AD-A273 329

PAGE

Form Approved
OMB No. 0704-0188

(2)

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE November 17, 1993	3. REPORT TYPE AND DATES COVERED Technical

4. TITLE AND SUBTITLE

The Photodissociation Dynamics of ICN at 304.67 nm by State-Selective One Dimensional Translational Fragmentation Spectroscopy

5. FUNDING NUMBERS

GRANT N00014-89-J-1350
R&T Code 4131015
Ronald A. De Marco

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research N00014
Chemistry Branch
Arlington, VA 22217

NOV 2 4 1993
E

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

This document has been approved for public release and sale; distribution of this document is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS	15. NUMBER OF PAGES 24
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18

OFFICE OF NAVAL RESEARCH

GRANT N00014-89-J-1350
Ronald A. De Marco

R&T CODE 4131015

Technical Report N. 76

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Prepared for Publication

in the

Journal of Chemical Physics

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November 9, 1993

The Photodissociation Dynamics of ICN at 304.67 nm by State-Selective One Dimensional Translational Fragmentation Spectroscopy

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The photodissociation dynamics of ICN to CN + I ($^2P_{3/2}$) are investigated by state selective one dimensional photofragmentation translation spectroscopy at 304.67 nm. Translational energy release, laboratory anisotropy factors, and energy distributions are obtained from analysis of the velocity and spatial distributions of the photodissociated iodine atoms. Two velocity distributions peaks are deconvoluted which are found to be separated by 2000 cm^{-1}, which is the CN stretching vibration of the CN radical. The high intensity velocity peak is assigned to dissociation to I + CN($X^2\Sigma^+$) in v=0 (channel I), while the weak lower velocity peak is attributed to dissociation to I + CN($X^2\Sigma^+$) in v=1 (channel II). More than 80% of the iodine are produced from channel I and are found to have a relatively small anisotropy parameter, β, that is independent of velocity, suggesting a mixed absorption polarization leading to rapid dissociation. The weak shoulder, representing less than 20% of the photodissociated iodine, is formed via channel II and found to have a β value that decreases with velocity and produces CN with more of the available excess energy appearing in rotation, suggesting longer dissociation time that allows for more energy redistribution prior to dissociation. The dissociation mechanisms involved in these two channels are discussed in terms of these results, the theoretically predicted properties of the $^3\Pi_{0^+}$ and $^3\Pi_1$ surfaces of ICN, our previous conclusion that suggests that ICN bends prior to dissociation via channel II, the laser wavelength used, and curve crossing between the $^3\Pi_{0^+}$ and $^1\Pi_1$ surfaces.

I. Introduction

The photodissociation dynamics of ICN have been extensively studied both experimentally[1-8] and theoretically[9-16]. Interest in this molecule stems from several factors. ICN is a triatomic molecule that has potentially simple dissociation dynamics and whose photofragments can be easily studied using a variety of techniques such as LIF, time-of-flight and Doppler profile spectroscopy. ICN has an absorption region, the A continuum, located between 210-350 nm which is readily accessible by conventional laser systems. In addition, the large spin- orbit coupling of the iodine atom creates a number of interesting problems in the photodissociation dynamics due to possible curve crossings and other non-adiabatic interactions. Overall, the photodissociation of ICN presents a reasonably tractable problem in which to study both dissociation dynamics and the effects of spin-orbit interactions on the photodissociation dynamics.

It is well established[1,7,19,21,24,26] that ICN dissociates via two product channels to form ground state ($^2P_{3/2}$) and excited state ($^2P_{1/2}$) iodine atoms following excitation to ICN's first absorption band, the A continuum (210 nm $\leq \lambda \leq$ 350 nm).

$$ICN + h\nu \rightarrow I^*(^2P_{1/2}) + CN(X^2\Sigma^+) \tag{1}$$

$$ICN + h\nu \rightarrow I(^2P_{3/2}) + CN(X^2\Sigma^+) \tag{2}$$

At wavelengths longer than ≈ 300 nm, energy conservation does not allow the production of $I^*(^2P_{1/2})$. At 266 nm the photofragments are formed from an initial transition that is predominantly parallel in character with a smaller perpendicular component that becomes more important at shorter wavelengths.[6,23-25,27,29] Measurements of CN product distributions in the range of λ = 210 - 350 nm indicate that the CN photofragment in both dissociation channels are formed predominately in the ground electronic state ($X^2\Sigma^+$) and vibrationally cold.[4,20] For example, at 266 nm the CN radical[1,21,28] has > 98% in v=0, while at 308 nm[18] the CN radical is approximately 88% in v=0, 10% in v=1, and 2-3% in v=2. In the dissociation to give excited state iodine atoms, CN fragments are formed rotationally cold, with rotational distributions that peak at low quantum numbers.[1,4-6,19-23,29] In contrast, the channel forming ground state iodine produces rotationally hot CN fragments.[1,4,18,20-22] Initial parent rotation has been shown to be unimportant as a source of CN rotational excitation.[1,19,27]

