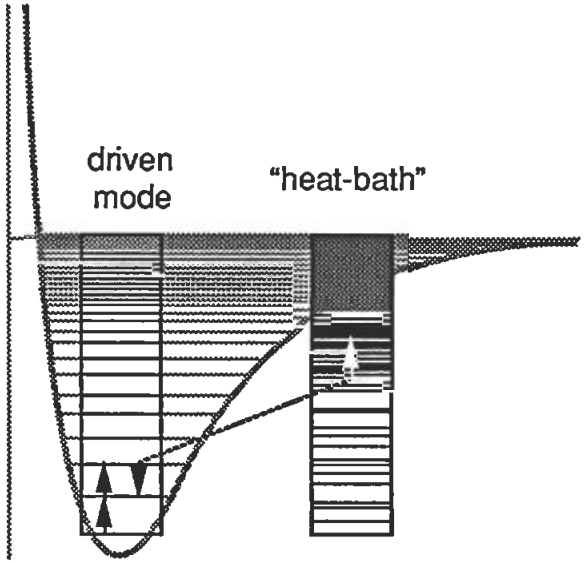
- Physical picture of IRMPE
- Raman experiments
- Discussion

N.R. Isenor, V. Merchant, R.S. Hallsworth and M.C. Richardson, Can. J. Phys. 51, 1281 (1973)

INFRARED MULTIPHOTON EXCITATION

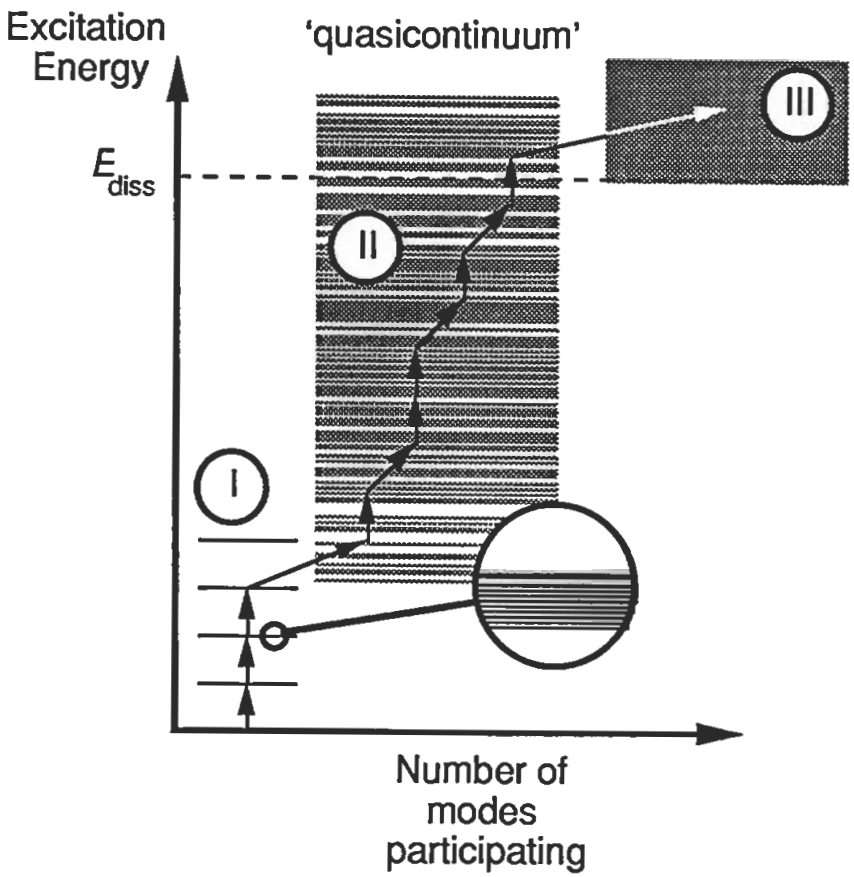


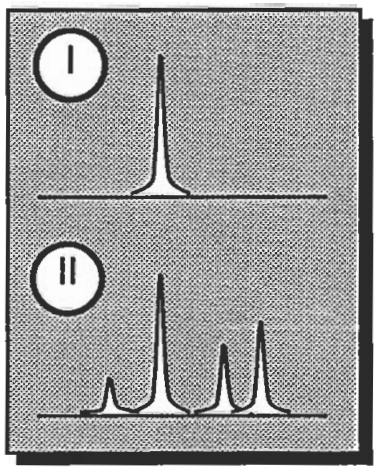
diatomic molecule



polyatomic molecule

'QUASICONTINUUM' MODEL





- incoherent step-by-step excitation
- fluence dependence
- bottleneck-effect
- loss of selectivity at high excitation

N. Bloembergen and E. Yablonovitch, Physics Today 5, 23 (1978)

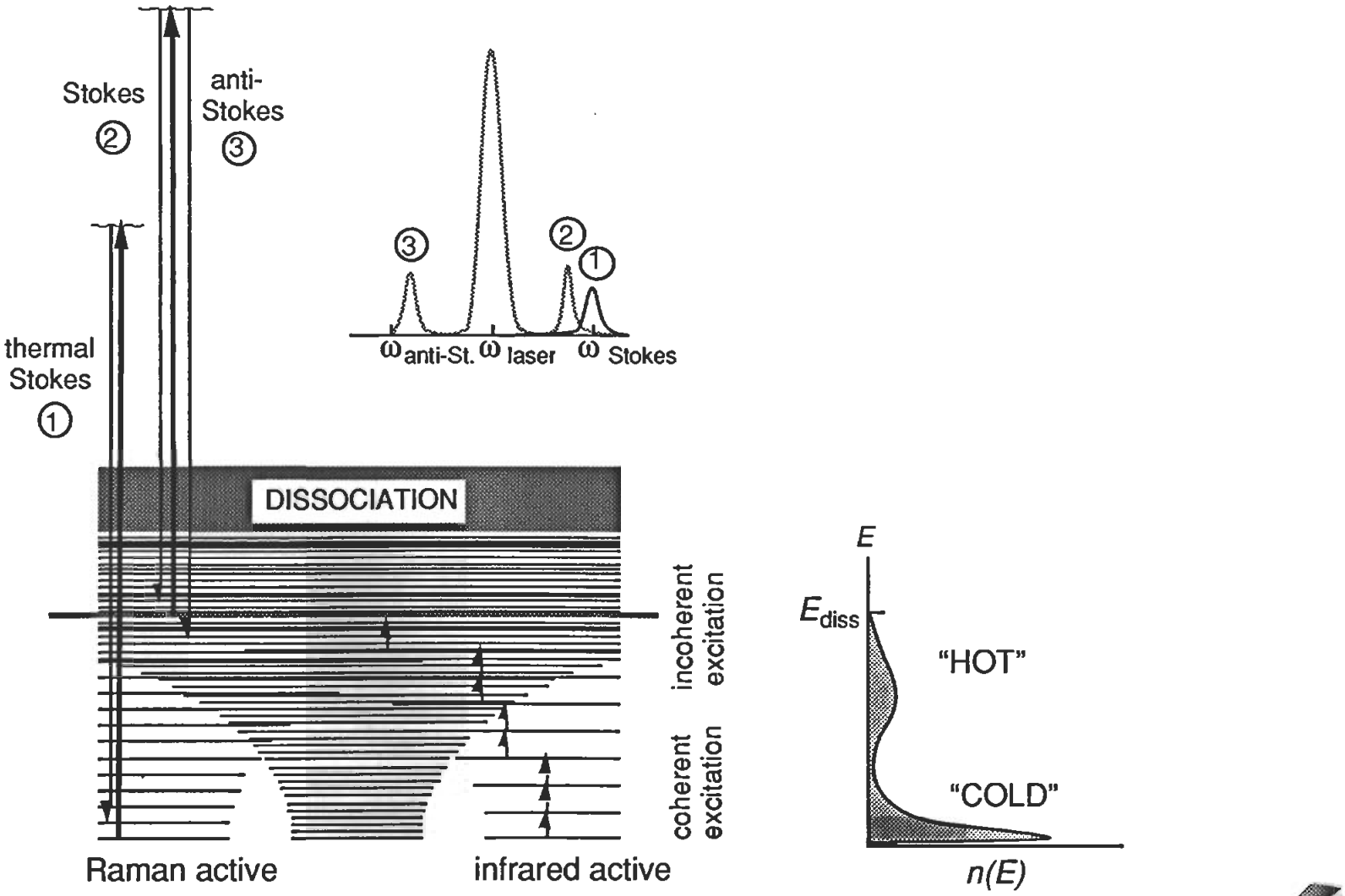
OBJECTIVES

- Measure intramolecular energy distributions
- Study dynamics at intermediate excitation

Spontaneous Raman		CARS
• Integrated energy over mode • Best at high excitation	⟷	• State-to-state distribution • Best at low to intermediate excitation

SPONTANEOUS RAMAN

V.N. Bagratashvili, et al., Opt. Lett. 6, 148 (1981)



