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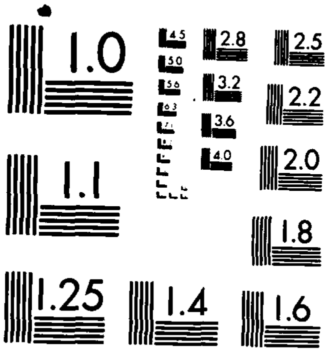

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(12)

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Contract N00014-80-C-0472

Task No. NR 056-749

TECHNICAL REPORT No. 71

Thermalization in Multiphoton Excitation of Molecules

by

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Prepared for Publication

in

Physics Letters A

Departments of Chemistry and Physics
State University of New York at Buffalo
Buffalo, New York 14260

November 1985

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

AD-A162 113

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
UBUFFALO/DC/85/TR-71

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Depts. Chemistry & Physics
State University of New York

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS *(City, State and ZIP Code)*
Fronczak Hall, Amherst Campus
Buffalo, New York 14260

7b. ADDRESS *(City, State and ZIP Code)*
Chemistry Program
800 N. Quincy Street
Arlington, Virginia 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Contract N00014-80-C-0472

8c. ADDRESS *(City, State and ZIP Code)*
Chemistry Program
800 N. Quincy Street
Arlington, Virginia 22217

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.

11. TITLE
Thermalization in Multiphoton Excitation of Molecules

12. PERSONAL AUTHOR(S)
Xi-Yi Huang and Thomas F. George

13a. TYPE OF REPORT
Interim Technical

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Yr., Mo., Day)*
November 1985

15. PAGE COUNT
12

16. SUPPLEMENTARY NOTATION
Physics Letters A

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
THERMALIZATION
MULTIPHOTON EXCITATION
LASER-DRIVEN ANHARMONIC OSCILLATOR
ENERGY RELAXATION
PHASE RELAXATION
DENSITY MATRIX

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Dr. David L. Nelson

22b. TELEPHONE NUMBER *(Include Area Code)*
(202) 696-4410

22c. OFFICE SYMBOL

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE.

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Physics Letters A, in press

THERMALIZATION IN MULTIPHOTON EXCITATION OF MOLECULES

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Abstract

The thermalization of coherent multiphoton excitation of molecules is examined. An inspection of the level distribution of a driven anharmonic oscillator, which is subject to energy and phase dissipation to a bath, reveals that phase relaxation (dephasing) due to the bath perturbation plays a major role in the thermalization process.

I. Introduction

Rapid advances in laser photochemistry and isotope separation have generated considerable interest in the selective absorption of electromagnetic radiation leading to either molecular dissociation[1,2] or adspecies desorption from an interface.[3-5] The theoretical treatment of the problem of many degrees of freedom for a polyatomic molecule and/or admolecule-surface system is very complicated and generally an insoluble problem. Besides the complexity of multiphoton excitation which is nonresonant for high transitions due to the presence of molecular anharmonicity, interactions between the resonant photon-active vibrational mode and the other inactive modes, and/or between the admolecule and surface modes,[6-8] i.e., surface phonons, surface plasmons, reflected photons (photons emitted by the admolecule and reflected by the surface), etc., create a large number of dissipative channels by which selective absorption, dissociation and desorption at the surface are strongly influenced. A major motivation for many of the studies in photochemistry is the attractiveness of mode-selective chemistry: under appropriate conditions, molecules prepared in a state of high vibrational energy by absorption of monochromatic laser radiation would be markedly different from the ergodic ensemble which results if the same energy is imparted by heating, i.e., by collisions with a thermal bath. Unfortunately, experimental and theoretical studies have shown[9,10] that near the dissociation threshold for the multiphoton excitation process of a polyatomic molecule or near the desorption threshold for such excitation of an admolecule-surface system,[5] a statistical thermodynamic process occurs, so that the dissociation (or adsorption) reaction proceeds in a roughly similar manner as for a thermally-excited unimolecular reaction. In this letter, we use a simple model for a laser-driven damped anharmonic oscillator for the active vibrational mode which is subject to both energy and phase dissipation to a bath (the inter- or intramolecular nonactive modes and the surface excitations) to discuss the role of dissipative mechanisms in the thermalization coherent multiphoton excitation processes. We shall see that phase relaxation (dephasing) is more important than energy relaxation in the active-mode thermalization process. The transformation of the level population distribution to the Planck distribution in the driven damped anharmonic active mode is mainly due to the phase dissipation provided by the bath.