Black, *et al.*[23] measured the anisotropy parameter (β) at 249 nm and found a complex dependence on CN rotational level. For the ground state I channel, β is negative at low N and positive at high N. For the excited state I channel, β is always positive, ranging from 1.8-1.9 at low N to approximately 1.2 at $N = 35$. Quantum yield measurements indicate that at 266 nm approximately 66% of the iodine atoms are formed in the $I(^2P_{1/2})$ state with decreasing excited state I production at both longer and shorter wavelengths. At 284 nm and 248 nm, Hess and Leone found I* quantum yields of 53.4 ± 2% and 44.0 ± 4%, respectively.[7]

There has been much discussion as to the number, symmetries, geometries, and non-adiabatic interactions of the low lying electronic states of ICN which could explain the observed photodissociation dynamics. It has been proposed[1,7,8,10,11,13,16,23,25-29]that the high rotational excitation observed for CN fragments produced in dissociation to $I(^2P_{3/2}) + CN(X^2\Sigma^+)$ is a result of strong non-adiabatic interaction in the Franck-Condon region between an initially excited linear state correlated with excited state $I^*(^2P_{1/2})$ and a bent excited state correlated with ground state $I(^2P_{3/2})$. However, two state empirical potential energy surfaces proposed by Goldfield, *et al.*[16] successfully predict branching ratios at 266 nm and longer wavelengths but fail at 249 nm. Guo and Schatz[11] utilized Goldfield, *et al.*'s two state potential surfaces with a quantum coupled-channel method and found that the surfaces were not accurate enough to describe the ICN photodissociation dynamics. However, there was qualitative reproduction of I*/I quantum yields, the bimodal rotational distribution, and total cross section.

In order to correct the shortcomings of Goldfield, *et al.*'s two state potential energy surfaces at shorter wavelengths, Black, *et al.*[8] suggest a model involving three interacting potential surfaces. The high value β observed for the $I^*(^2P_{1/2})$ exit channel is close to the limiting value of $\beta = 2$ for a purely parallel transition, and is thus thought to indicate a primarily collinear dissociation on a repulsive surface reached via a parallel initial absorption. The decreasing trend in β is a reflection of an increasing contribution from a perpendicular transition at higher N with subsequent curve crossing to a bent surface correlated with $I^*(^2P_{1/2})$. The $I(^2P_{3/2})$ production also involves a mixed transition . The positive values of β at high N result from an initial parallel transition to the $^3\Pi_{0^+}$ followed by crossing to a state with $\Omega = 2$ symmetry, while the negative values of β at low N result from direct dissociation along a state populated by an initial perpendicular transition, e.g. $^1\Pi_1$

More recent *ab initio* calculations by Yabushita and Morokuma[14] of the low lying electronic states of ICN show that only two electronic states are involved in the A band photodissociation. In contrast to others, the authors report that both surfaces are bent at all geometries, including the Franck-Condon region. The calculations predict a conical intersection between the states with symmetries $\Omega = 0$ ($^3\Pi_{0^+}$) or $\Omega = 1$ ($^1\Pi_1$) located beyond the Franck-Condon region. In addition, they find that the $^3\Pi_{0^+}$ potential energy surface has an attractive well of about 0.45 eV at R_{CI} = 3.22 A. At 266 nm, the initial parallel absorption is from the linear $^1\Sigma_{0^+}$ ground state to a linear excited potential surface with $^3\Pi_{0^+}$ symmetry. The probability of crossing to the $^1\Pi_1$ is governed by the ICN bending angle, θ. Those trajectories with small θ correlate with I* production diabatically, giving CN fragments with low N. Those trajectories with large θ cross to the $^1\Pi_1$ surface to give I and CN fragments with high N. Yabushita and Morokuma propose that there is no need for a third excited state to explain the photodissociation dynamics of ICN at longer wavelengths. Instead, a small perpendicular contribution from excitation to a potential energy surface with $^1\Pi_1$ symmetry becomes more important at shorter wavelengths and results in the observed behavior for the anisotropy factor at 249 nm.

In spite of the wealth of experimental and theoretical work in the literature, the photodissociation dynamics of ICN in the A continuum are not clearly understood. State-selective photofragment translational spectroscopy allows examination of translational energy distributions, anisotropy parameters, and quantum yield for both the $I^*(^2P_{1/2})$ and $I(^2P_{3/2})$ exit channels in the dissociation of ICN. In addition, it is possible to correlate the spatial anisotropy with the recoil velocity of the dissociating fragments[34,40,41] to give information about the dissociation mechanism and the determination of the rate of energy redistribution. Hopefully this will lend some insight into the nature of the ICN excited state potential energy surfaces and their non-adiabatic interactions in the low energy region at an excitation wavelength of 304.67 nm.