RAMAN INTENSITY AND MODE-ENERGY

Raman transition probabilities are proportional to quantum number *n*

$$W_{n\to n+1} \sim n+1, \qquad W_{n\to n-1} \sim n$$

So Raman intensities are proportional to the energy in the mode

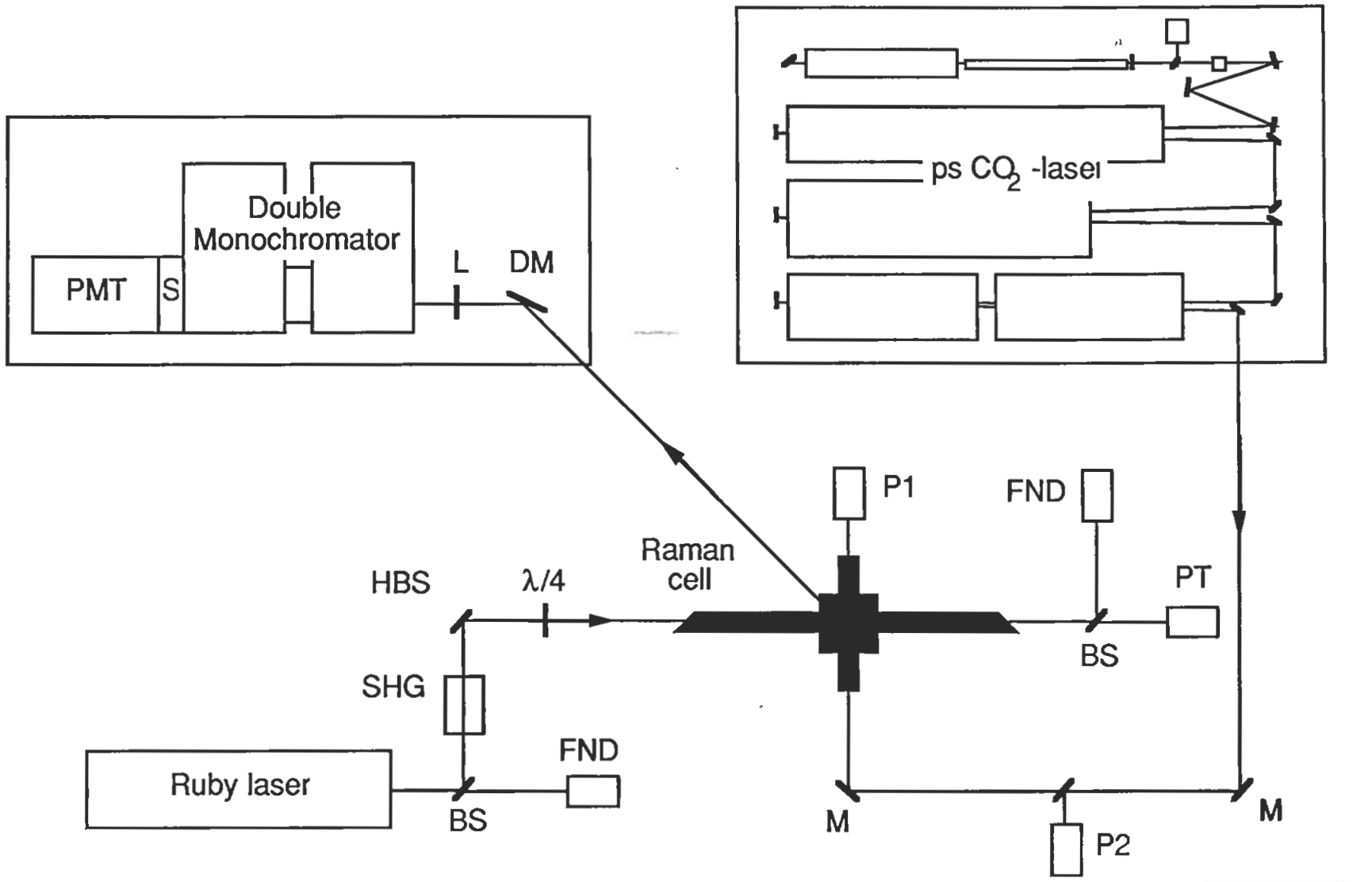
$$I_{AS} \sim \sum_{n=0}^{\infty} W_{n\to n-1} N(n) \sim \sum_{n=0}^{\infty} nN(n) \sim \sum_{n=0}^{\infty} nN(n) = E_R/h\nu_R$$

$$I_S \sim \sum_{n=0}^{\infty} W_{n\to n+1} N(n) \sim \sum_{n=0}^{\infty} (n+1)\, N(n) \sim 1 + \sum_{n=0}^{\infty} nN(n) = 1 + E_R/h\nu_R$$

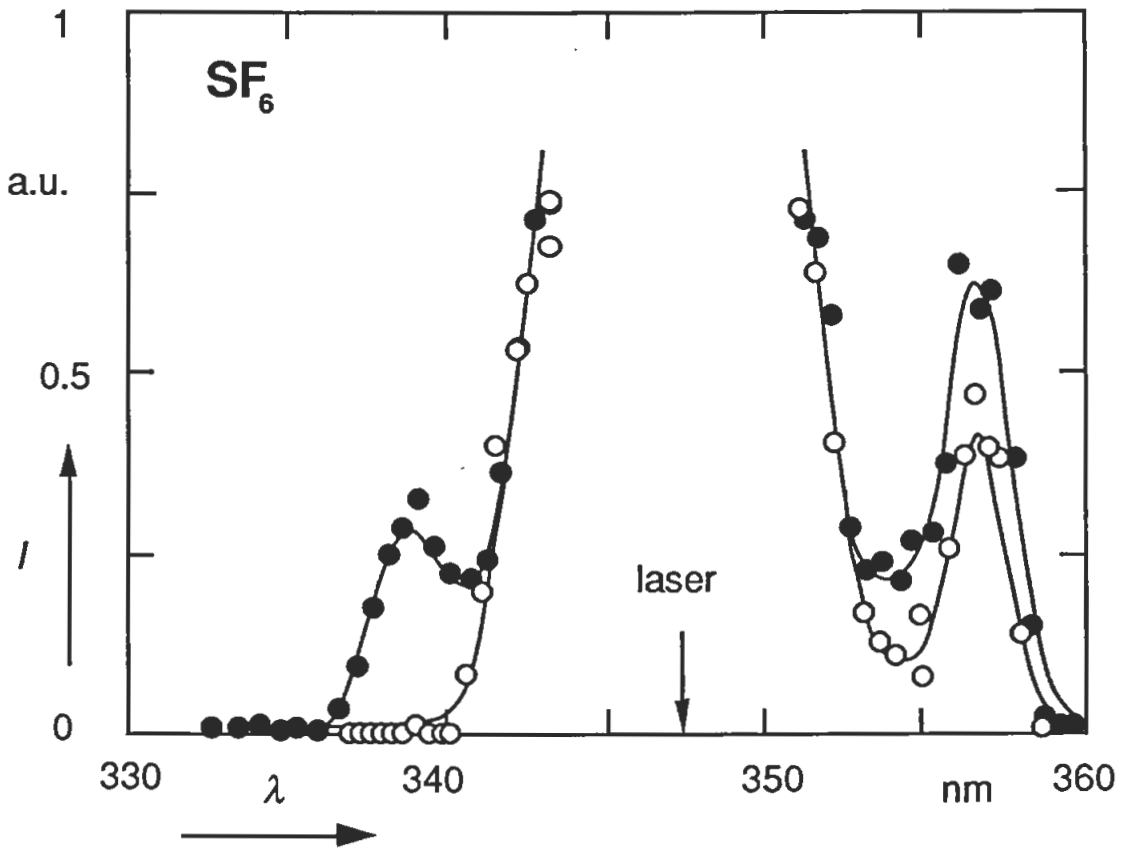
The anti-Stokes signal divided by the room temperature Stokes signal is a direct measure of the mode energy