II. The Model

The excitation and relaxation of the active vibration mode in a collisionless multiphoton process can be visualized in terms of an anharmonic oscillator which is driven by a near resonant coherent laser field and controlled by both energy (T_1) and phase (T_2) relaxation. The many other inactive modes and/or surface excitations (phonons, plasmons, reflected photons, etc.) are treated as a large thermal bath, by which the dissipative mechanisms are provided. A reduced density operator W for the resonant mode obeys the master equation[12]

$$\frac{dW}{dt} = [-iL_C+\Lambda_1+\Lambda_2]W \quad . \tag{1}$$

The first term in Eq. (1), $-iL_CW = -(1/\hbar)[H,W]$, is a coherent (reversible) term, where $H = H_M + H_F$ is the sum of molecular anharmonic oscillator and driving field interactions,

$$H_M = \hbar(\omega-\omega_L)a^\dagger a - \hbar\varepsilon a^\dagger a(a^\dagger a+1) \tag{2}$$

$$H_F = \mu E(t)(a^\dagger+a). \tag{3}$$

Here $a^\dagger$ and a are oscillator ladder operators, μ is the molecular dipole, E(t) is the applied field, ω_L is the laser frequency, and ε is the (positive) molecular anharmonicity. The last two terms in Eq. (1) are dissipative terms, which are given by[11,12]

$$\Lambda_1 W = \gamma_\downarrow([a,Wa^\dagger] + [aW,a^\dagger]) + \gamma_\uparrow([a^\dagger,Wa] + [a^\dagger W,a]) \tag{4}$$

$$\Lambda_2 W = \eta([a^\dagger a, Wa^\dagger a]+[a^\dagger aW, a^\dagger a]) \ . \qquad (5)$$

$\Lambda_2 W$ is responsible for a pure phase relaxation mechanism (dephasing), $\gamma_\uparrow$, $\gamma_\downarrow$ and η contain implicit information about the bath, and $\Lambda_1 W$ is responsible for the energy relaxation mechanism, which governs the population loss in the active mode. In the Born approximation, i.e., where the characteristic rate of the coherent exchange induced by the system Hamiltonian is sufficiently smaller than the largest decay rate of the dissipation process, the diagonal parts of the density matrix obey

$$\frac{d}{dt} W_n = \langle n|\Lambda_1 W_r|n\rangle - \int_0^t d\tau \, \langle n|PL_I e^{-iL_M(t-\tau)} e^{\Lambda_2(t-\tau)} L_I W_r(\tau)|n\rangle \ , \qquad (6)$$

where L_I is a Liouville operator due to the oscillator-field interaction, and P is a projection operator used to obtain the diagonal part of the density operator.[13]

To solve the difficult problem of explicitly evaluating the matrix element that appears within the integrand in Eq. 6, we have used the Weidlich eigenfunction-expansion method.[12,14] The "eigenstates" of the super operators Λ_2 and $\Lambda_2^\dagger$ are $||Apq)$ and $||Bpq)$, respectively. For a normal situation in molecular excitation, the phase-relaxation rate η is always much larger than the energy relaxation,[18] i.e., $\eta >> \kappa$, so that the Markoff approximation is applicable. Within this approximation, the equations of motion for the diagonal parts of the density matrix are then given as

$$\dot{W}_n = \langle n|\Lambda_1 W_r|n\rangle - \int_0^t d\tau \sum_{pq} e^{-\eta q^2(t-\tau)} Tr(B_{pq}^\dagger L_I W(\tau))\langle n|L_I e^{-iL_M(t-\tau)} A_{pq}|n\rangle \ . \qquad (7)$$

Equation (7) can be explicitly written as

$$\dot{W}_n = 2\kappa(\frac{1}{z})[(n+1)W_{n+1}-nW_n] + 2\kappa(\frac{1}{z}-1)[nW_{n-1}-(n+1)W_n]$$

$$+ [\frac{\Omega_R}{(\frac{1}{z}-1)^2}]^2 \{\sum_{m=0}^{\infty} W_m(t)[\sum_{p=0}^{m}(\frac{1}{1-z})^p P_p^{(m-p,0)}(2z-1)/(p+1)$$

$$+ \sum_{p=m+1}^{\infty}(-1)^{m+p}(\frac{1}{1-z})^m P_m^{(p-m,0)}(2z-1)/(p+1)]G(n,p)\} \quad , \qquad (8)$$