III. Experimental

The experimental method and apparatus are described in detail elsewhere.[30] Briefly, gaseous ICN molecules from an effusive beam are photodissociated by linearly polarized nanosecond laser pulses to produce cyanogen and iodine radicals. Photodissociation experiments are performed at polarizations parallel and perpendicular to the detection axis i.e., polarization angles of a = 0° and a = 90°, respectively. For the 304 nm dissociation experiments, the iodine atoms are produced in either the ground or spin orbit excited states and are state-selectively ionized within the same pulse (304.67 or 304.02 nm for I and I*, respectively). The iodine ions are then allowed to move in a field free region for a delay time τ of 1.5 μs. During the delay time the photoions spread out from their initial positions with the same velocities as the recoil velocity of their respective atoms since the electron carries the excess photon energy above ionization threshold. The photoions are accelerated by applying a pulsed acceleration voltage of approximately -1500 volts for 1 μs to an extraction electrode in a home built time-of-flight mass spectrometer (TOF-MS). In addition to propelling the ions to the detector, the acceleration increases the kinetic energy of the photoions which in turn is used to amplify the signal at the detector and enhances detection sensitivity. The ions travel across a second field free region to a discrimination pinhole 6.00 mm in diameter placed on the detection axis. When the acceleration field is applied, the ions acquire new velocities dependent on their initial position in the extraction region. Consequently, the arrival time of a photoion at the detector is directly related to its recoil velocity component along the detection axis (a line connecting the laser focus and the center of the discrimination pinhole). The pinhole eliminates ions that have a large component of velocity perpendicular to the detection axis (greater than 120 m/s), and thus permits detection of only those ions that are aligned along the detection axis. Typical TOF spectra consist of two peaks, with the negative velocity peak corresponding to the photoions with their initial recoil direction towards the detector and the positive velocity peak corresponding to the photoions with their initial recoil direction away from the detector.

ICN was obtained from Sigma and used without further purification. Prior to use the sample underwent several freeze-pump-thaw cycles to remove lower vapor pressure contaminant molecules. Experiments were performed at pressures on the order of 1.0×10^{-6} torr and laser power of 15-25 mJ/pulse. To ensure that there was no significant multiphoton processes occurring, experiments were performed with similar laser power at wavelengths slightly off resonance from the I and I* resonance adsorption wavelengths of 304.67 and 304.02 nm, respectively. No multiphoton dissociation was observed.

IV. Results and discussion

a. Translational energy distribution

The translational energy distribution for production of $I(^2P_{3/2})$ at 304 nm is shown in Figure 1. The peaks at negative and positive velocities correspond to iodine atoms whose initial recoil velocity were towards and away from the detector, respectively. For a one photon electric dipole transition it has been shown that the lab recoil velocity distribution can be related to the center of mass distribution[31,36] by

$$f(v,\theta) = (4\pi)^{-1} [1 + \beta(v) P_2(\cos\theta)]\, g(v) \qquad (3)$$

where $f(v,\theta)$ is the lab. recoil velocity distribution, θ is the lab recoil angle with respect to the electric vector of the photon, $P_2(\cos\theta)$ is the second order Legendre polynomial, $g(v)$ is the recoil speed distribution, and $\beta(v)$ is the anisotropy parameter as a function of velocity. Both $g(v)$ and $\beta(v)$ are shown in Figure 2.

It appears that there are two overlapping $I(^2P_{3/2})$ peaks, as evidenced by the non-symmetrical character of the recoil speed distribution of Figure 2. The two overlapping peaks were deconvoluted assuming that the higher velocity peak is symmetric with respect to its high velocity side. The resulting deconvoluted peaks for the lower and higher velocity distributions are shown in Figure 3. The lower velocity distribution peak is broader than the higher velocity peak by a factor of about 2.1. ΔE between the two peaks is ≈ 5.7 ± 0.2 kcal/mol (i.e. 2.0 x 10^3 cm^{-1}). Using the relation for CN vibrational levels of the CN radical:

$$E_{vib} = (2071.16v - 13.82v^2)\ cm^{-1} \tag{4}$$

ΔE for v=0 to v=1 transition is found to be 2056.66 cm^{-1}. Thus, it is possible that the two peaks in the deconvoluted spectrum correspond to production of I + CN in v=0 (channel I) and v=1 (channel II), with the peak at lower velocity corresponding to channel II. It is known that at 308 nm the CN radical from ICN dissociation is produced 87% in v=0 state and 10% in v=1. At 299 nm this distribution changes slightly to 91% in v=0 and 9% in v=1. From the deconvolution it appears that approximately 80% of the CN radicals are in v=0.

The separation into v=0 and v=1 allows examination of c.m. translational energy of both product states independently. The total energy available, E_{avl}, for translation (E_t) or internal excitation (E_{int}) is given by

$$E_{avl} = h\nu - D_0{}^0(\text{I-CN}) + E^p{}_{int} = E_t + E_{int} = E_t + E_{vib} + E_{rot} \tag{5}$$

where hν = 94 kcal/mol, $D_0{}^0$(I-CN) = 74 kcal/mol[32], and $E^p{}_{int}$ = 1.2 kcal/mol.[33] It should be noted that this is assuming that ICN is initially in the v=0 state. If dissociation is occurring from vibrationally excited states then E_{avl} will be slightly higher by ~ kT = 0.6 kcal/mol. $\langle E_t \rangle$ for v=0 and v=1 are obtained from the recoil velocity distributions, $g_{v=0}(v)$ and $g_{v=1}(v)$, transformed into the energy domain using conservation of momentum

$$\langle E_t \rangle = \frac{m_I\,(m_I + m_{CN})\,\langle v \rangle^2}{2m_{CN}} \tag{6}$$

where m_I and m_{CN} are the mass of the iodine atom and CN radical, respectively. It is possible to calculate the amount of energy that goes into the CN rotation (E_{rot}) from the relation

$$\langle E_{int} \rangle = \langle E_{rot} \rangle + E_{vib} \tag{7}$$

where E_{vib} is the vibrational energy of the CN in the v=0 or v=1 vibration level. Dissociation via channel I gives $\langle E_{rot} \rangle$ = 3.3 kcal/mol, while via channel II $\langle E_{rot} \rangle$ this increases to 3.7 kcal/mol.