$$I_{norm} = \frac{E_R/h\nu_R}{1 + E_R/h\nu_R} \approx \frac{E_R}{h\nu_R}.$$

EXPERIMENTAL SETUP

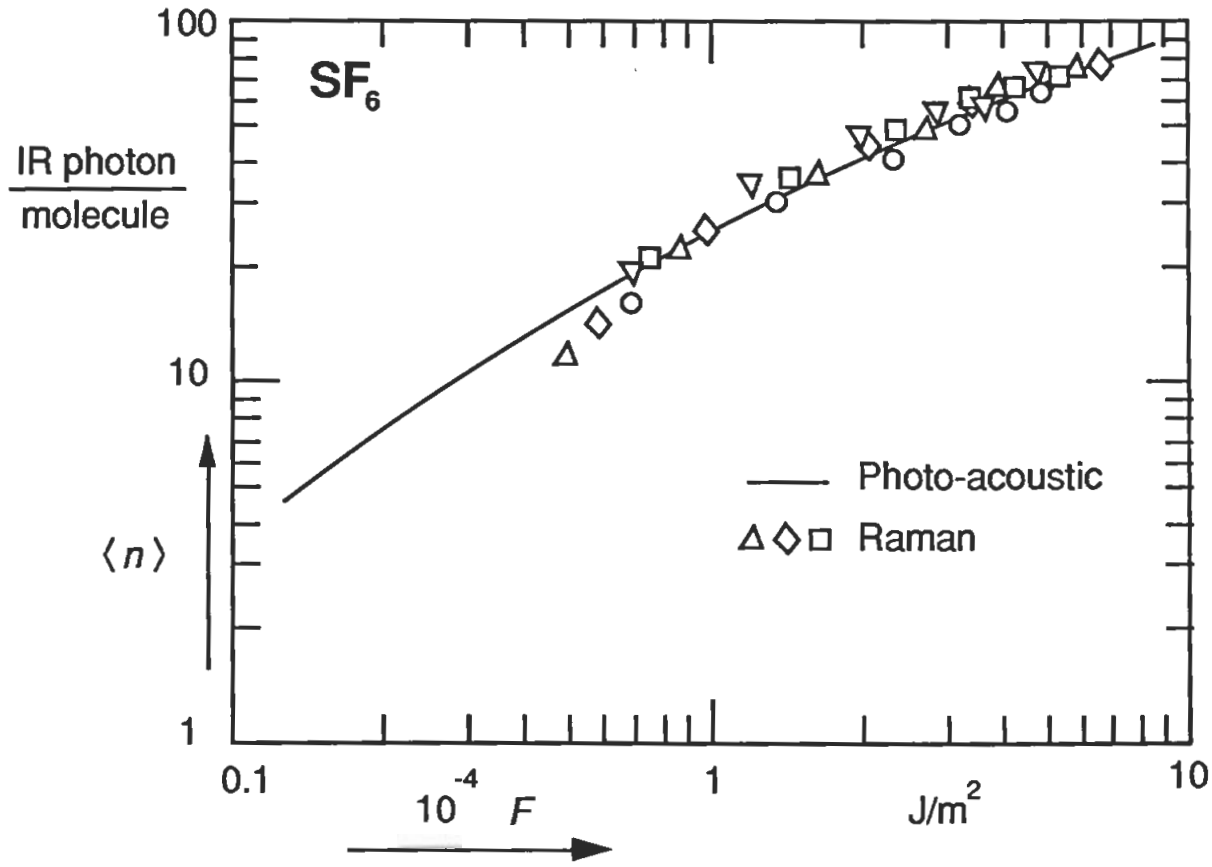


RAMAN SPECTRUM



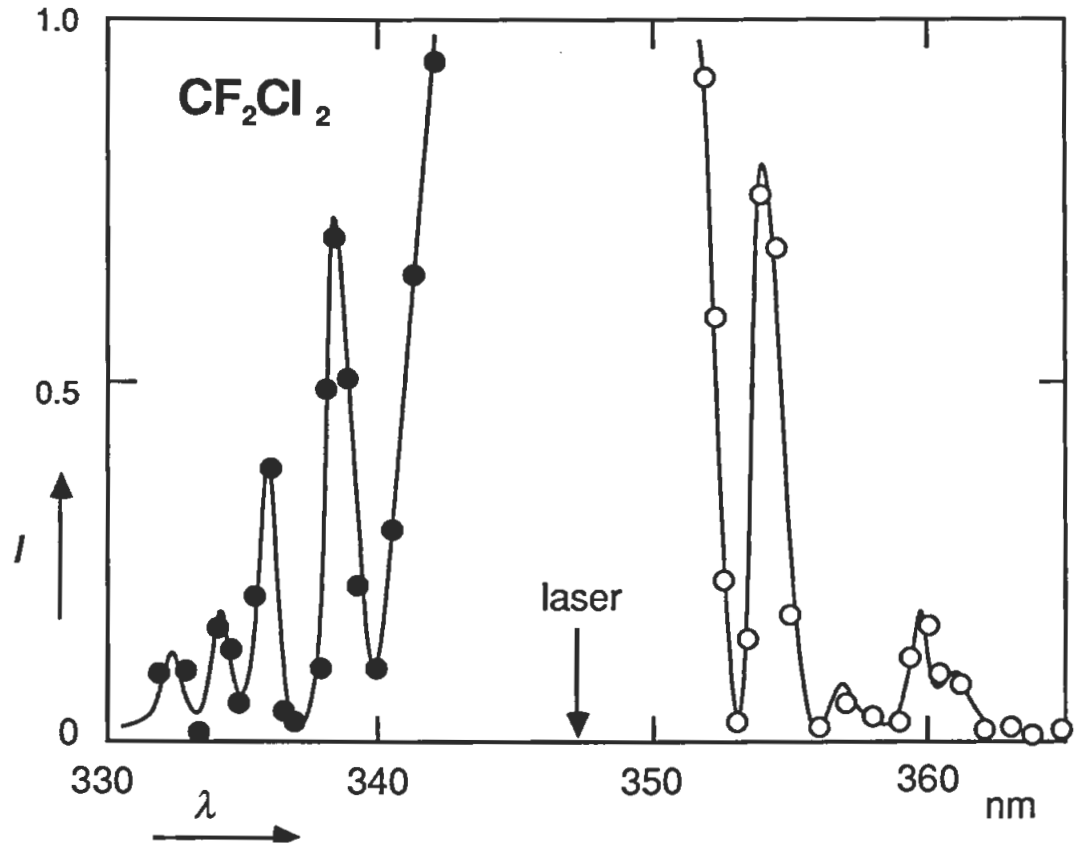
Jyhpyng Wang, Kuei-Hsien Chen, and Eric Mazur, Phys. Rev. A 34, 3892 (1986)

INTRAMOLECULAR EQUILIBRIUM



Jyhpyng Wang, Kuei-Hsien Chen, and Eric Mazur, Phys. Rev. A 34, 3892 (1986)

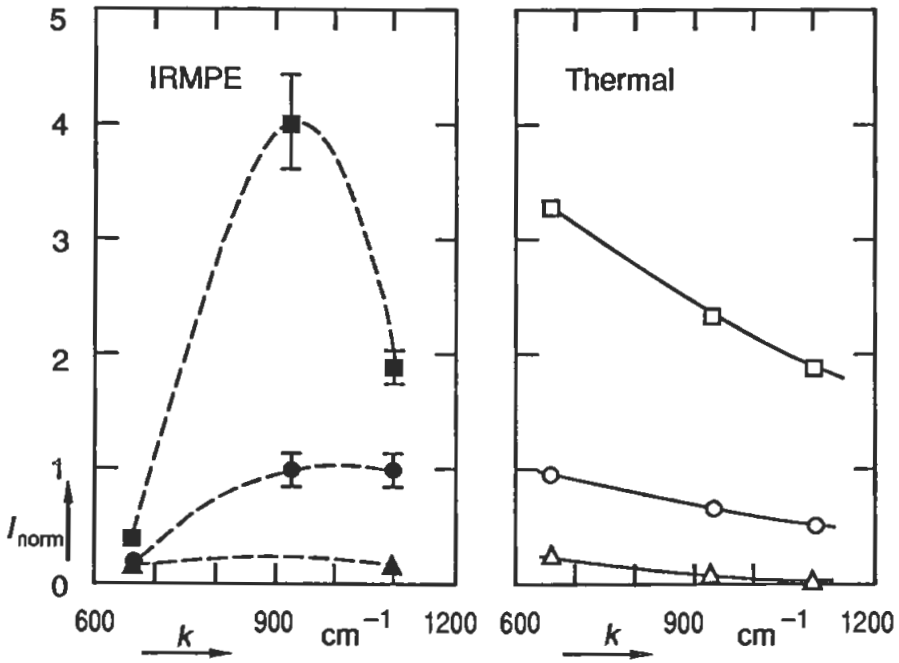
RAMAN SPECTRUM



INTRAMOLECULAR NONEQUILIBRIUM

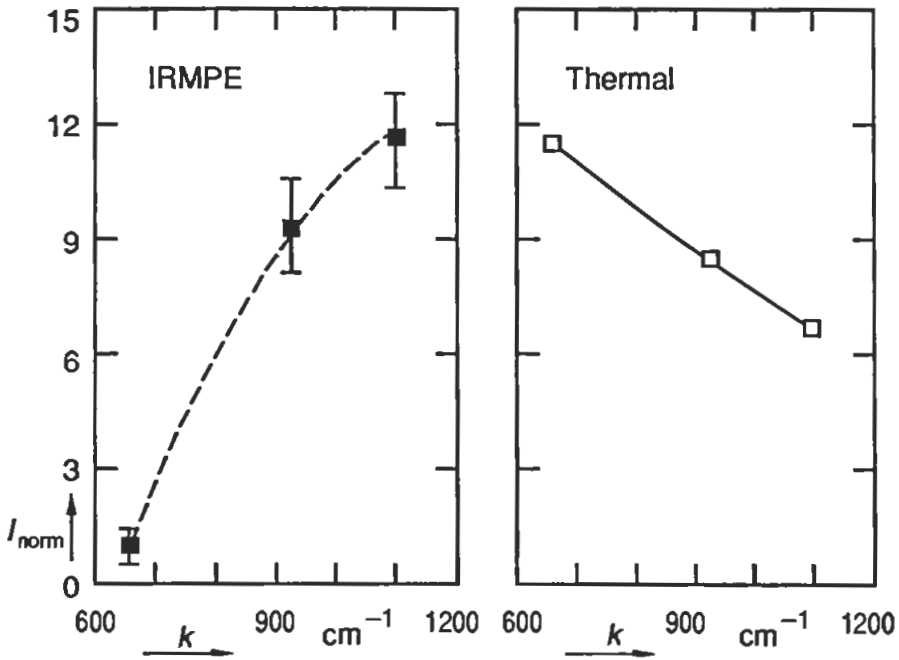
ν_8 pumping

(923 cm^{-1})



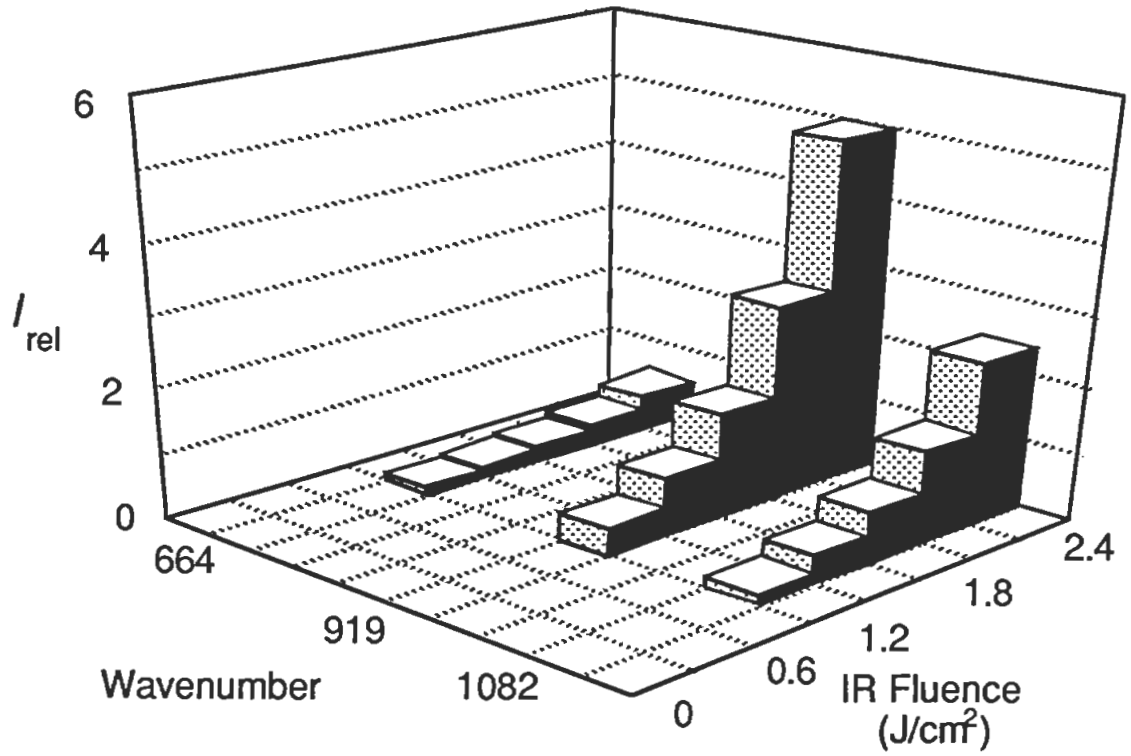
ν_1 pumping

(1098 cm^{-1})



