

PICOSECOND-PULSE LASER STUDY OF PREDISSOCIATION

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الخلاصة

ان ثابت السرعة لعملية التفكك السابق - حوالي ١٠ ١١ ثانية - لا يمكن قياسه مباشرة بالطرق التقليدية . الليزر المقفل نسقياً الحديث التطوير يمكن من توليد نبضات لا تتجاوز مددها ١٠-١٢ ثانية . في هذه المقالة تستعرض طريقة مستحدثة لقياس ثابت السرعة مباشرة باستخدام تلك الليزر . مقدار الثابت قد يعطي فكرة عن نوعية الحالات الالكترونية المتضمنة والأشكال العامة لمنحنيات الطاقة الكامنة لها . يستعرض تطبيق الطريقة على جزيء Te_2 كثال .

ABSTRACT

The rate constant for predissociation k_p , of the order of 10^{11} sec^{-1} , does not lend itself to direct measurement by conventional methods. Recently developed mode-locked lasers can generate pulses whose duration is of the order of a picosecond. This paper introduces an original method for direct measurement of k_p using such lasers. The magnitude of k_p can provide significant insight into the types of electronic states involved and the general shapes of their potential energy diagrams. The applicability of the method to Te_2 , as an example, is studied.

INTRODUCTION

Predissociation may be defined as radiationless transition from a discrete state of the molecule to a continuous state. When a discrete state of a molecule is overlapped by a dissociation continuum, a mixing of the eigenfunctions occurs as a result of which the discrete energy levels of the stable state assume, to a certain extent, properties of the continuous energy levels. For a molecule undergoing a transition to the region of overlap, there is a finite probability of crossing over to the continuous state. Once in the continuous state, the molecule dissociates within a time comparable with the period of a vibration. The molecule is then said to predissociate.

The term predissociation was coined by Henri[1], although his interpretation of the process was inaccu-

rate. It was Farkas[2] and Kronig[3,4] who explained it as a radiationless transition from a discrete state to a continuous state resulting in dissociation.

Figure 1 represents a situation that may lead to predissociation in the case of a diatomic molecule. If absorption of radiation excites the molecule to the neighborhood of v' or above, then there is a finite probability that the system in the discrete excited electronic state will cross over to the continuous state and decompose.

Three criteria[5] have been so far used to identify predissociation.

1. Diffuseness of Absorption Bands:

The vibronic absorption bands corresponding to transitions to the region where the two potential

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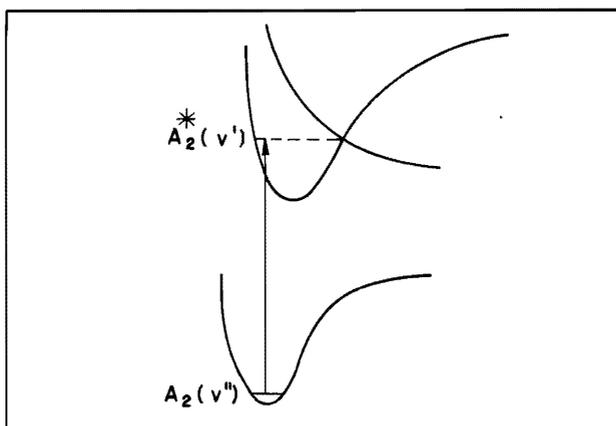


Figure 1. Potential Energy Curves for a Predissociative System.

energy curves cross usually appear diffuse, though not continuous. However, this criterion has its limitations, the most obvious one being the spectral natural line width. In the case of fluorescence with a lifetime of the order of 10^{-8} sec., the line width is about 0.0005 cm^{-1} . In addition, broadening due to the Doppler effect contributes approximately 0.1 cm^{-1} . Consequently, the diffuseness will be noticeable only when the broadening of the line due to predissociation is greater than the Doppler broadening, and this will be the case only when predissociation is extensive.

2. Breaking-off of Emission Bands:

Assuming the diffuseness of the bands in absorption to be due to predissociation, one would expect the corresponding bands in emission to be completely missing or weak, depending on the extent of predissociation. This is a good criterion if one is certain that the radiationless transition carries the molecule to a continuum from which it can dissociate. However, if the radiationless transition carries the molecule to another discrete state then the breaking-off of the bands is not an indication of predissociation.