From equation (5) above, one can write:

$$E_{avl} - E_{vib} = (h\nu - D_0{}^0(\text{I-CN}) + E^P{}_{int}) - E_{vib} = E_t + E_{rot} = E_{avl(rot)} \qquad (8)$$

then $<E_{rot}>/E_{avl(rot)}$ is 17% for channel I and 28% for channel II. This agrees well with the results reported by Fisher, *et al.*[18] at 308 nm where $<E_{rot}>/E_{avl(rot)} = 18\%$ for v=0 and 30% for v=1. This supports our assignment of the observed two peaks for I resulting from dissociation to the CN in the v=0 and v=1 levels. It further confirms the conclusion that the dissociation leading to vibrationally hot CN leads to more rotational energy as well.

The above assignment of the two distributions to channel I and II is not completely unambiguous. The v=0 rotational distribution is not exactly symmetric[18] as is clearly shown in Figure 10 of reference 18, which plots the relative rotational population as a function of E_{int} (E_{rot} + E_{vib}) and evidences a shoulder at approximately 1800cm^{-1} higher internal energy than the peak maximum. Thus it is possible that the lower velocity (higher internal energy) distribution is in fact this shoulder of the v=0 rotational distribution. However, the agreement of the separation with CN vibration frequency, the agreement between our calculated % of available energy that goes into rotation for the v=0 and v=1 with those obtained by Fisher, *et al.*[18] using a different technique, and the moderate agreement of the relative intensity of the iodine produced from channel I and II with the previously determined branching ratio determined by a quite different method all support our assignment.

b. Anisotropy parameter and dissociation time

Deconvolution of the recoil velocity distribution g(v) allows examination of the anisotropy parameter β(v) for both v=0 and v=1 distributions. The anisotropy parameter is deconvoluted taking into account the anisotropic broadening of the distribution to the low velocity side resulting from thermal velocity of the parent molecule.[34] $\beta_{v=0}(v)$ for v=0 can be found using the following relation

$$\beta_{v=0}(v) = \frac{g(v)\beta(v) - g_{v=1}(v)\beta_{v=1}(v)}{g(v) - g_{v=1}(v)} \qquad (9)$$

where $g(v)$ and $\beta(v)$ are the experimental speed distribution and anisotropy parameter and $g_{v=0}(v)$ and $\beta_{v=0}(v)$ are for the v=0 distribution. The results of this deconvolution are shown in Figure 3.

1) Photodissociation via channel I (I + CN (v=0)):

The observed anisotropy parameter (β) of ICN dissociation at 304 nm exhibits interesting behavior. For the dissociation via channel I, $\beta(v)$ is constant at approximate value of 1.2 This is comparable to the value of β = 1.2 reported for the 266 nm dissociation of ICN for the ground state I channel. Houston, *et al.*[35] showed that a decrease from the limiting value of $\beta = 2$ for a purely parallel transition in ICN cannot be attributed solely to parent rotation prior to dissociation or the molecule bending prior to or during dissociation. Instead, the drop is assigned to a mixed parallel and perpendicular character of the excitation (absorption) process Our results support this conclusion, since $\beta(v)$ for v=0 does not change with velocity, i.e. it is time independent.

The relative contributions of the parallel and perpendicular transitions to the mixed transition producing CN via channel I can be calculated using the following relation

$$\beta = X_{\parallel}\beta_{\parallel} + X_{\perp}\beta_{\perp} \qquad (10)$$

where $X_{\parallel}$ and $X_{\perp}$ are the fractional contributions of the parallel and perpendicular transitions, respectively. It is necessary to know $\beta_{\parallel}$ and $\beta_{\perp}$. For a purely parallel transition ($\beta_{\parallel} < \beta_{cm,\parallel} < 2$) $\beta_{\parallel}$ is taken[34] as 1.63. This value is the limiting value of β found in our apparatus.[34] Assuming a similar decrease in β for $\beta_{\perp}$ gives $\beta_{\perp} \approx 0.8$–$0.9$. Thus, for absorption leading to CN with v=0, the transition has approximately 85% parallel and 15% perpendicular character. This result is a lower limit for the amount of parallel character as it assumes no depolarization due to rotation or bending of the excited state molecule prior to dissociation.

Since the photodissociation time of ICN via this channel is faster than its rotation time, one cannot clock its rate of energy redistribution into the bending motion which appears as CN (v=0) rotation excitation. Thus the width of the iodine translation energy spectrum formed via channel I is a reflection of the extent of energy redistribution prior to dissociation via this rapid channel.