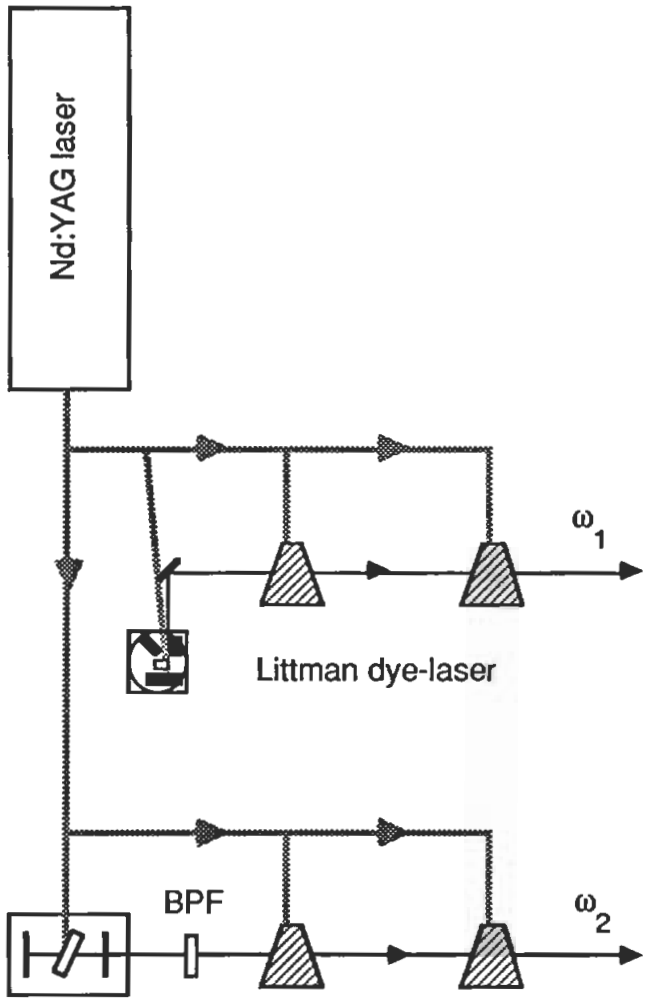
Kuei-Hsien Chen, Jyhpyng Wang, and Eric Mazur, Phys. Rev. Lett. 59, 2728 (1987)
Jyhpyng Wang, Kuei-Hsien Chen and Eric Mazur, Int. Quantum Electr. Conf., Tokyo (1988)

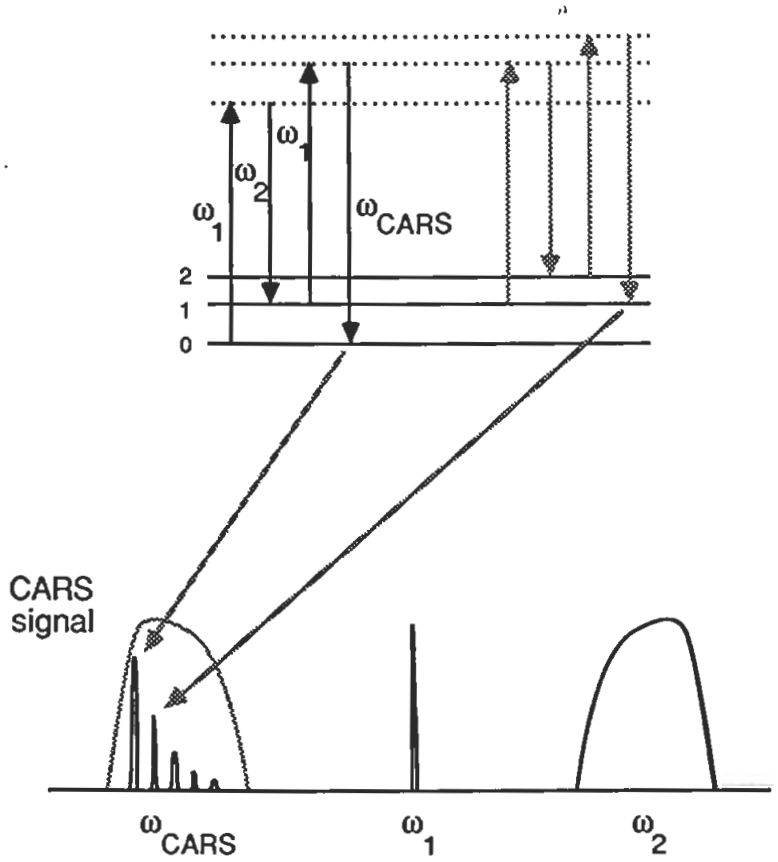
FLUENCE DEPENDENCE



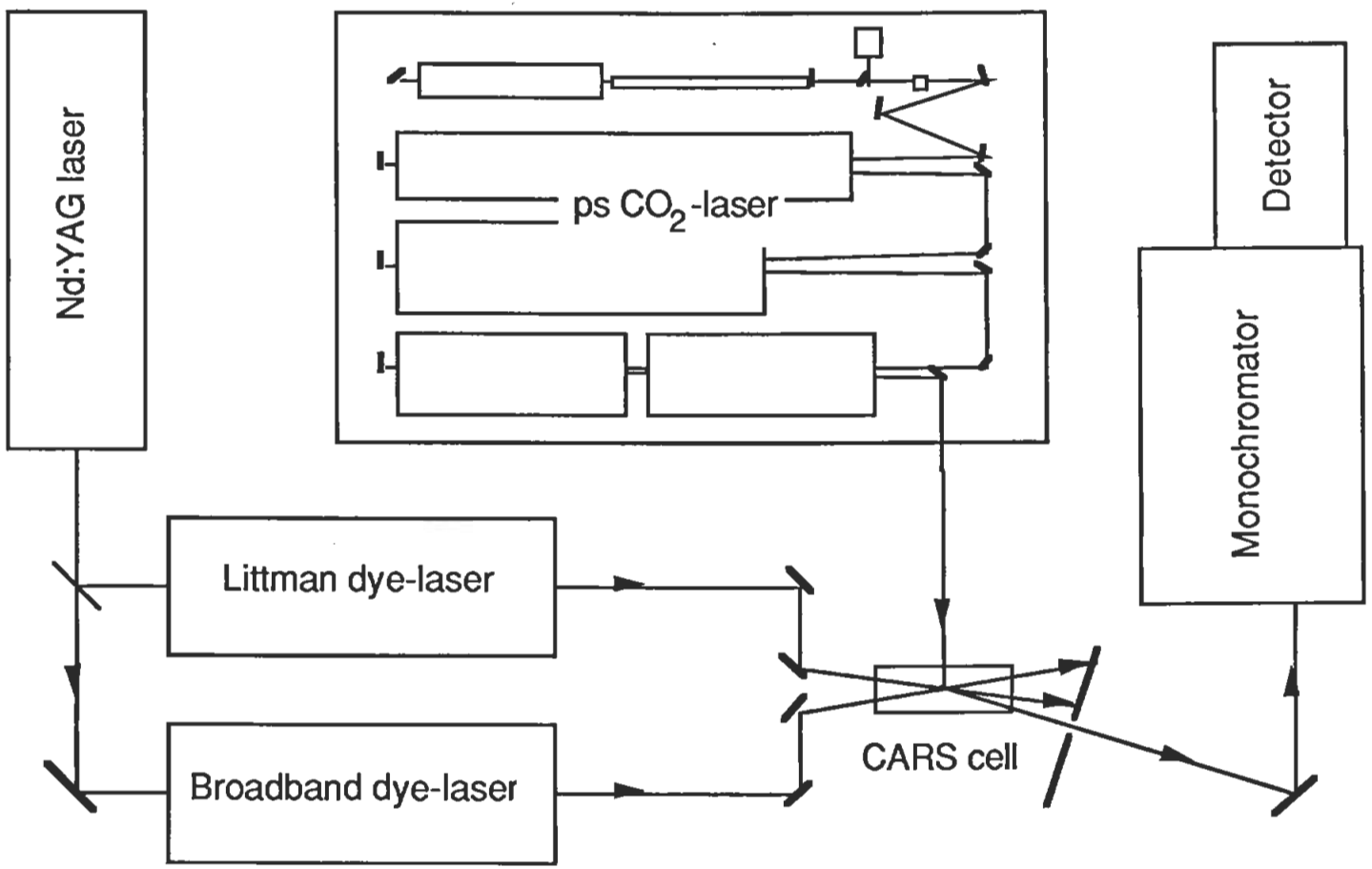
Kuei-Hsien Chen, Jyhpyng Wang, and Eric Mazur, Phys. Rev. Lett. 59, 2728 (1987)