where $G(n,p) = F(\omega_n^-,t)(1-z)^{n+1}nP_p^{(n-p-1,1)}(2z-1) - F(\omega_n^\dagger,t)(1-z)^{n+2}(n+1)P_p^{(n-p,1)}(2z-1)]$,
$F(\omega_n^\pm,t) = -\left[2\eta/(\eta^2+\omega_n^{\pm 2})\right]\left[e^{-\eta t}(\cos\omega_n^\pm t - (\omega_n^\pm/\eta)\sin\omega_n^\pm t) - 1\right]$;
$\omega_n^- = 2(n-1)\varepsilon - \Delta$, $\omega_n^+ = 2n\varepsilon - \Delta$, $z = (\bar{n}_B+1)^{-1}$, $\bar{n}_B$ is the averaged excitation of the bath, which is dependent on temperature, Δ is the laser detuning with respect to the fundamental frequency of the oscillator, $P_\ell^{(\alpha,\beta)}(x)$ are Jacobi polynomials of the indicative argument, and Ω_R is Rabi frequency.

For the case of low bath temperature, i.e., where the average excitation of bath quantum $\bar{n}_B \ll 1$ and the rate of phase relaxation is much larger than the energy relaxation and the Rabi frequency, i.e., $\eta \gg \kappa$, Ω_R, Eq. (8) can be evaluated by a lengthy but straightforward algebraic calculation. This leads to the following set of coupled differential equations, which takes both the laser coherent excitation and the thermal excitation and relaxation into account:

$$\dot{W}_n = 2\kappa(\bar{n}_B+1)[(n+1)W_{n+1}-nW_n] + 2\kappa\bar{n}_B[nW_{n-1}-(n+1)W_n]$$

$$+ 2\eta\Omega_R^2(t)\{\frac{n(W_n-W_{n-1})}{\eta^2+[2\varepsilon(n-1)-\Delta]^2} + \frac{(n+1)(W_n-W_{n+1})}{\eta^2+(2\varepsilon n-\Delta)^2}\} \quad . \qquad (9)$$

The first two terms of Eq. (9) correspond to low-temperature thermalization processes due to the energy relaxation, which causes the active mode to approach the steady state by sharing its energy with other degrees of freedom. The last two terms correspond to coherent processes due to the laser excitation, where the influence of the bath still cannot be neglected since the phase relaxation parameter η is governed by the bath interaction.

As is already known,[15] the level population distribution of a pure driven harmonic oscillator is a Poisson distribution, i.e., the oscillator has a single degree of freedom with no coupling to the other degrees of freedom and its initial state is coherent. It is further known that the level population distribution of a single driven anharmonic oscillator can also be approximately described by a Poisson distribution.[16] As for a fully statistical thermalized system, i.e., an incoherently driven quantum oscillator, the level population should be in a Planck distribution at a well-defined temperature determined by the total energy deposited in the oscillator.[17] It is hence quite interesting to know how the population distribution looks for an anharmonic vibrator which is coherently driven by a laser field but is subject to (incoherent) energy and phase dissipation.

III. Numerical Results

What kind of dissipative channel is more important in the thermalization processes for molecular multiphoton excitation? To answer this question, we evaluate the vibrational level population of a driven damped anharmonic oscillator subject to both energy and phase relaxation [Eqs. (8) and (9)] and compare it with the Planck distribution and the Poisson distribution having the same average vibration excitation, $\bar{n} = \Sigma_{n=0}^{\infty} nW_n$. We see that when the phase relaxation rate constant η is rather small (i.e., $\eta=5$ in Fig. 1), the population distribution over the vibrational levels of the driven damped anharmonic oscillator (D curve) is markedly different from the Poisson distribution (P curve) and the thermal Planck distribution (T curve). However, if we let the phase relaxation constant become larger, (e.g., $\eta=15$ in Fig. 2), the curves for the driven damped oscillator (D curves) become closer to the thermal distribution curves (T)(see Fig. 2). We also notice that the curves for the driven damped oscillator never behave as a Poisson distribution, hinting that the coherence has been diminished in the excitation due to the existence of the relaxation pathway.

To determine the effect of energy relaxation on the population distribution, we have also computed curves for different values of the energy relaxaton parameter (κ=0.1,0.5,0.9,etc.), but with the other parameters remaining the same as in Fig. 1. Given the resulting constant proximity of the D curve to the fully thermalized T curve, we conclude that energy relaxation has a minor influence on the thermalization of the driven anharmonic oscillator.

IV. Summary

We have used a model for a driven anharmonic oscillator, which is subject to energy and phase dissipation, in order to evaluate thermalization effects in the initial stage of coherent multiphoton excitation. It is shown that the main effect in the thermalization of the vibrational level population in the active mode is due mainly to the dephasing agitation coming from the bath interaction. In a normal situation, the dephasing rate η is very large (η^{-1} is on the order of a picosecond), and it is much larger than the energy relaxation rate κ. To achieve mode-selective chemical reactivity, an ultra-short pulse, i.e., sub-picosecond laser pulse, may be necessary. The mode-selective reaction must take place in the period of the short duration of laser pulse in order to prevent fast dephasing.