Actually, the width divided by the dissociation time should be related to the rate of energy redistribution via this channel.

*2. Photodissociation via channel II (I + CN(*v*=1)):*

For channel II, there is a significant correlation between the observed value of β for the iodine produced and the observed recoil velocity as can be seen in Figure 3. $\beta(v)$ ranges from 0.1 to 1.0. This suggests that the energy redistribution time which is related to β is comparable to both the dissociation time and the molecular rotation or excited state distortion. The depolarization of the spatial distribution (i.e. the decrease of β) with dissociation time of channel II is either due to molecular rotation or due to loss of the linear structure of ICN during or prior to dissociation. Each of these limits is investigated below.

i) <u>*Rotational depolarization:*</u> Yang and Bersohn[36] have shown the relation between the orientation of the transition dipole moment and the dissociation direction. In this model, the dependence of the anisotropy parameter on the average dissociation lifetime (τ^*) of the molecule is determined through use of the molecular rotational correlation function. For the dissociation of ICN via channel II (to CN (v=1)) the dependence of β on velocity implies that for each β there is a unique excited state lifetime (dissociation time). Thus, the average value used by Yang and Bersohn[36] over excited state lifetimes (t^*) to give the average dissociation time (τ^*) is omitted for our case[40]. The observed value of β/β_0 (where β_0 is the rotationally undepolarized value, i.e. for rapid dissociation prior to rotation) reflects the extent of the change of the dissociation axes from the initial laboratory excitation axis. Obviously this depends on the time $t^* = t/\tau$ (scaled by the molecular rotation time $\tau = (I/kT)^{1/2}$, where I is the moment of inertia) that has elapsed between excitation and dissociation. $(\beta/\beta_0)_{t^*}$ is related to the time dependent rotation correlation function[36] $<D_{00}(t^*)>$ averaged (over the initial rotation configuration) as follows.

$$\beta(t^*)/\beta_0 = <D_{00}(t^*)> \qquad (11)$$

$<D_{00}(t^*)>$ vs. t^* for ICN is shown in Figure 4.

The β_0 used is = 1.2, the limiting value of β for the prompt dissociation channel of ICN at 304 nm. This value for β_0 thus takes into account any electronic depolarization effects on β. Further depolarization of β below 1.2 can be due to molecular processes occurring prior to photodissociation after the initial excitation, rotation of the parent molecule during dissociation, or bending of the molecule. From the limits on v for the v=1 peak and Fig. 3, an estimate of the range of dissociation times for v=1 is found to be 100-500 fs greater than that for the v=0 channel. Converting $\beta(v)$ to $\beta(E_t)$ through the following relation

$$E_t = \frac{(mv^2)\, m_r}{2m_p} \tag{12}$$

where m_r and m_p are the masses of the CN radical and ICN parent molecules, the range of E_t for β = 1.0 to 0.1 can be found, giving dE_t/dt = 34 kcal/ps. This suggests that the time to transfer 2000 cm^{-1} into the CN vibration would require ~ 0.18 ps, which is comparable to the CN vibration period. This implies the absence of a barrier to the conversion of electronic to vibrational energy in the excited state. Molecules that have longer dissociation times are capable of converting more of the electronic energy into the bending mode, which has a larger projection on the dissociative coordinate and results in more rotational excitation of the produced CN radical.

ii) Depolarization due to bending excitation and the structure of the transition state in channel II dissociation: The depolarization of β observed for the v=1 channel could be due to bending distortion of the I-CN bond prior to dissociation, leading to both rotational excitation of the CN product and a new recoil direction of the photofragments. The bending motion results in a recoil direction for the iodine radical that is at an angle θ to the original ICN axis as defined by the polarization of the absorbed light. There are a number of reasons to believe that this is actually the cause of the observed change of β of the iodine atoms formed in this channel: 1) Theoretically it has been predicted that ICN is bent in the excited state[14]; 2) in order to transfer energy from the excess available energy to CN vibration, the dissociation time for this channel is expected to be longer, thus allowing for the excited state to sample it minimum; 3) our recent work[42] has shown that the calculated deviation from ICN linearity required to account for the observed value of β at the maximum of the I signal produced in channel II (38°) is similar to that needed to give the CN (v=1) radical its observed rotation energy by use of the impulsive model (36°). All these facts suggest that the iodine atoms produced in this channel are formed from excited ICN molecules that live sufficiently long to allow sampling of its bent equilibrium configuration. During such time, vibration excitation of the CN group takes place, leading to dissociation with the CN radical in v=1 and a larger fraction of the excess energy being deposited in its rotation (0.28 compared to 0.17 for the CN produced in channel I)

c. Discussion of the Dissociation Dynamics:

The important results regarding the photodissociation of ICN at 304.67 nm, which can only produce iodine in the ground electronic state, can be summarized as follows:

i) Photodissociation via channel I: Over 80% of the molecules dissociate through this channel(s). Since β is small, over 85% of these (i.e. > 68% of the absorbing molecules) have parallel absorption, i.e. could involve the $^3\Pi_{0+} \leftarrow X^1\Sigma$ transition.[14] In order to produce I in the $^2P_{3/2}$ state, crossing to the $^1\Pi_1$ state should occur prior to dissociation. The other 12% of the absorbing molecules that lead to CN in v=0 excite a $\perp$ transition, e.g. the $^3\Pi_1$ surface. According to the latest calculations of the energy surfaces by Yabushita and Morokuma[14], only molecules that are in higher vibration (I-CN bending) and rotational levels will be able to reach these levels via the absorption of 304.67 nm photons. Furthermore, since the ground state surface is very shallow along the carbon-iodine coordinate, molecules with a slight stretched I-C bond (by 0.07 A) could yield vertical absorption to the $^3\Pi_1$ surface and slightly more (i.e. by 0.13 A) would reach the $^3\Pi_0{}^+$ surface by photon absorption at 304.67 nm. This would suggest that the population that could absorb and reach the $^3\Pi_{0+}$ surface is smaller, not larger, than that absorbing to the $^3\Pi_1$ surface. However, the $^3\Pi_{0+}$ has an energy minimum at a longer C-I distance than the ground state equilibrium distance. This would increase the Franck-Condon factors, and thus the absorption probability, for molecules with more "stretched" C-I bond. This, together with the fact that the electronic transition probability to the $^3\Pi_0{}^+$ is much larger than to the $^3\Pi_1$ state, makes it possible for more molecules to reach the ${}^3\Pi_0{}^+$ surface by absorbing the 304.67 nm laser photon than the ${}^3\Pi_1$ surface. In absolute numbers, this might not make for very large numbers of molecules, however, laser ionization or LIF detection is sufficiently sensitive to make it possible to observe dissociation via this channels.

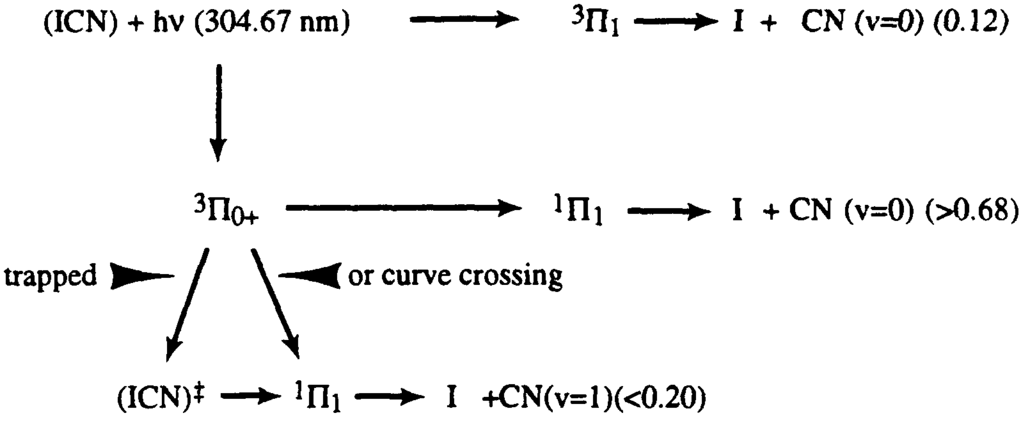
In summary, over 68% of the ICN molecules give I + CN (v=0) by absorption to the ${}^3\Pi_{0+}$ (n,σ^*) state and then curve crossing rapidly to the ${}^1\Pi_1$ surface (which correlates with the I(${}^2P_{3/2}$)). 12% of the molecules give I + CN (v=0) by absorption and rapid dissociation along the ${}^3\Pi_1$ surface. ICN molecules with either stretched C-I bond and/or rotationally and vibrationally hot (along the I-CN bending coordinate) can reach the excited state surface by photon absorption at 304.67 nm. Since ICN is bent in the excited states[14], vibrationally hot molecules are expected to absorb better due to the more favorable Franck-Condon factors.

ii) *Photodissociation via channel II:* The correlation between β and the recoil velocity of the iodine formed via this channel suggests that the dissociation time is comparable to the energy redistribution and molecular rotation times or the I-CN bending vibrational period (or both). This suggests that this channel has either a longer dissociation time or a faster energy redistribution rate compared to that producing CN in the v=0 level. The latest theoretical calculations[14] suggest that the ${}^3\Pi_{0+}$ state has a shallow minimum and curve crosses the ${}^1\Pi_1$ surface at a C-I distance longer than the ground state equilibrium distance.

An attractive proposal for the dissociation mechanism for this channel involves absorption to the ${}^3\Pi_{0+}$ state. In order to account for a longer dissociation time, it is possible that a small fraction of the molecules absorbing to this surface get trapped in its minimum for a time necessary to transfer some of the excess energy into C-N stretching. This trapping would also allow for the excited state to sample the ICN distorted equilibrium configuration[42]. Upon dissociation, these distorted molecules give CN in v=1 and more of the available energy appears as rotation (as the ICN bending motion goes into CN rotation upon dissociation).