CARS EXPERIMENT

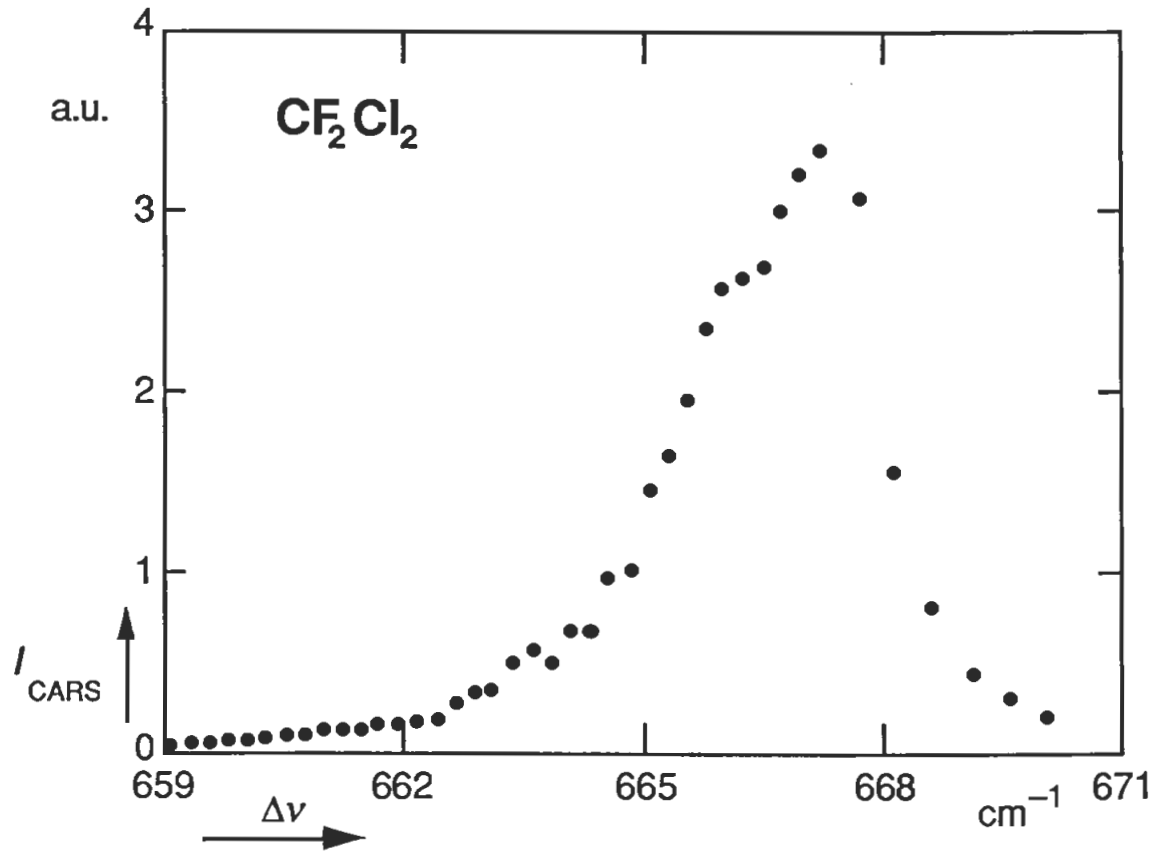




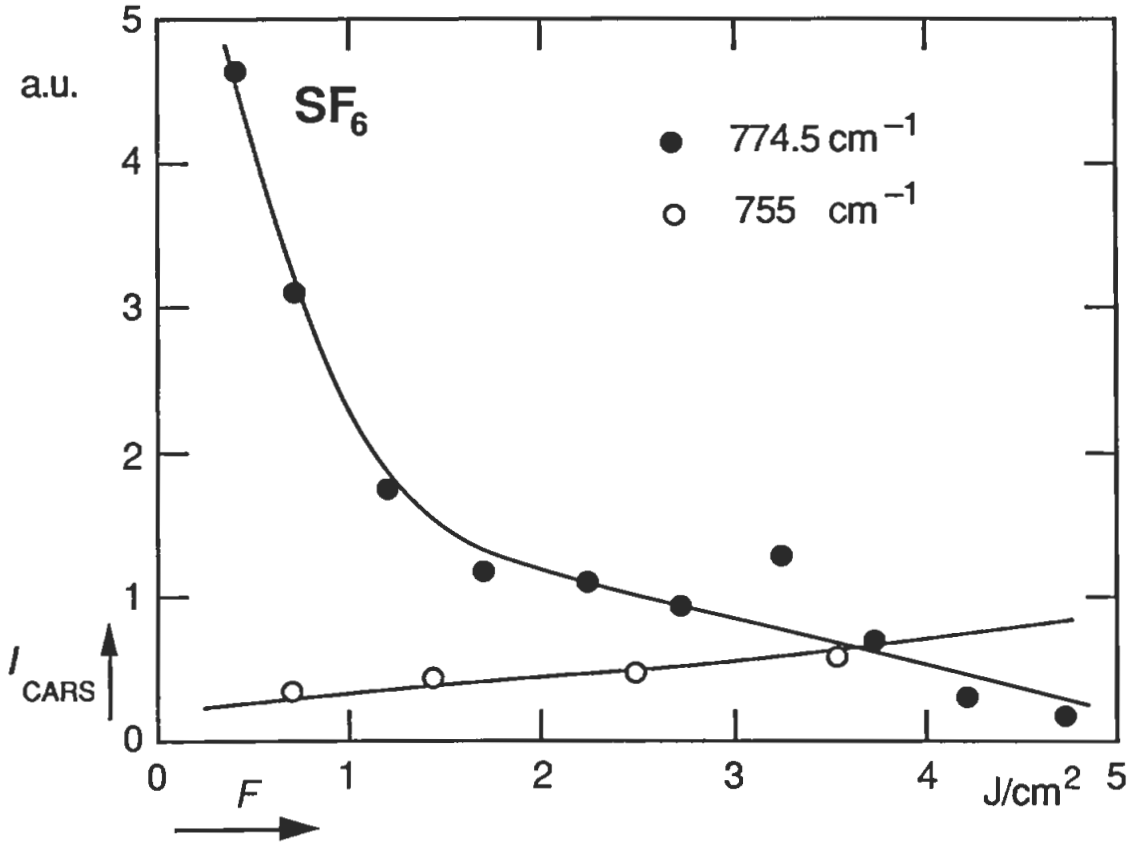
EXPERIMENTAL SETUP



CARS SPECTRUM



GROUNDSTATE DEPLETION



OVERVIEW OF RESULTS

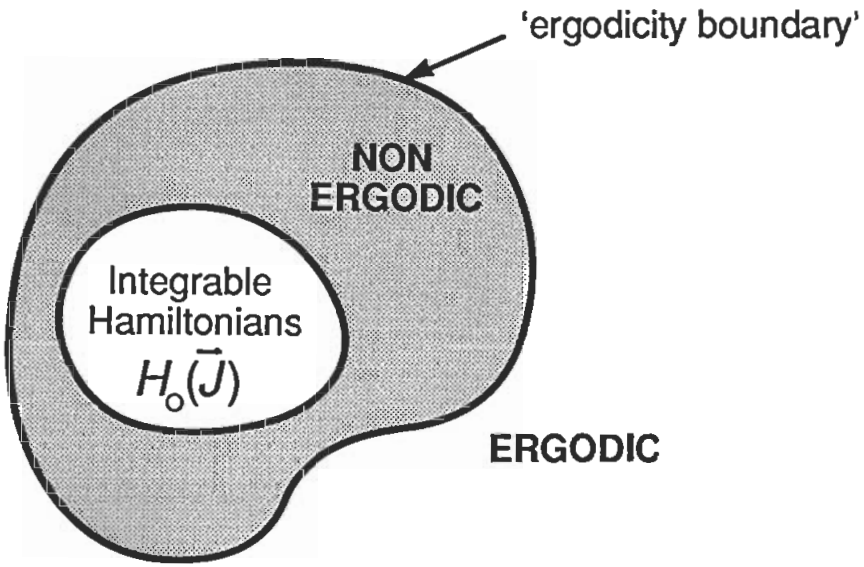
Spontaneous Raman:

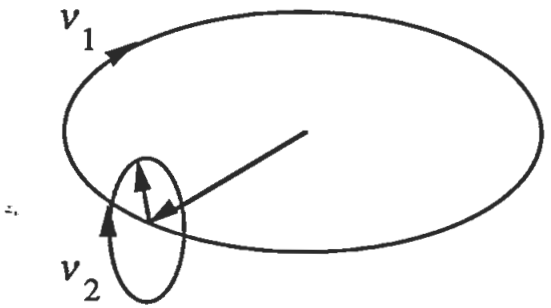
SF_6	Equilibrium vibrational energy distribution is reached within 20 ns
CF_2Cl_2	Nonequilibrium vibrational energy distribution for two modes
	Total vibrational energy at least 21,000 cm^{-1}
	Pump mode contains most energy
	Buffer gas equilibrates the energy distribution

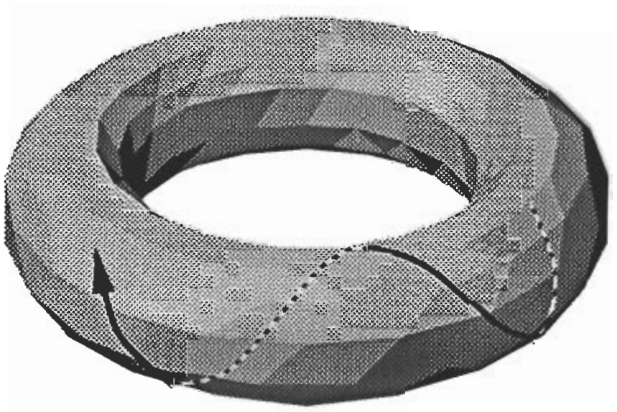
CARS:

Complete ground state depletion

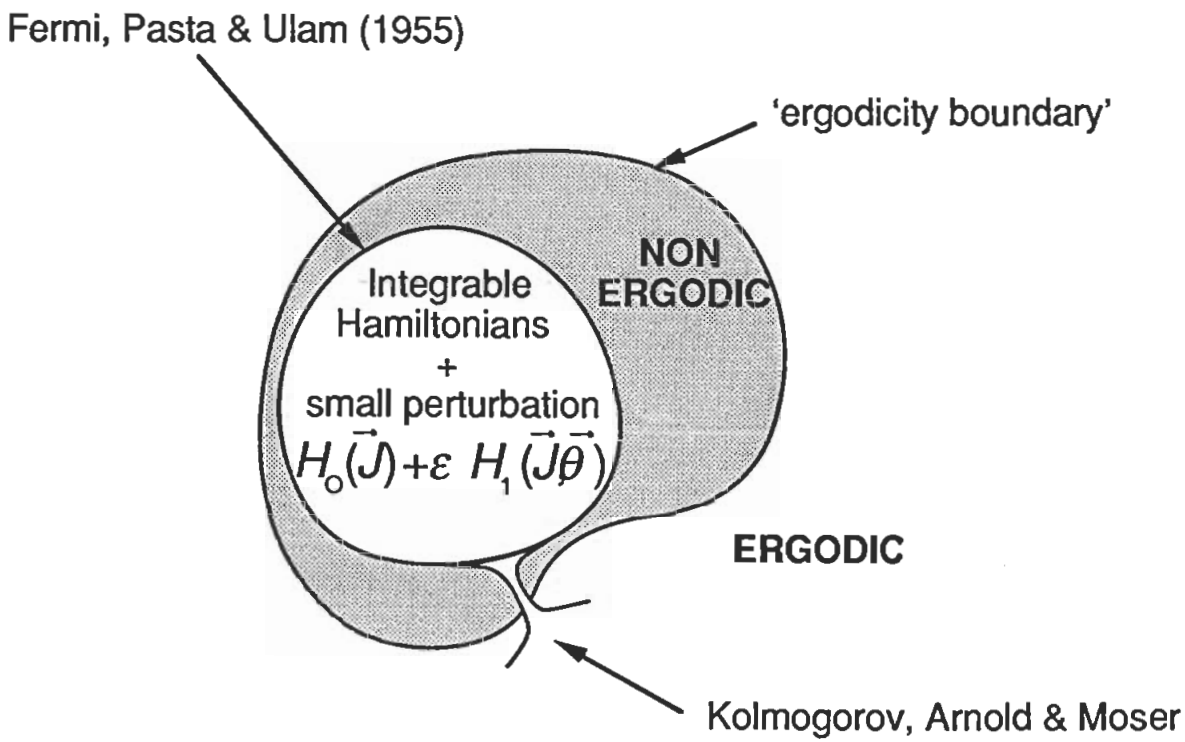
INTEGRABLE HAMILTONIANS







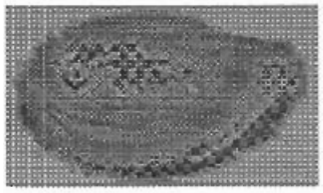
NONINTEGRABLE PERTURBATIONS



$$\sum_{\{n\}} n_i \nu_i = 0$$

KAM THEOREM: If ν's linearly independent and perturbation small $\rightarrow$ trajectory surfaces are not destroyed, just distorted.

PHASE SPACE TRAJECTORIES

	frequencies linearly independent	frequencies linearly dependent
low excitation		
high excitation		

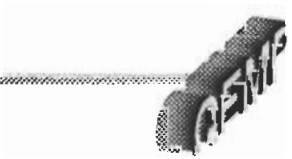
COMMENSURATE FREQUENCY COMBINATIONS

$$\left|\sum_{\{n_i\}} n_i \nu_i\right| < 0.02 \sum_{\{n_i\}} |n_i| \nu_i \qquad \text{with } |n_i| \leq 2, \text{ and } \sum_{\{n_i\}} |n_i| \leq 4.$$

Molecule	Number of combinations	Measured distribution
SF_6	220	equilibrium
CF_2Cl_2	17	nonequilibrium

CONCLUSIONS

- Results consistent with KAM theorem
- High 'selectivity' below dissociation possible
- Rotational states play an important role
- Study intermolecular distribution and state-to-state distributions



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Discussion: Prof. N. Bloembergen

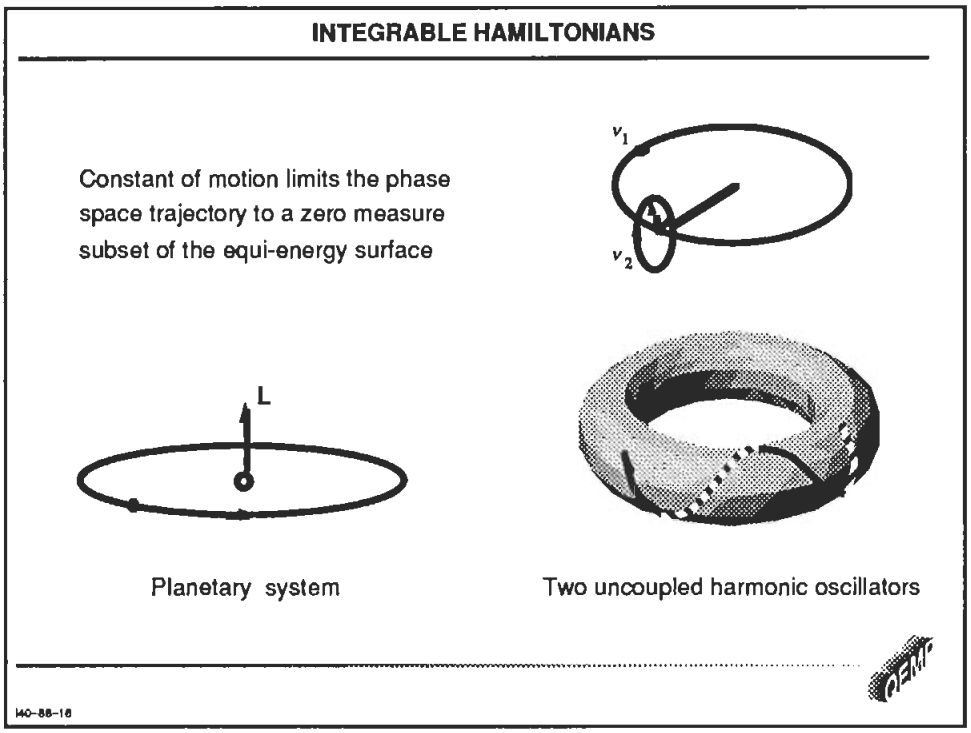
Prof. A.H. Zewail

Support: ARO DAAG29-85-K-0060

JSEP N00014-84-K-0465

Hamamatsu Photonics

NOTES



In the rest of this presentation, we will look at IRMPE from a classical nonlinear dynamics point of view.

In classical mechanics, a polyatomic molecule can be modeled as a system of coupled nonlinear oscillators.

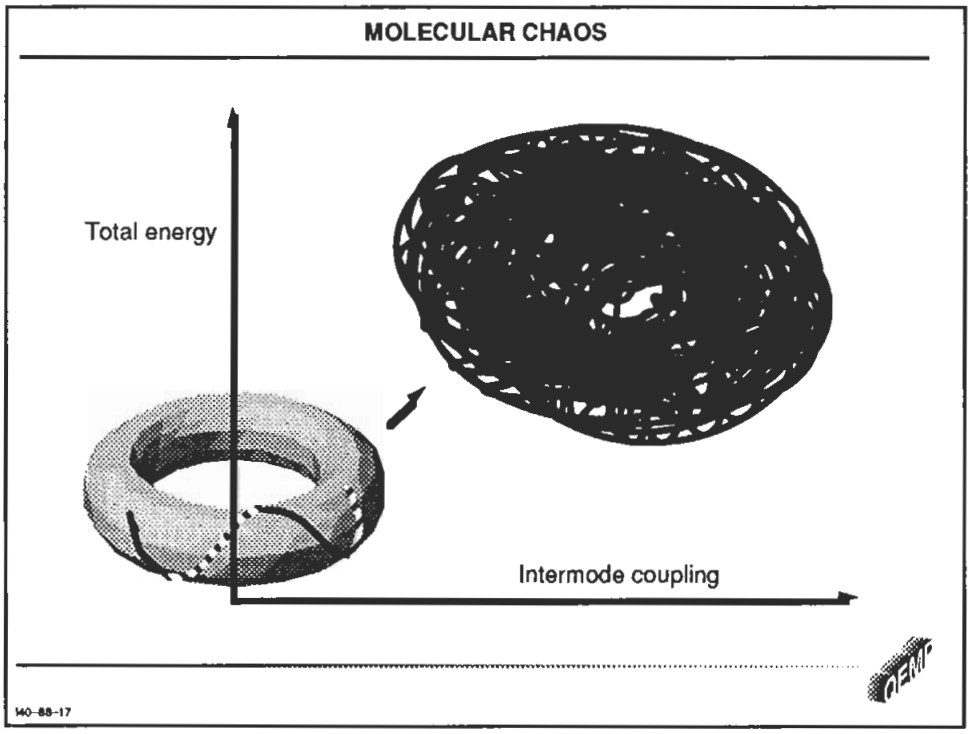
Then, IRMPE can be thought of as a system of coupled nonlinear oscillators driven by an external oscillatory force.

From experiments we know that at low excitation, the energy is localized in the pump mode, while at high excitation the energy can be transferred to other modes.

The question of interest here is how the state of the molecule evolves from one with localized vibrational energy to one with distributed energy. Also, one would like to know what determines the final energy distribution.

