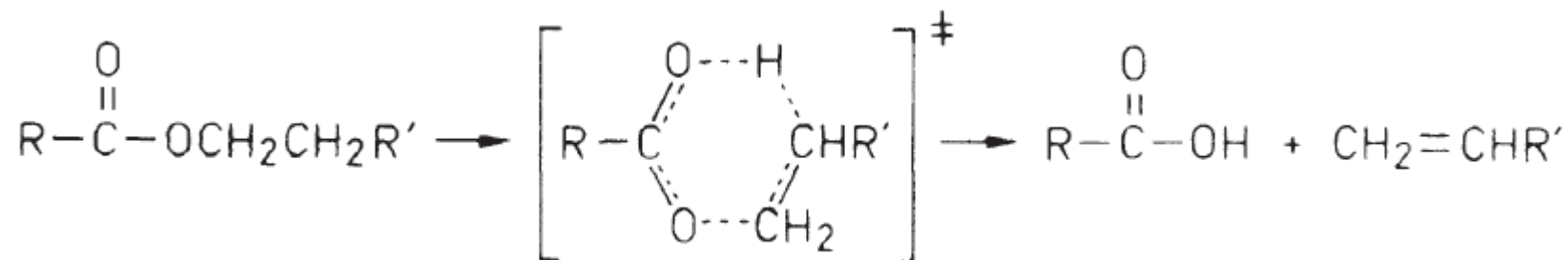


Molecular structures of (I) 7-dehydrocholesterol;(II) previtamin D<sub>3</sub>; (III) vitamin D<sub>3</sub>

- Most unimolecular laser-induced reactions involve multiphoton infra-red dissociation
- Some good examples are provided by elimination reactions involving esters, which proceed as follows



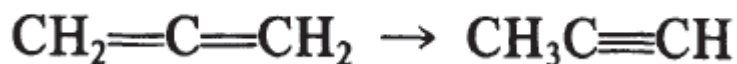
- Such reactions can be very effectively induced by laser irradiation at a frequency of around  $1050\text{ cm}^{-1}$ , which produces excitation of the stretching mode of the O-CH<sub>2</sub> bond and ultimately results in its fission.

- There are certain cases, especially in comparatively small molecules, where irradiation at different laser frequencies genuinely results in different products.
- Cyclopropane, where it is found that multiphoton excitation at around  $3000\text{ cm}^{-1}$  corresponding to the C-H stretching frequency results in isomerisation to propene. However, irradiation at around  $1000\text{ cm}^{-1}$ , corresponding to the  $\text{CH}_2$  'wagging', produces both isomerisation and fragmentation in roughly equal amounts.

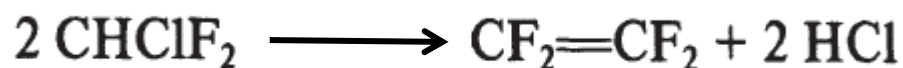
# Laser-Sensitised Reactions

- It involves the sensitisation of reactions by the excitation of a species which does not itself undergo chemical change; this can be regarded as a form of *laser-assisted homogeneous catalysis*.
- This kind of reaction generally proceeds as a result of the collisional transfer of vibrational energy, often referred to as *V-V transfer*, from molecules of the laser-excited species (the sensitizer) to reactant molecules.
- The major advantage of laser sensitisation becomes apparent if the reactants do not themselves strongly absorb in the emission region of a particular laser.

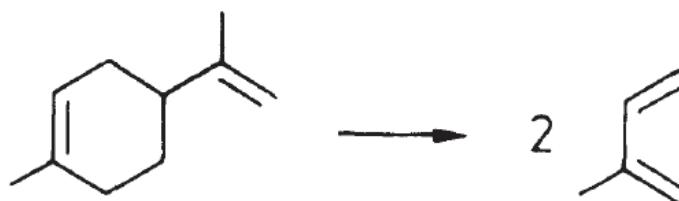
- By choosing a strongly absorbing sensitizer to initiate the reaction, the rate of reaction induced by laser stimulation can be greatly increased.
- Both **sulphur hexafluoride** and **silicon tetrafluoride** have been widely employed as sensitizers
- In the presence of  $\text{SiF}_4$ , various types of sensitised gas-phase reaction have been observed.