If, however, the dissociation time remains unchanged but the rate of energy redistribution is enhanced, one may blame this on the curve crossing process between the $^3\Pi_0{}^+$ and $^1\Pi_1$ surfaces. It is possible that as the excited ICN molecule crosses from one surface to the other, a quarter of the molecules succeed in converting their electronic energy into CN stretching and ICN bending vibrations. Hwang and El-Sayed[34] have shown that curve crossing between the corresponding surfaces in C_2F_5I indeed results in an enhancement of energy redistribution. In order to distinguish between these two mechanisms, a femtosecond laser experiment is required. The population of the produced CN radical in v=1 should show oscillation with delay time between photolysis and the CN detection if the trapping mechanism is correct but not if the curve crossing enhancement mechanism is correct.

In summary, the overall possible mechanisms giving rise to the observed iodine produced by absorption of 304.67 nm radiation in our experiment are:



The $(ICN)^\ddagger$ species is electronically and vibrationally excited. The vibrational excitation occurs either at curve crossing or by being trapped within the minimum of the $^3\Pi_{0+}$ state.

There are a few observations that might support the above proposed mechanism. If a laser of longer[18,19] or shorter wavelength[1,21,28] is used, the channel producing the CN in v=1 becomes less probable. Absorption at 266 nm is known to excite the $^3\Pi_{0+}$ state. However, with more excess energy, the time spent either at the minimum or in the curve crossing region is greatly reduced due to an increased velocity of the dissociating I and CN parts of the molecules as the excited ICN molecule changes on the $^3\Pi_0{}^+$ repulsive surface. This would decrease the probability of converting electronic into vibration energy for the excited ICN molecules in the $^3\Pi_0{}^+$ state. Absorption at $\lambda > 304.67$ nm. does not lead to the excitation of the $^3\Pi_{0+}$ surface and thus cannot lead to the conversion of electronic into vibration excitation.

Acknowledgments: Jennnifer A. Griffiths wishes to thank Dr. Hyun Jin Hwang and Dr. John Freitas for their assistance. The financial support of the Office of Naval Research is greatly appreciated.

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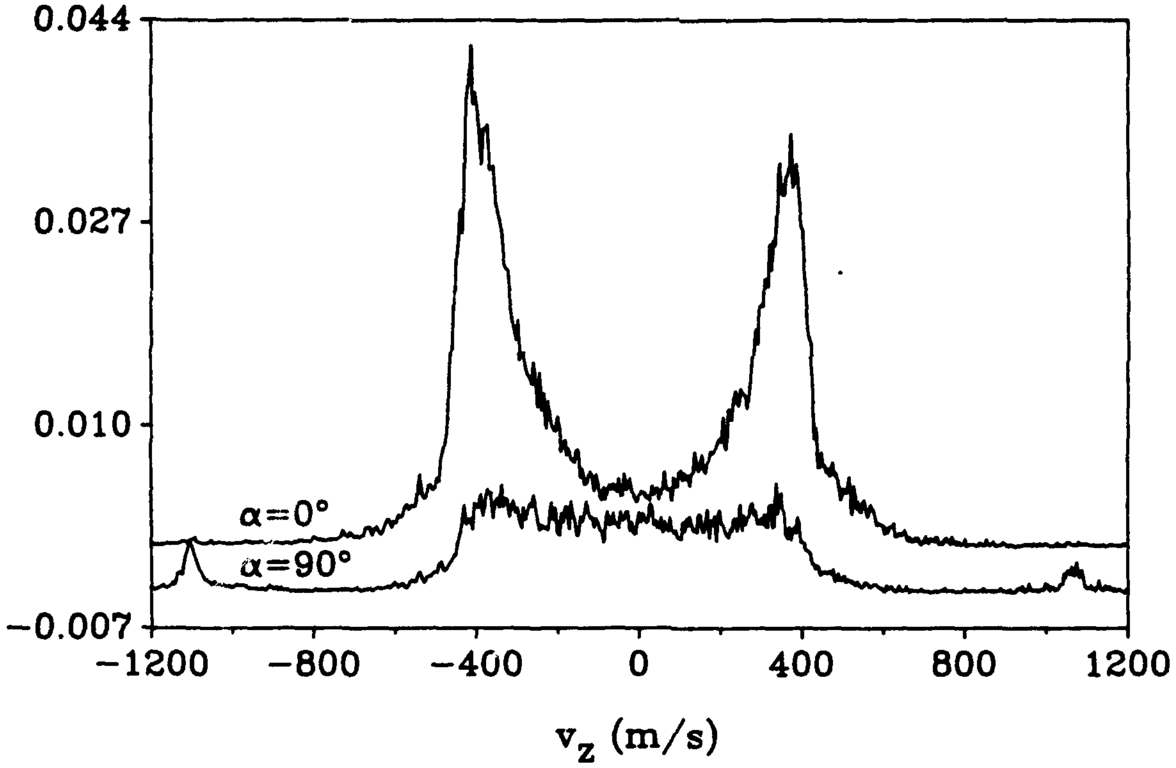
Figure 1. The experimentally measured one dimensional recoil velocity distributions of resonantly ionized iodine atoms produced in the photodissociation of ICN at 304.67 nm with incident laser polarization at an angle $\alpha = 0°$ (top) or 90° to the detection axis. The positive and negative energy peaks correspond to molecules whose initial recoil velocity is either away from or towards the detector, respectively.