For an integrable system, the trajectory is limited in a small part of the available phase space because of the constants of motion. And the energy is always localized For example:

NOTES

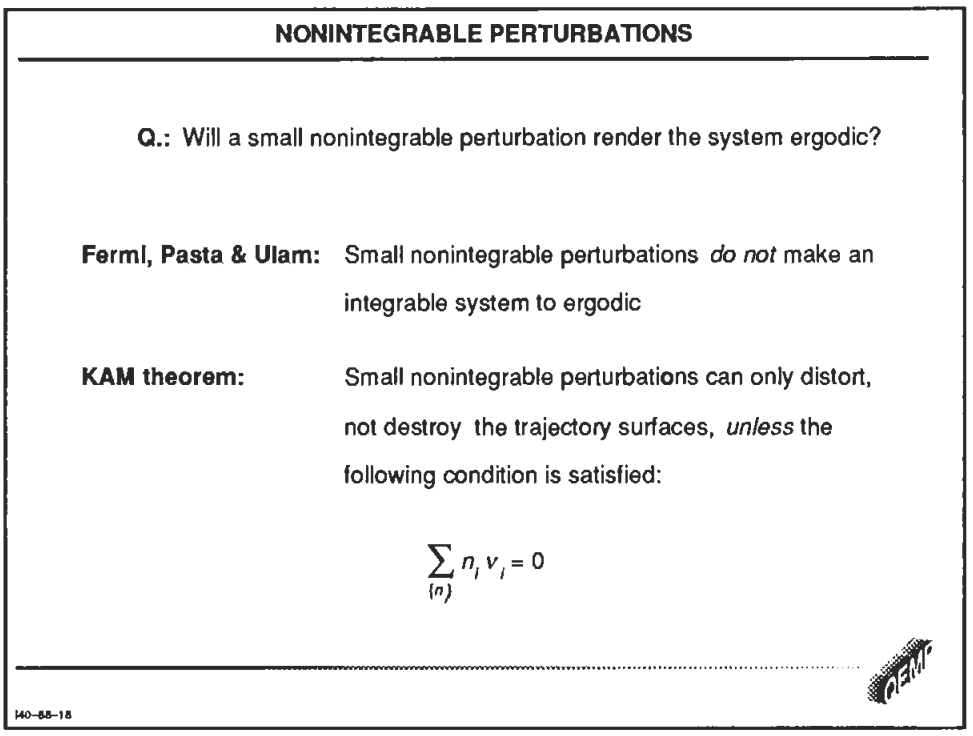


While for nonintegrable systems the trajectory can be very irregular.

For sufficiently high excitation or strong intermode coupling, the trajectory may cover the entire available phase space.

In this case, the energy distribution is equilibrium.

NOTES



Since nonintegrable perturbations such as mode-couplings can render the trajectory chaotic and energy distribution equilibrium, it was thought that these perturbations is responsible for the ergodicity of the system.

Intended to show that the general assumption of ergodicity in Boltzmann's statistical mechanics is a nature consequence of the inevitable small nonintegrable perturbations, Fermi, Pasta & Ulam studied the following question:

Both Fermi's experiment and the KAM theorem suggest that, in general, a system of nonlinear oscillators can become ergodic only when the energy involved is large enough, or when condition ** is satisfied.

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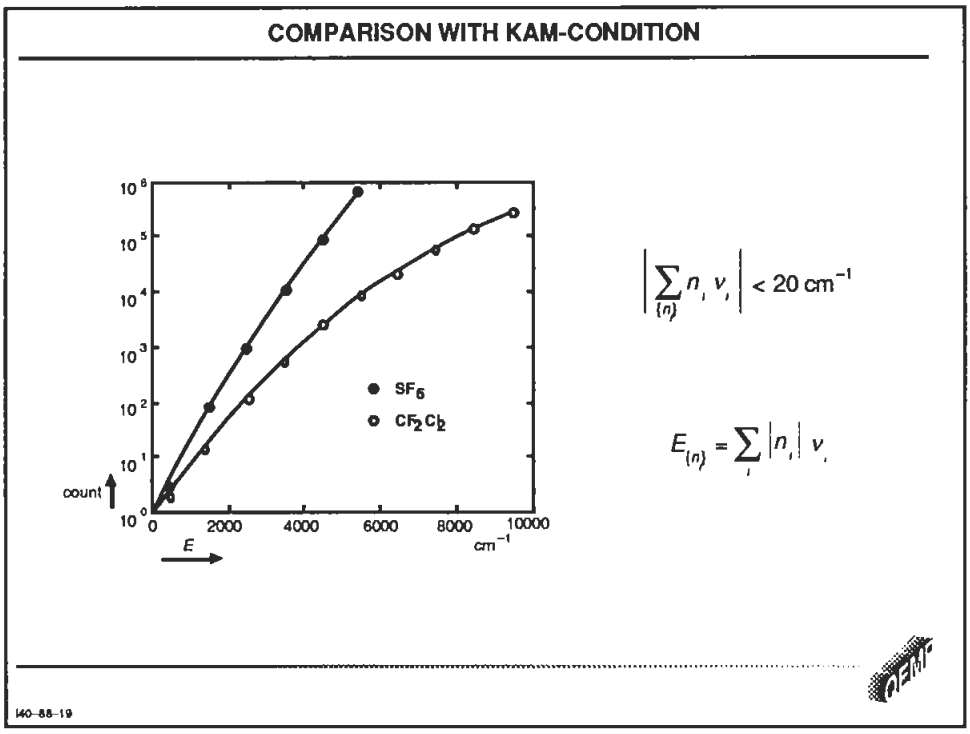


It is interesting to compare the number of times condition ** is satisfied for the two molecules, SF6 and CF2Cl2, whose energy distribution have been measured experimentally.

According to the KAM theorem, the more often condition ** is satisfied, the more likely the molecule will behave ergodically after infrared multiphoton excitation. For SF6 and CF2Cl2, one can calculate the number of times condition ** is satisfied as a function of the excitation energy, and compare the results of the calculation with the experimental results.

of the equation is chosen close to the total anharmonicity of a typical vibrational mode, which can be roughly thought of as the linewidth of a typical ν_i. Since our goal is to compare the number of incidences where Eq. (1.1) is satisfied for different molecules under the same conditions, the choice of the number on the right hand side of Eq. (1.2) is not critical. In the calculation the set $\{n_i\}$ is permuted to cover all possible combinations, and the number of incidences is sorted according to the total internal energy of the molecule,

$$E = \sum_i |n_i| \nu_i . \tag{1.3}$$

As one can see from Fig. 1.5, for SF_6, the number of incidences where Eq. (1.2) is met, is orders of magnitude larger than for CF_2Cl_2. Also, the larger the excitation energy is, the bigger the difference between the two molecules. Note that for both molecules N increases rapidly with energy .

Figure 1.5 strongly suggests that SF_6 will behave ergodically at a much lower excitation energy than CF_2Cl_2. Indeed, the experimental results presented in chapter 4 and 5 show that the intramolecular vibrational energy distribution of SF_6 after infrared multiphoton excitation is an equilibrium one, while the one of CF_2Cl_2 is not.

1.6 Mode-selective excitation vs. intramolecular vibrational energy equilibrium

The experimentally observed intramolecular equilibrium for dissociating molecules raised serious doubts regarding the feasibility of selective chemical bond breaking by infrared lasers. Experimental studies indicate that intramolecular energy relaxation takes

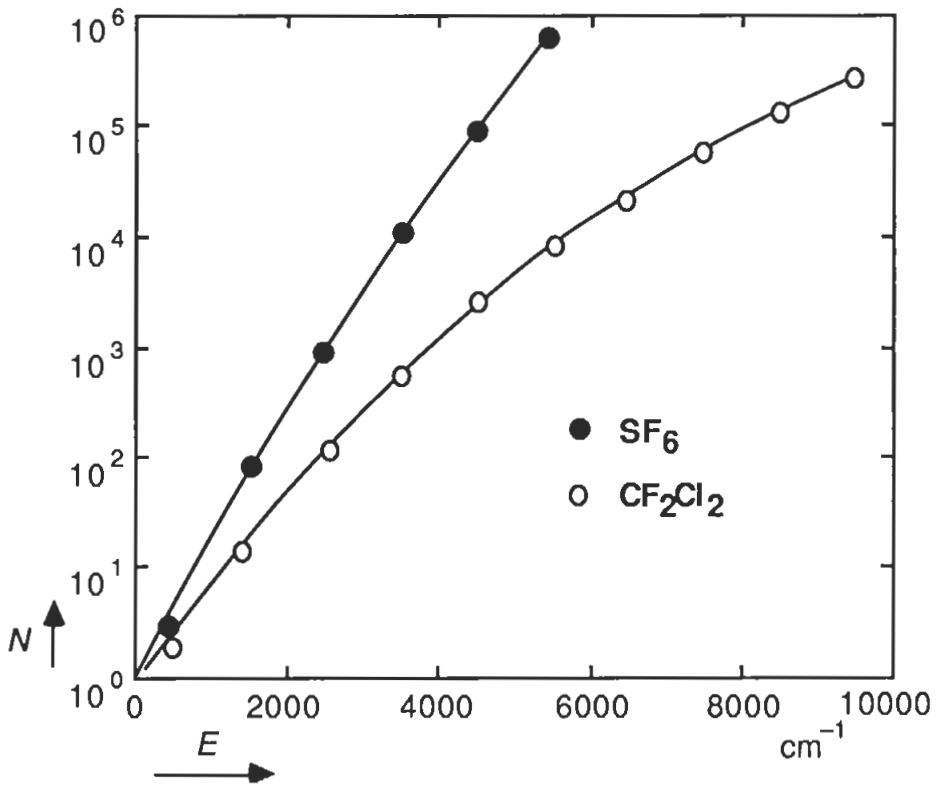


Fig. 1.5. Number of times, N, where Eq. (1.1) is satisfied as a function of excitation energy for SF_6 and CF_2Cl_2. For SF_6 N is one to two orders of magnitude larger than for CF_2Cl_2. This graph suggests that SF_6 will behave ergodically at a much lower excitation energy than CF_2Cl_2.