Isomerization



Condensation



Retro Diels – Alder Reaction



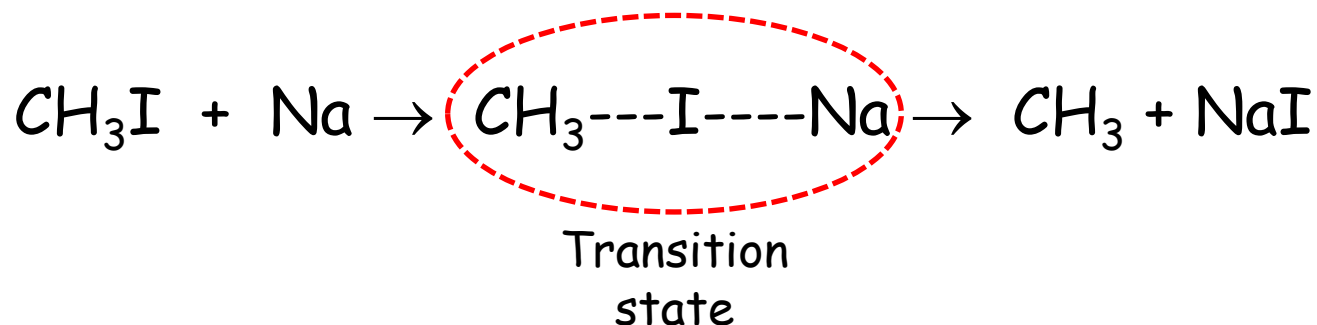
- Many such reactions which are normally carried out at high temperatures, or even with CW laser heating, produce chemically cleaner products if they are induced indirectly by laser sensitisation since the reaction vessel remains cold.
- Such reactions may also be strongly influenced by the choice of sensitizer and the pressure ratio of sensitizer to reagent.
- Because the reactants in a sensitised reaction do not need to possess absorption bands in any particular infra-red region, then with a good sensitizer like  $\text{SiF}_4$ , the range of gas-phase reactions which can be laser-induced is almost limitless.

- Another related topic is *laser-catalysed* reaction, a term which is a very definite misnomer but is applied to a reaction in which the catalyst is itself produced by laser chemistry.
- For example, the laser pyrolysis of OCS using 248 nm radiation from a KrF laser produces ground state  $S_2$  molecules, which can catalyse the isomerisation of cis-2-butene to *trans-2-butene* with an effective quantum yield of about 200.