3. Photochemical Decomposition:

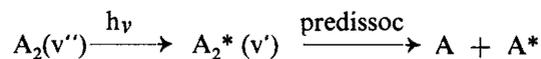
The detection of products of photochemical decomposition, by itself, will obviously not distinguish between predissociation and direct dissociation. It is only in conjunction with the two previously mentioned criteria that this criterion becomes of any use.

It is pertinent to mention here that very few molecules will exhibit these three phenomena. Consequent-

ly, one encounters frequent contradictions in the literature as to whether predissociation is occurring in a given region of the spectrum.

THE PROPOSED METHOD:

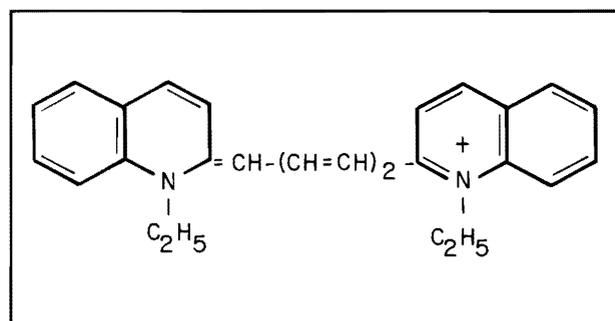
The main object of the proposed method is to measure the rate constant of predissociation. Since the upper limit of the rate constant of predissociation is of the order of $1 \times 10^{11} \text{ sec}^{-1}$, the rate constant will constitute a very strong criterion for predissociation in cases where its occurrence is doubtful. The idea of the method is as follows: Consider the hypothetical case of predissociation in a diatomic molecule whose ground state is $A_2(v'')$.



where $A_2^*(v')$ is the electronically excited molecule which predissociates to two differently excited atoms A and A^* . First, the molecules, A_2 , are excited to the region where predissociation is suspected of occurring (i.e. to $A_2^*(v')$) by means of a laser pulse of picosecond duration [6]. Shortly thereafter, a probing picosecond pulse with a wavelength capable of exciting A is passed through the system. The intensity of absorption of the probing pulse provides a measure of the concentration of atoms A formed after a certain delay time corresponding to the delay time between the exciting and the probing pulses. This delay time is varied and the rate of formation of A is obtained. Similarly the rate of formation of A^* is determined by using a probing pulse with a wavelength capable of exciting A^*

THE Te₂ SYSTEM :

Predissociation in Te₂[7] is suspected of occurring upon absorption of radiation whose wavelength is 3897 Å. This wavelength can be obtained by using the output of a ruby laser (6943 Å) to stimulate emission from the cyanine dye [8] dissolved in glycerol.



The output of the stimulated mission can be varied from 7500 Å – 7900 Å by adjusting the concentration.

The concentration of the dye in glycerol is adjusted so as to give stimulated emission whose wavelength is 7794 Å. This radiation is then frequency doubled and the 3897 Å harmonic is isolated and used to excite Te₂.

The products of predissociation are most likely atoms in the states ³P₂, ³P₁ or ³P₀. The rate of formation of ³P₂ can be obtained from the rate of absorption for the transition:



The probing pulse can be obtained from stimulated emission by 1, 1'- diethyl-2,2'- quinotricarbocyanine iodide in acetone at a concentration of 6×10^{-3} [9].

THE EXPERIMENTAL PROCEDURE:

Figure 2 represents a sketch of the experimental setup. The ruby laser is simultaneously mode-locked and Q-switched by means of a passive bleachable-dye shutter[10] whose relaxation time is faster than the round-trip time of the laser pulse in the laser cavity. Kodak 9860 dye would be suitable for this purpose.

The output of the laser actually consists of a train of pulses, with those at the beginning and the end generally weaker than those in the middle. For this experiment it is essential to use a single pulse for