place on a picosecond time scale.[34,35] With today's molecular laser technology it is still hard to beat this time scale. It has been proposed that it may be possible to use laser pulses with a complicated preprogrammed coherence structure to match the evolution of the molecular states in such a way that the collective motion of the atoms leads to a selective bond breaking state.[36] However, this approach will work only when the time scale of the

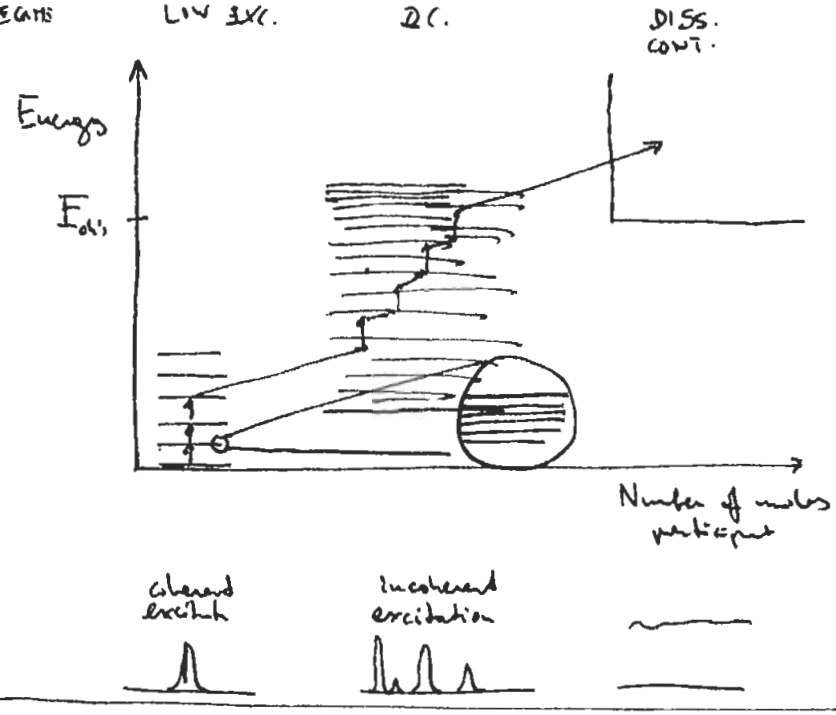
coherence structure of the pumping pulse is shorter than the transverse relaxation time of the vibrational states. Practically, there is not yet a way to control the coherence structure of an infrared laser pulse on such a short time scale.

1.7 Objective of this work

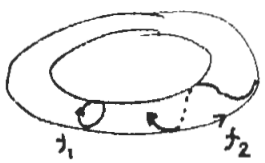
Although the quasicontinuum model explains the general features of infrared multiphoton excitation, one cannot obtain a clear picture of intramolecular vibrational energy relaxation without measuring the intramolecular vibrational energy distributions. Most of the experiments done before this thesis do not supply mode-specific information other than for the pumped mode. Spectroscopic measurements on modes which do not interact directly with the infrared pumping laser are necessary for understanding how the nonresonant background modes participate in the infrared multiphoton excitation. In the first stage of this research project, time-resolved spontaneous Raman spectroscopy was employed to measure the vibrational energy of each accessible Raman active mode after infrared multiphoton excitation for molecules with different sizes and symmetries (see chapter 2–5). The intramolecular vibrational energy distributions were obtained as functions of infrared fluence, frequency and time. In the second stage, a high resolution coherent anti-Stokes Raman experiment was set up to measure the state-to-state population within each vibrational mode. In both cases, the realization of low density, high time resolution Raman spectroscopy provides direct measurements of the state of the molecules.

QC.

REGIME LIN EXC. QC. DISS. CONT.

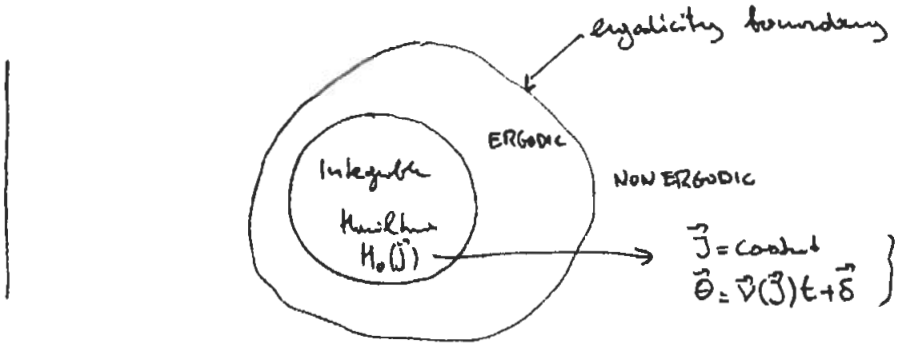


GV excitation



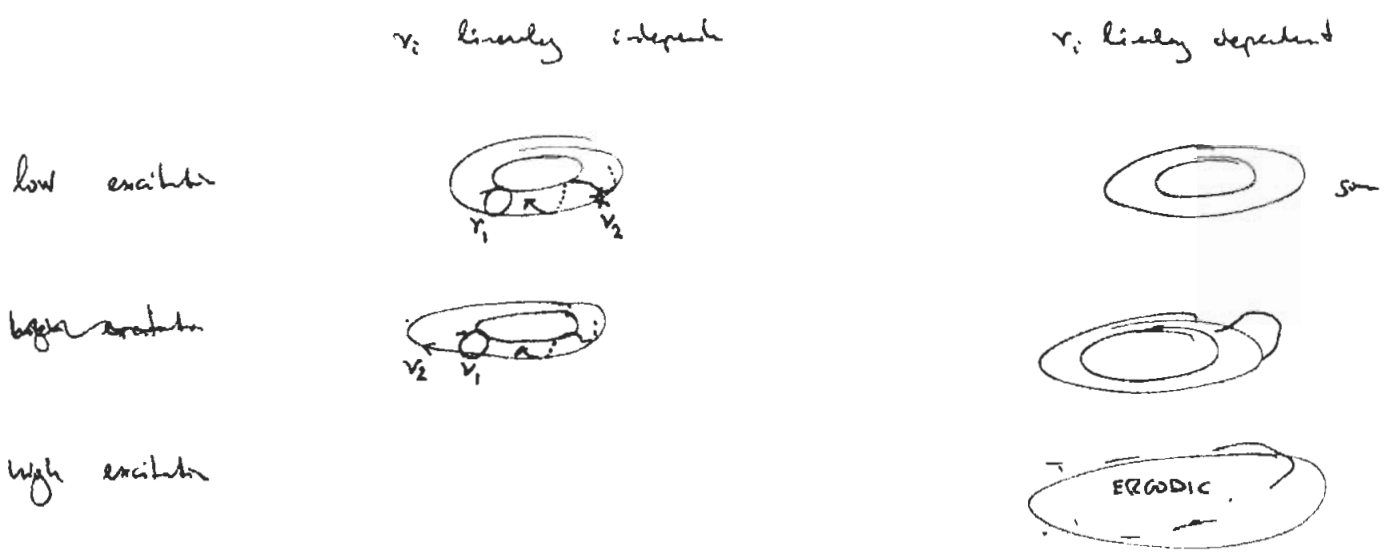
N degrees of freedom ⇒ 2N dimensional phase space
N constants of motion

} motion on N dim surface in 2N dim. space

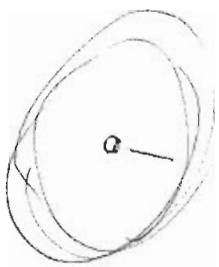


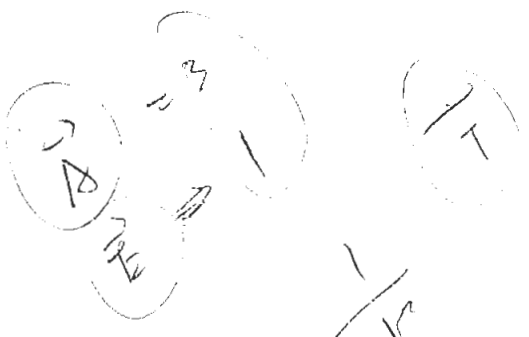
3, 4 or more action-angle variables

KAM THEOREM: if ν_i linearly independent and perturbation sufficiently small → phase space trajectories are distorted but bounded



- RESULTS consistent with KAM theorem
- high selectivity below dissociation possible
- rotational states play important role
- need to look in more detail at intermolecular dist. and state-to-state distr.

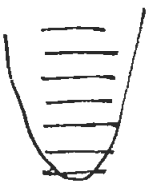




1. Isomor paper
2. Raman Theory
3. Overview of result of Sp. Raman
4. Cars Results
5. ~~Correct ergodic~~
6. ~~Correct cars set up~~
7. degree of freedom and constant
8. ~~draw a planetary system~~ of motion
9. ~~Two frequency torus~~
10. ~~KAM~~ condition in transparency 19
11. finish the tori

CLASSICAL SPECTRUM Q M

Uncoupled HO δ-linewidth



$$\ddot{x}_i + k_i x_i = F_i \qquad p^2 + q^2 = 1$$

coherent IRMPE, high selectivity

Finite linewidth

$$\ddot{x}_i + \gamma_i \dot{x}_i + k_i x_i = F_i \qquad ?$$

coherent IRMPE, high selectivity

Small coupling

$$\ddot{x}_i + \gamma_i \dot{x}_i + k_i x_i + \sum_{j,k} g_{kj} x_j x_k = F_i \qquad ?$$

Coupled

$$\ddot{x}_i + \gamma_i \dot{x}_i + k_i x_i + f(\dot{x}_j, x_k) = F_i \qquad ? \qquad ?$$

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integrable Hamiltonian → system never becomes ergodic (because of constants of motion)

small non-int. perturb. → still no ergodicity (Fermi Pasta Ulam strings, ...)
intermode transfer

Kolmogorov Arnold Moser

only distortion of trajectories in phase space
impossible to destroy
except when $\sum_i m n_i \nu_i = 0$