# Ultrafast Chemical Reaction Dynamics with Ultrashort-Pulsed Lasers

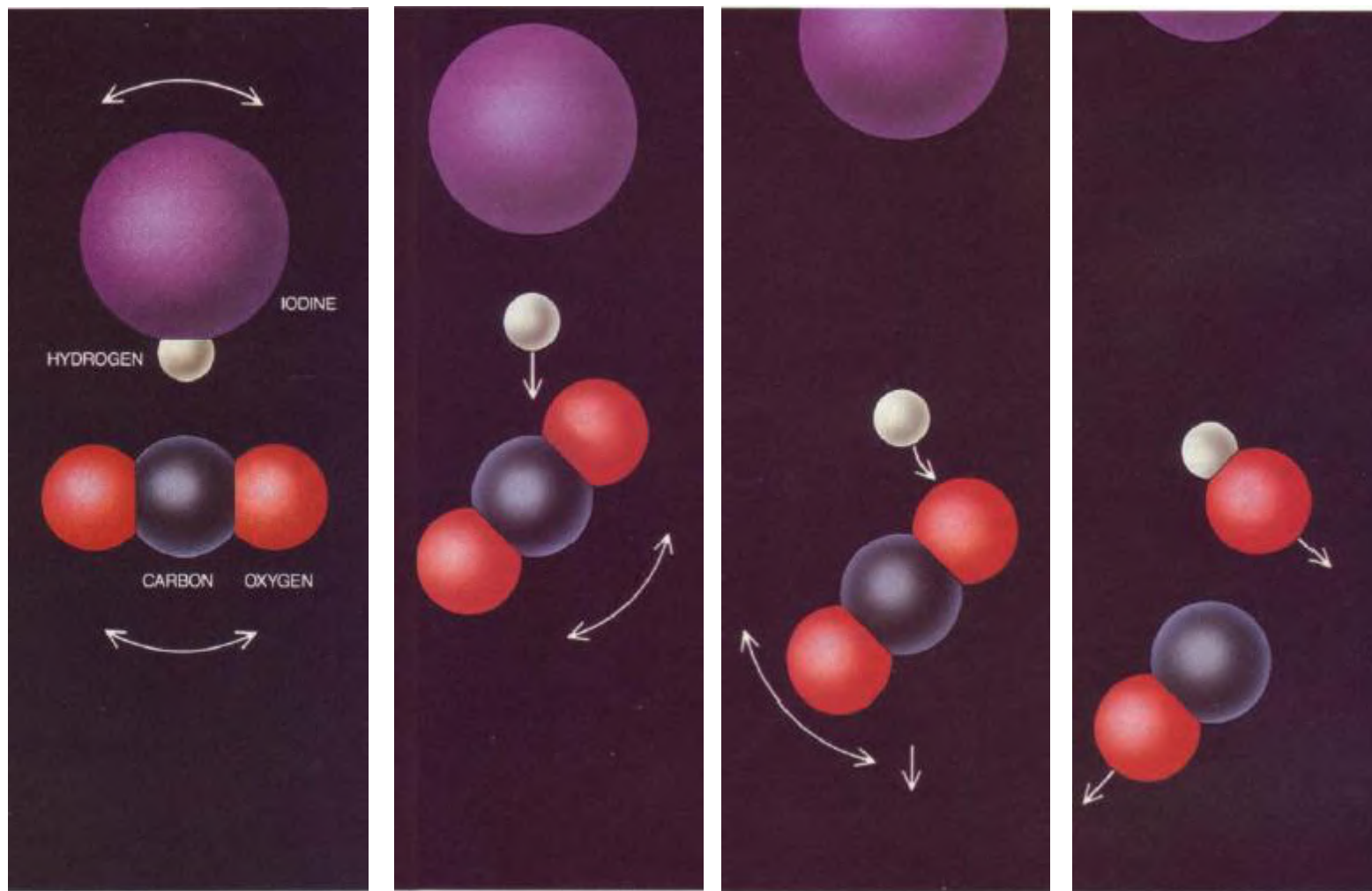


Consider a chemical transformation



In any chemical reaction the motions of the electrons and nuclei of atoms determine how the molecules interact, and those interactions in turn create the forces that govern the reaction's dynamics.

If one can determine how molecular motions change during the critical transition phase, we can understand how new chemical bonds form and old ones disappear.



Molecular structures for a reaction in progress involving two molecules (bimolecular).

## Question

How can one study transition state(s) in real time?