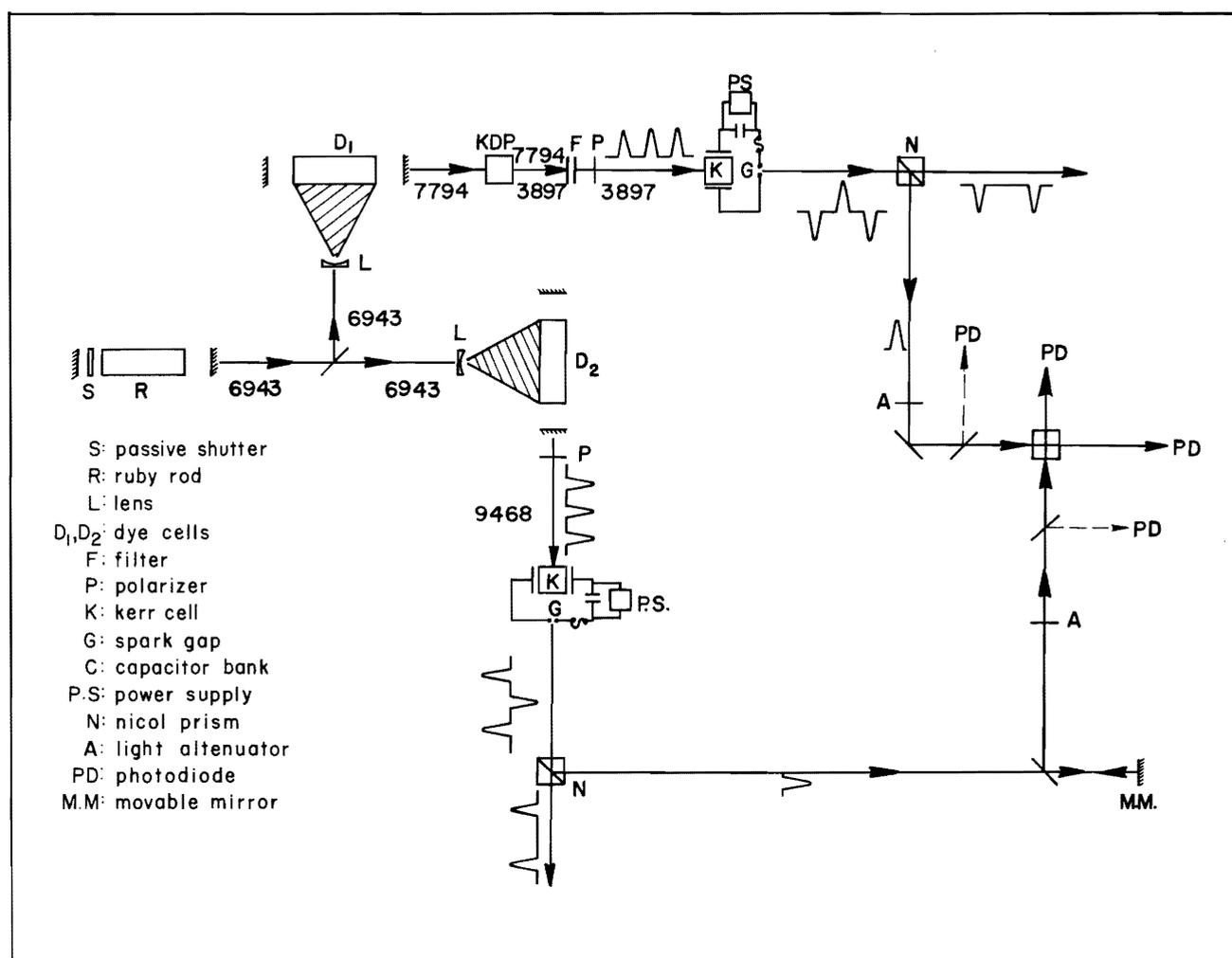


Figure 2. Schematic Experimental Setup.

excitation and another for probing. The single pulse may be isolated from the train as follows (Figure 2): For simplicity it will be assumed that the train consists of only three pulses, but the same procedure could be applied to isolate a single pulse from a train consisting of a large number of pulses. The 6943 Å output of the ruby laser is partially reflected towards the dye laser D₁, the output of which is frequency doubled, filtered and then polarized. The pulses then pass through a Kerr cell activated by a spark gap. The timing is such that the first pulse triggers the spark gap which activates the Kerr cell at the instant the middle pulse is passing through the Kerr cell. Thus the polarization of the middle pulse will be 90 degrees in relation to the polarization of the other pulses. A nicol prism resolves the polarizations, isolating the middle pulse. The pulse is attenuated, and part of it reflected towards a photodiode to obtain the initial intensity. The pulse excites the Te₂ sample and its intensity after absorption is indicated by another photodiode.

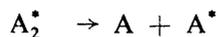
A similar procedure is followed to isolate the probing pulse, and the delay time between the exciting pulse and the probing pulse is regulated by means of the movable mirror (MM).