Acknowledgments

This research was supported in part by the Office of Naval Research, the National Science Foundation under Grant CHE-8519053, and the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-009. The United States Government is authorized to reproduce and distribute reprints for governental purposes notwithstanding any copyright notation hereon. TFG acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1975-86).

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Figure Captions

1. Level population distribution W_n for: (a) a laser-driven damped anharmonic oscillator (D curve); (b) Poisson distribution (P curve); (c) thermal Planck distribution (T curve). Cases (a)-(c) all have a same averaged excitation energy $\bar{n}$. The parameters needed to calculate the D curve are $(\kappa, \eta, \Omega_R, \epsilon, \Delta) = (0.1, 5, 1.0, 1.5, 3.0)$, where all the rates are in the unit of the transverse relaxation rate.[12] n must be a positive integer, n = 0,1,2,..., and there are no values for W_n between adjacent n.
2. The same as Fig. 1, except η=15.

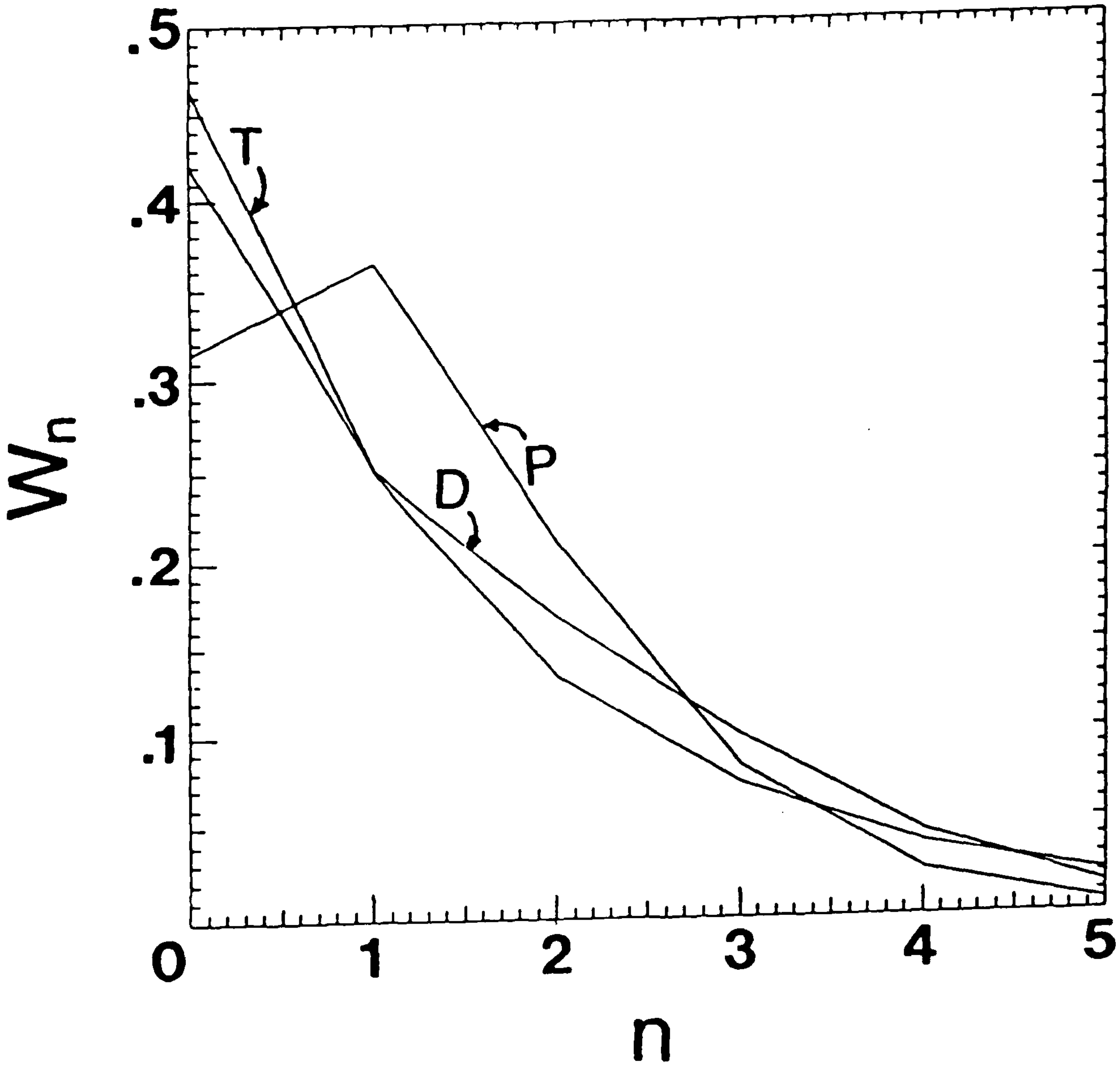

Fig 1

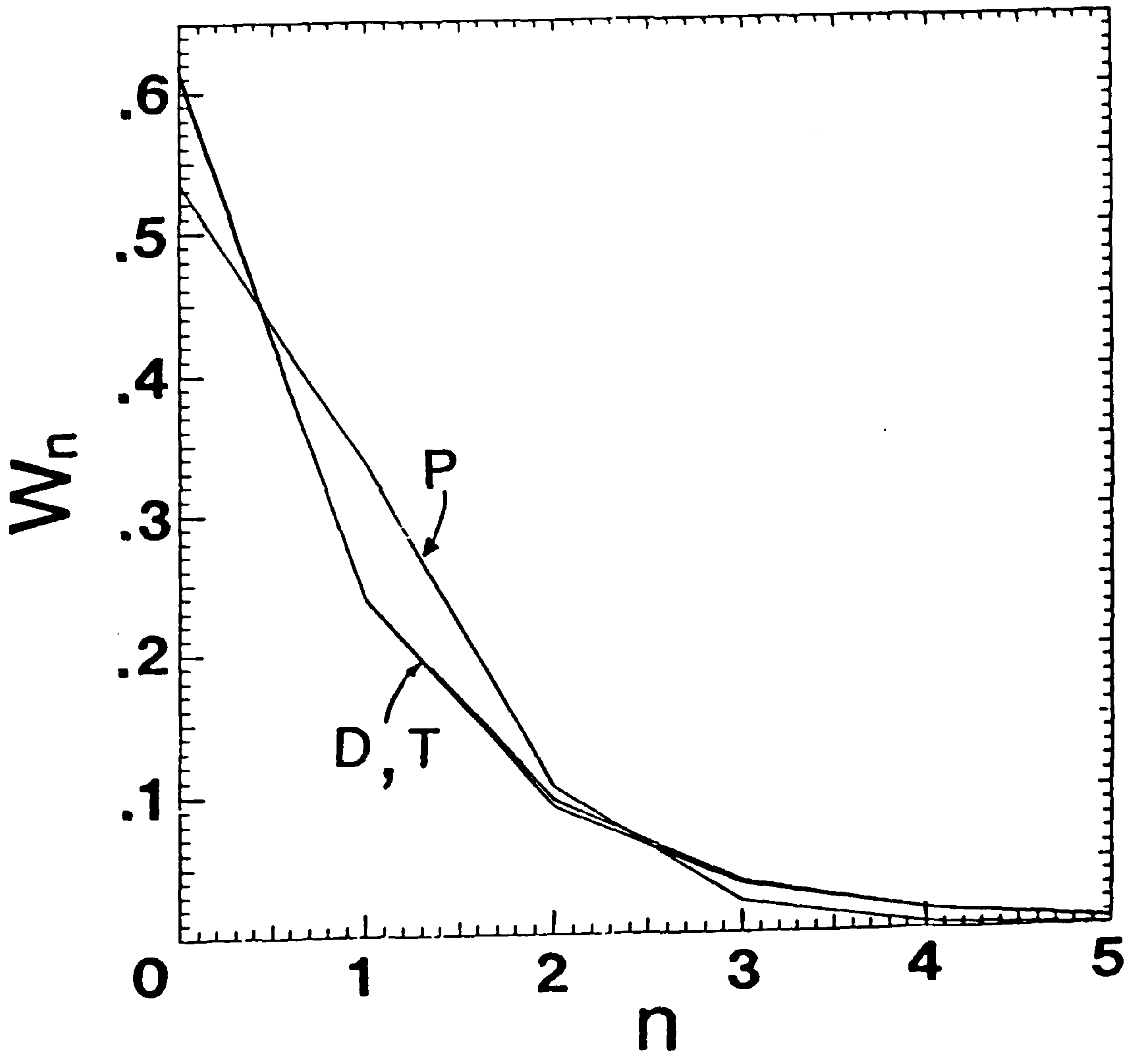

Fig 2