## Answer

Need ultrafast probe and detection technique

## **The Nobel Prize in Chemistry 1999**



**Ahmed  
Zewail**

**"for his studies of the transition states of chemical reactions using femtosecond spectroscopy"**

## Real-time femtosecond probing of "transition states" in chemical reactions<sup>a)</sup>

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(Received 3 June 1987; accepted 15 June 1987)

Transition state(s) (TS) of chemical reactions are fundamental in defining the region(s) of internuclear separation ( $R^*$ ) on the potential energy surface (PES) at which the reagent molecule is "passing on" to products.<sup>1</sup> In contrast to the many successes in applying spectroscopies to the characterization of *stable* reagents and *stable* products, TS spectroscopy has been very limited, because of the TS ultra-short lifetime (few vibrational periods) and the very low

density of TS molecules that can be probed at  $R^*$ . Recently, elegant ideas of time-integrated emission,<sup>2</sup> absorption,<sup>3</sup> and scattering<sup>4</sup> spectroscopy have been developed to infer the dynamics of the TS. Here, we offer a real-time technique that, because of its time resolution ( $\sim 40$  fs), promises to provide direct information concerning the TS and the spectroscopy of reaction intermediates in the process of falling apart (dissociation) or forming a chemical bond (associ-

## Femtosecond real-time probing of reactions. I. The technique

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(Received 12 July 1988; accepted 11 August 1988)

When a chemical bond is broken in a direct dissociation reaction, the process is so rapid that it has generally been considered instantaneous and therefore unobservable. But the fragments formed interact with one another for times on the order of  $10^{-13}$  s after the photon has been absorbed. On this time scale the system passes through intermediate transition configurations; the totality of such configurations have been, in the recent literature, designated as "transition states." Femtosecond transition-state spectroscopy (FTS) is a real-time technique for probing chemical reactions. It allows the direct observation of a molecule in the process of falling apart or in the process of formation. In this paper, the first in a series on femtosecond real-time probing of reactions, we examine the technique in detail. The concept of FTS is explored, and the interrelationship between the dynamics of chemical reactions and molecular potential energy surfaces is considered. The experimental method, which requires the generation of spectrally tunable femtosecond optical pulses, is detailed. Illustrative results from FTS experiments for several elementary reactions are presented, and we describe methods for relating these results to the potential energy surface(s).

## Femtosecond real-time probing of reactions. II. The dissociation reaction of ICN

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(Received 12 July 1988; accepted 11 August 1988)

Experimental results obtained for the dissociation reaction  $\text{ICN}^* \rightarrow [\text{I} \cdots \text{CN}]^{\ddagger*} \rightarrow \text{I} + \text{CN}$  using femtosecond transition-state spectroscopy (FTS) are presented. The process of the I-CN bond breaking is clocked, and the transition states of the reaction are observed in real time. From the clocking experiments, a "dissociation" time of  $205 \pm 30$  fs was measured and was related to the length scale of the potential. The transition states live for only  $\sim 50$  fs or less, and from the observed transients we deduce some characteristics of the relevant potential energy surfaces (PES). These FTS experiments are discussed in relation to both classical and quantum mechanical models of the dynamical motion, including features of the femtosecond coherence and alignment of fragments during recoil. The observations are related to the radial and angular properties of the PES.