KINETICS OF PREDISSOCIATION:

The kinetics of predissociation will fall into one of two categories:

Case 1: $k_p \gg k_f$

Where k_p is the rate constant of predissociation and k_f is the fluorescence rate constant. The reaction of interest here is,



$$\frac{-d(A_2^*)}{dt} = k_p (A_2^*)$$

$$\int_{(A_2^*)_0}^{(A_2^*)_0 - (A)} \frac{d(A_2^*)}{(A_2^*)} = -k_p t$$

$$\ln \frac{(A_2^*)_0}{(A_2^*)_0 - (A)} = k_p t$$

Assuming a quantum yield of unity for the absorption process,

$$(A_2^*)_0 = \frac{(I_0 - I)}{V} \text{ molecules/unit volume}$$

where I_0 and I are the initial and final intensities of the exciting pulse, measured in quanta, and V is the volume of the absorption cell. The concentration of A can be obtained from the relationship

$$(A) = \frac{1}{a_A l} \log \frac{I_0}{I}$$

where a_A is the absorptivity for atom A and l is the path length in the absorption cell.

a_A can be determined in another experiment using A with a known concentration, and then

$$I = I_0 10^{-a_A (A) l}$$

Thus plotting

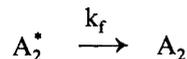
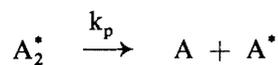
$$\ln \frac{(A_2^*)_0}{(A_2^*)_0 - (A)} \text{ versus } t \text{ gives}$$

a straight line with a slope equal to k_p .

A similar analysis applies when A^* is used in place of A .

Case 2. $k_p \simeq k_f$

Two reactions occur simultaneously,



$$\frac{-d(A_2^*)}{dt} = (k_p + k_f) (A_2^*)$$

$$\int_{(A_2^*)_0}^{(A_2^*)} \frac{d(A_2^*)}{(A_2^*)} = -(k_p + k_f) \int_0^t dt$$

$$(A_2^*) = (A_2^*)_0 e^{-(k_p + k_f)t}$$

and,

$$\frac{d(A)}{dt} = k_p(A_2^*) = k_p(A_2^*) e^{-(k_p + k_f)t}$$

Thus,

$$\frac{(A)}{(A_2^*)_0} = \frac{k_p}{k_p + k_f} \left[1 - e^{-(k_p + k_f)t} \right]$$

The plot of $\frac{(A)}{(A_2^*)_0}$ versus t would have the form

shown in Figure 3.

In the limit as $t \rightarrow \infty$, $\frac{(A)}{(A_2^*)_0} \rightarrow \frac{k_p}{k_p + k_f} = \alpha$

the quantum yield of predissociation.

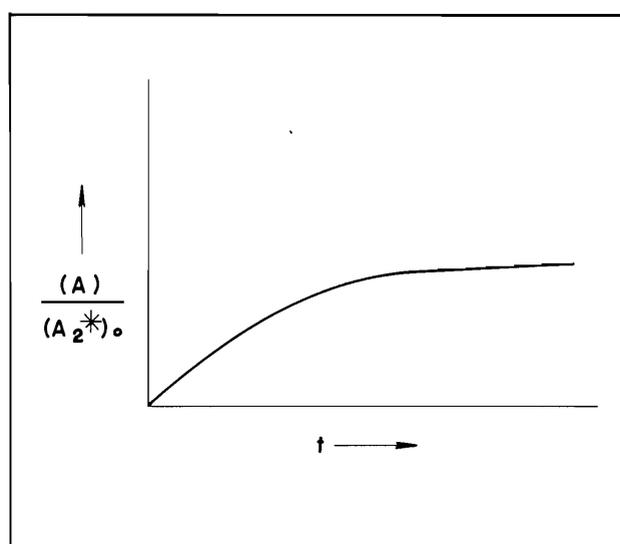


Figure 3. Graph of Ratio of Concentrations as a Function of Time for Case 2

k_p and k_f can then be obtained from the lifetime of the fluorescence,

$$\tau = \frac{1}{k_p + k_f} = \frac{\alpha}{k_p}$$

or,

$$k_p = \frac{\alpha}{\tau}$$

and,

$$\tau (k_p + k_f) = 1$$

$$\tau (\alpha/\tau + k_f) = 1$$

or,

$$k_f = \frac{1 - \alpha}{\tau}$$

INFORMATION DERIVED FROM EXPERIMENT

1. Identification of Predissociation:

The experimental results constitute a very strong criterion for predissociation in cases where its occurrence is doubtful. If no atoms can be detected, it is inferred that the diffuseness of the absorption bands and breaking-off of emission bands are probably due to some other radiationless transitions. If atoms are detected but their concentration as a function of the delay time is constant, it may be concluded that they are formed as a result of a direct dissociation process where their rate of formation is faster than the time scale of the experiment.