## Trotting Horse

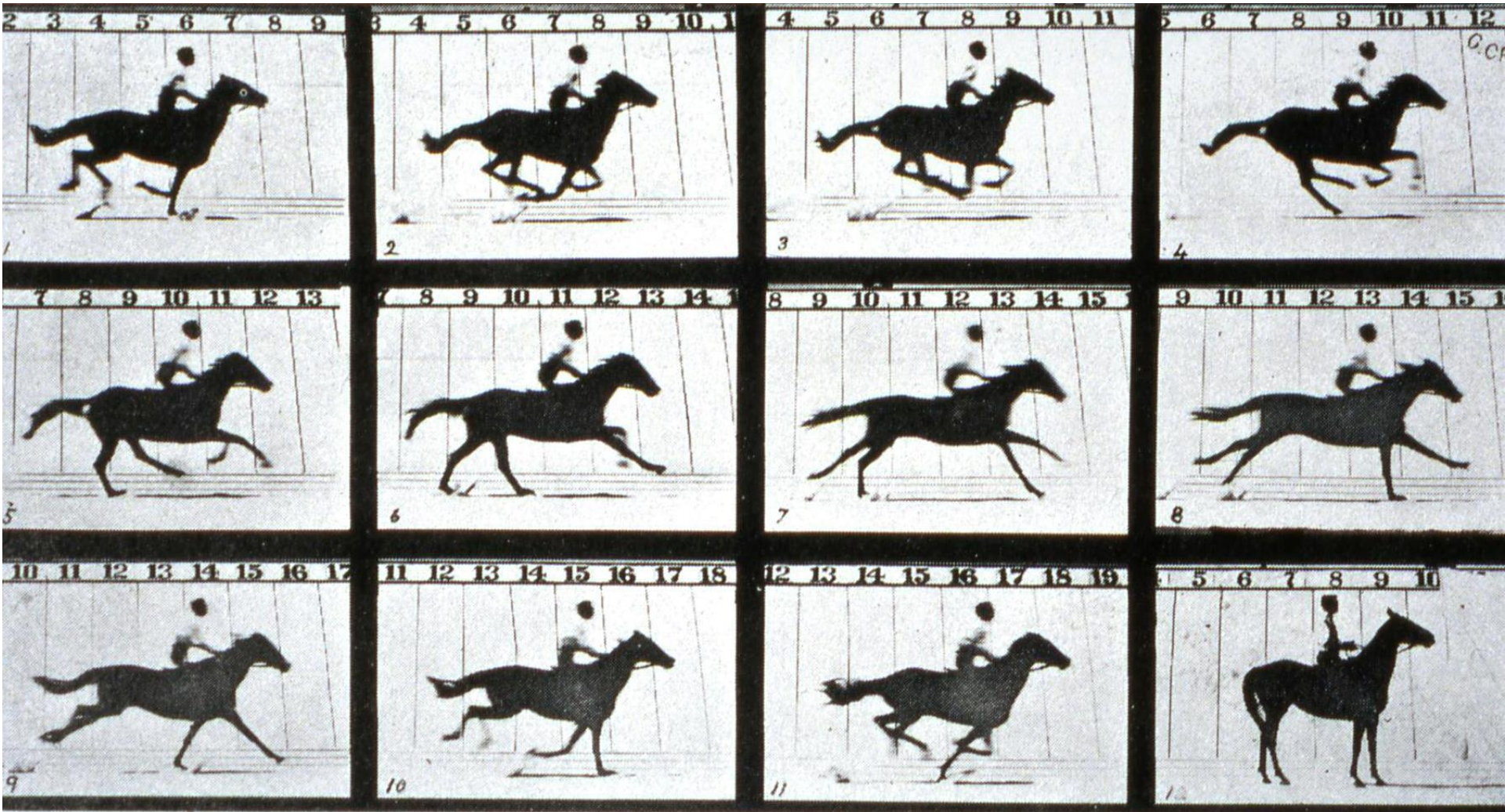
Movie →



There was a debate over the question of whether all four hooves of a trotting horse are simultaneously out of contact with the ground at any point in its stride.



Eadweard Muybridge resolved this!





Time sequence  
images of a  
falling apple



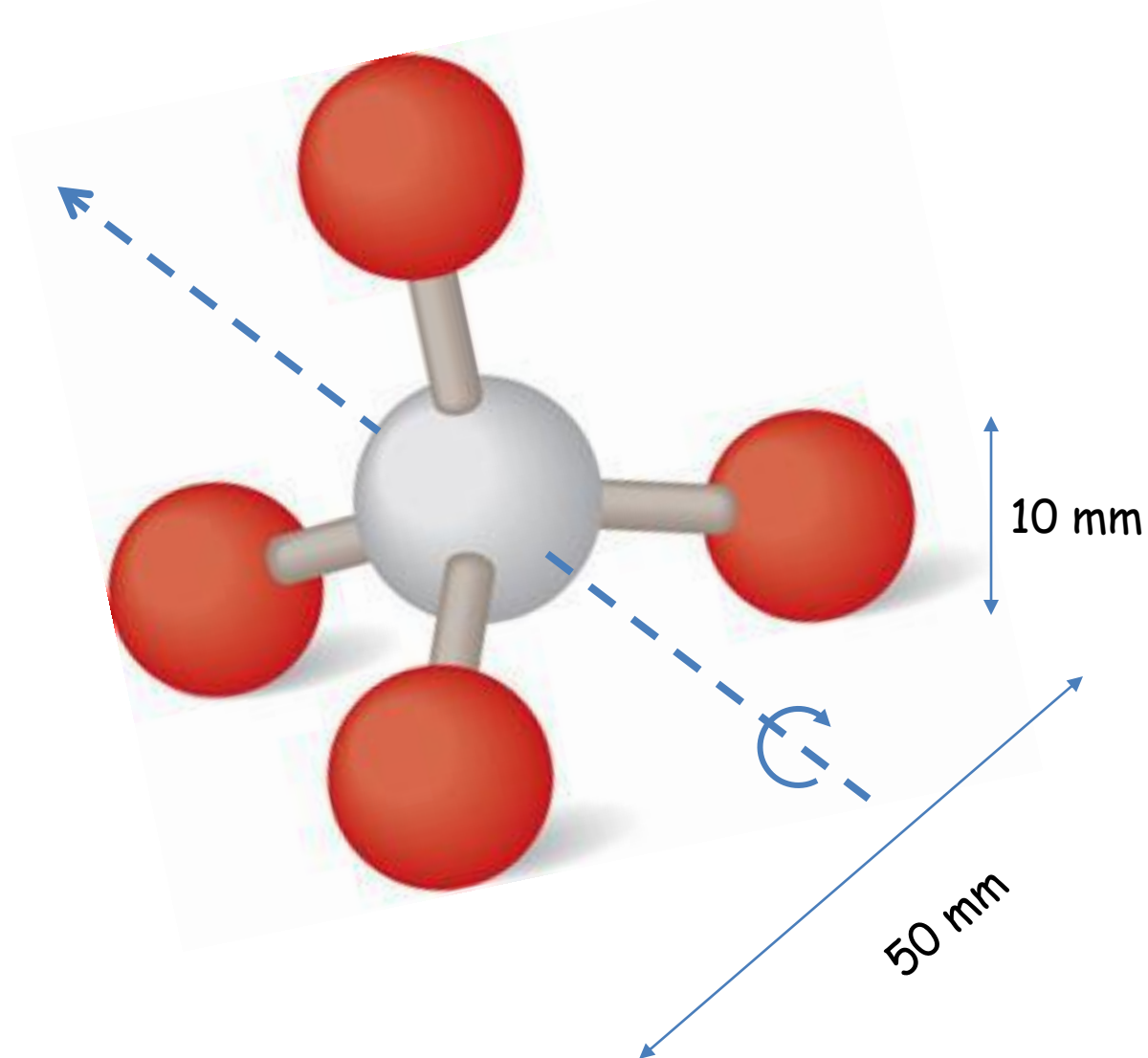
Q. How can you  
get these time  
sequence images?

A. Stroboscopy

What time  
resolution is  
needed to  
capture sharp  
images of the  
falling apple????

We can work it  
out

Let's take a molecular model, rotating at high speed (say -2600 rpm)