2. Rate Constants and Quantum Yields:

In cases where predissociation takes place, the rate constants and quantum yields of fluorescence and predissociation can be determined.

3. Potential Energy Curves and Heat of Dissociation:

In cases where the rate constant of formation of the atoms turns out to be a function of wavelength below the region of maximum predissociation (crossing point), it is implied that the potential curves cross as indicated in Figure 4a, where the rate constant of predissociation decreases at longer wavelengths because of a decrease in the extent of tunnelling as the potential barrier becomes broader. Where the rate constant is independent of wavelength at longer wavelengths, it becomes likely that the potential curves cross as shown in Figure 4 b, c. In the latter case it is possible to get an accurate number for the heat of dissociation of the state causing the predissociation. The heat of dissociation is defined as:

$$Q_0^0 = E_d - E_x$$

where E_d is the energy of the dissociation limit and E_x is the excitation energy of the products. E_x can be easily determined from the wavelength of the probing pulse.

4. Assignment of the Molecular Electronic States:

Once the states of the atoms formed are identified, the Wigner-Witmer correlation rules [11] can be used to derive the possible molecular states that correspond

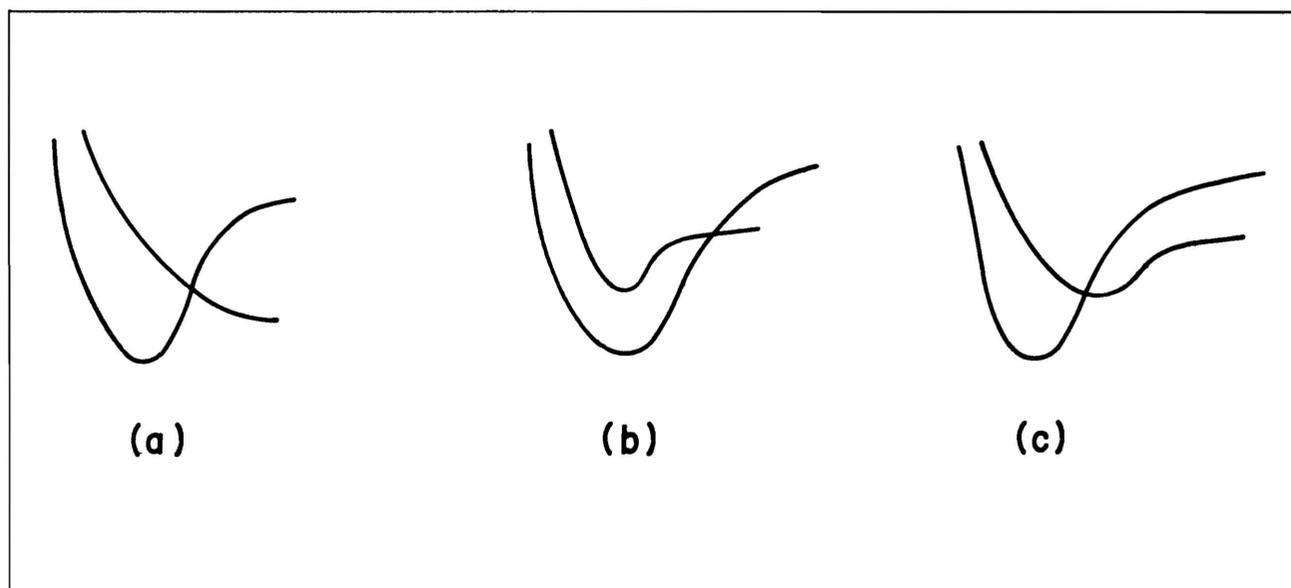
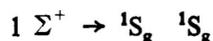


Figure 4. Possible Forms of Curve Crossings.

to the atomic states. As an example, if the atoms are formed in the states 1S_g and 1S_g , then,



and hence the state involved in the predissociation is a Σ_g^+ . If the rate of predissociation is very fast, ($k_p > 10^{10}$), the predissociation is allowed by Kronig's selection rules [3]

$$\Delta j = 0 \quad \Delta S = 0 \quad \Delta \Lambda = 0, 1$$

It is then implied that in this case the discrete state involved in the process is either $1 \Sigma^+$ or 1π .

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