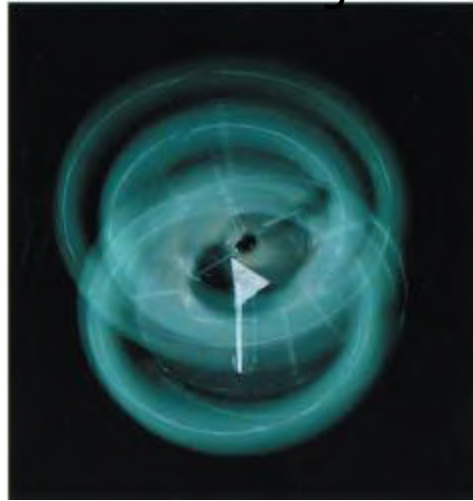


# Laser : Fundamentals and Applications

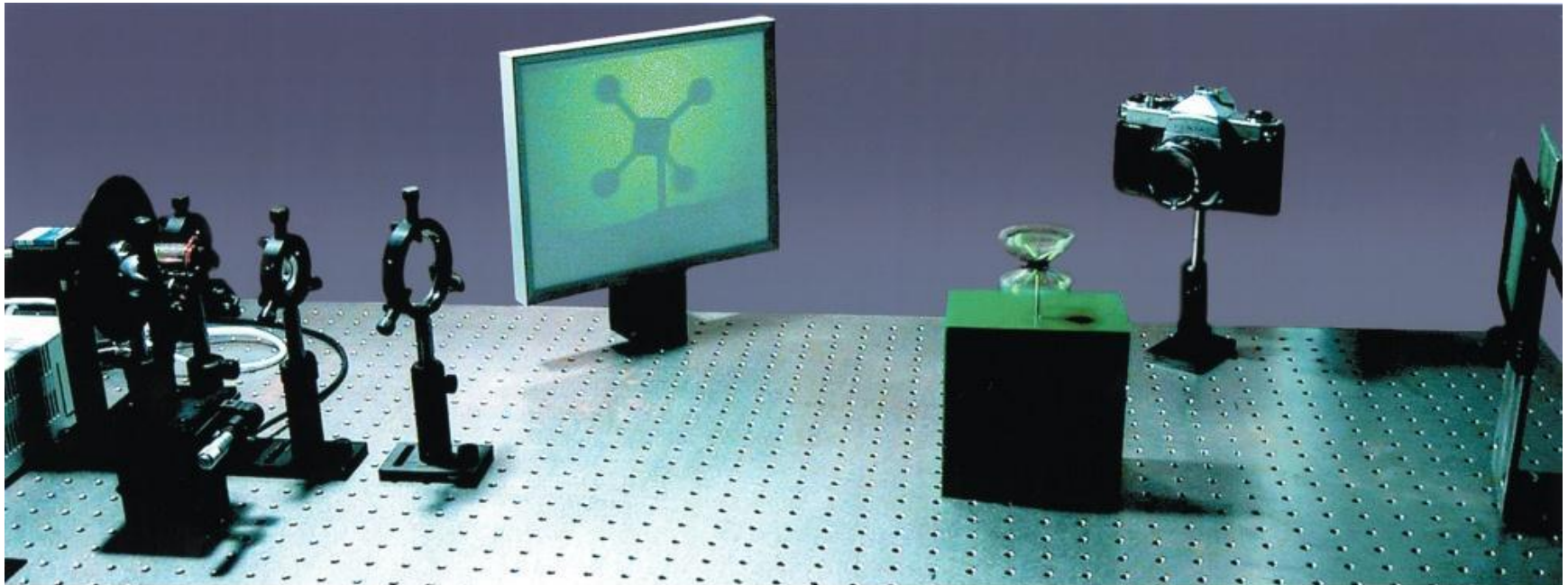
When static



View under room light  
:when rotating



Freezing motion using  
proper light pulse



What time resolution is needed to freeze this macroscopic molecular model in motion???? **Let's find it out** →  **$\sim 150 \mu\text{s}$  !!!** **Need short pulse!**

What about a real molecule (say methane)?  
 **$\sim 10^{-12} \text{ s}$  !!!** **Need ultrashort pulse!**

How can we generate light pulses???

**We have already learnt about it.**

**Is just achieving the time resolution good enough for our goal???**

**No. Need synchronization as well !!** **Why????**

# Laser : Fundamentals and Applications