Figure 2. The undeconvoluted recoil speed distribution, g(v), and anisotropy parameter, $\beta(v)$, for the dissociation of ICN at 304.67 nm. The non symmetrical nature with broadening to the lower velocity side of the g(v) distribution and the decrease in $\beta(v)$ with velocity suggest that there are two overlapping peaks and thus two different dissociation channels for ICN at this wavelength.

Figure 3. The deconvoluted recoil speed distribution and anisotropy parameter obtained from the full distribution shown in Figure 2. The higher velocity g(v) peak is assigned to dissociation of ICN to give the CN radical in v=0, while the lower velocity g(v) peak is assigned to dissociation to CN in v=1. Note that $\beta_{v=0}(v)$ is independent of velocity, while $\beta_{v=1}(v)$ shows a strong change with velocity, indicating that the dissociation time is comparable to energy distribution and rotation or ICN bending vibration times for this channel producing CN in the v=1 level. This correlation allows for the estimation of the time it takes for the electronic excitation energy of ICN to be transferred to vibrational and rotational modes of the CN photofragment prior to dissociation.

Figure 4. The time dependent rotational correlation function, $\langle D_{00}(t^*)\rangle$, vs time, t^*, for linear ICN molecule. t^* is the time scaled by the ICN rotation period, i.e. $t^* = t(I/kT)^{-1/2}$, where I is the moment of inertia of ICN around the axis perpendicular to the figure axis of the symmetric top molecule, k is the Boltzman constant, and T is the temperature of the parent molecule. Using this figure and the relation $\langle D_{00}(t^*)\rangle = \beta/\beta_0$, one can transform v vs. β into energy release vs. time, from which the rate of energy distribution can be determined assuming that rotation is responsible for the decrease in β with v.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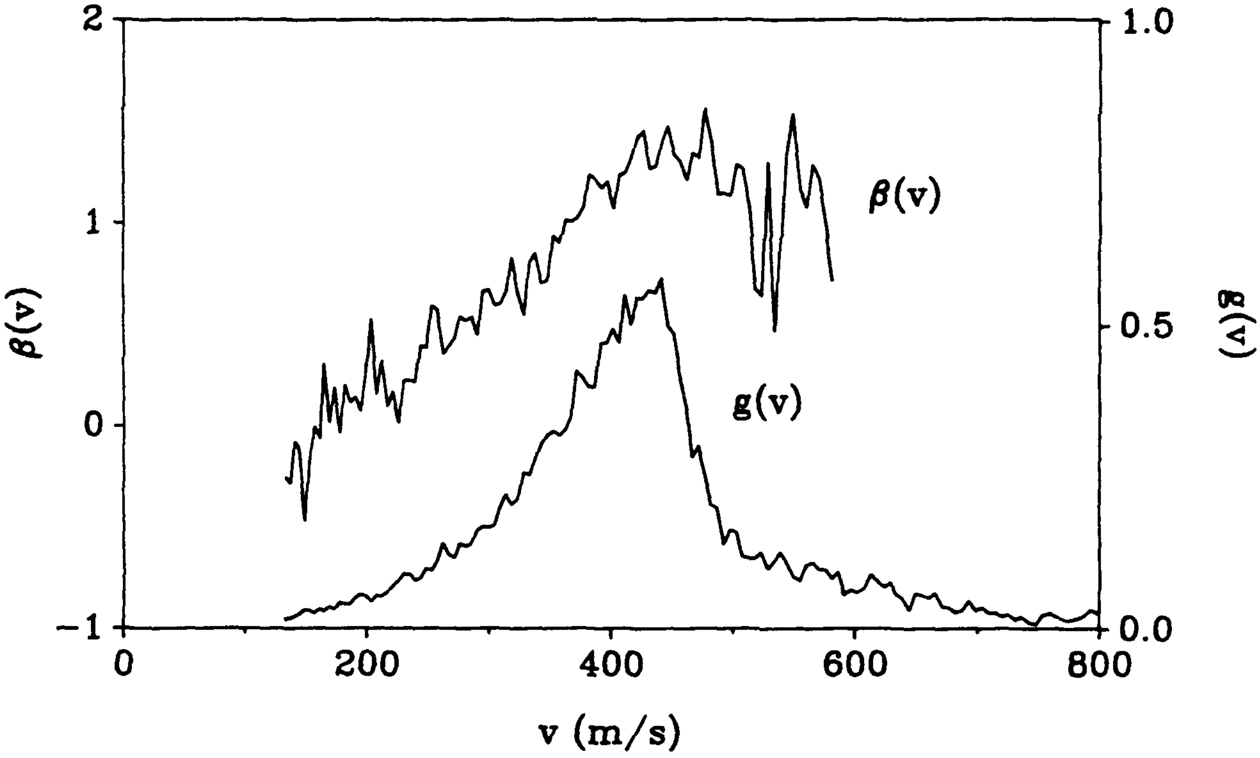
v_z (m/s)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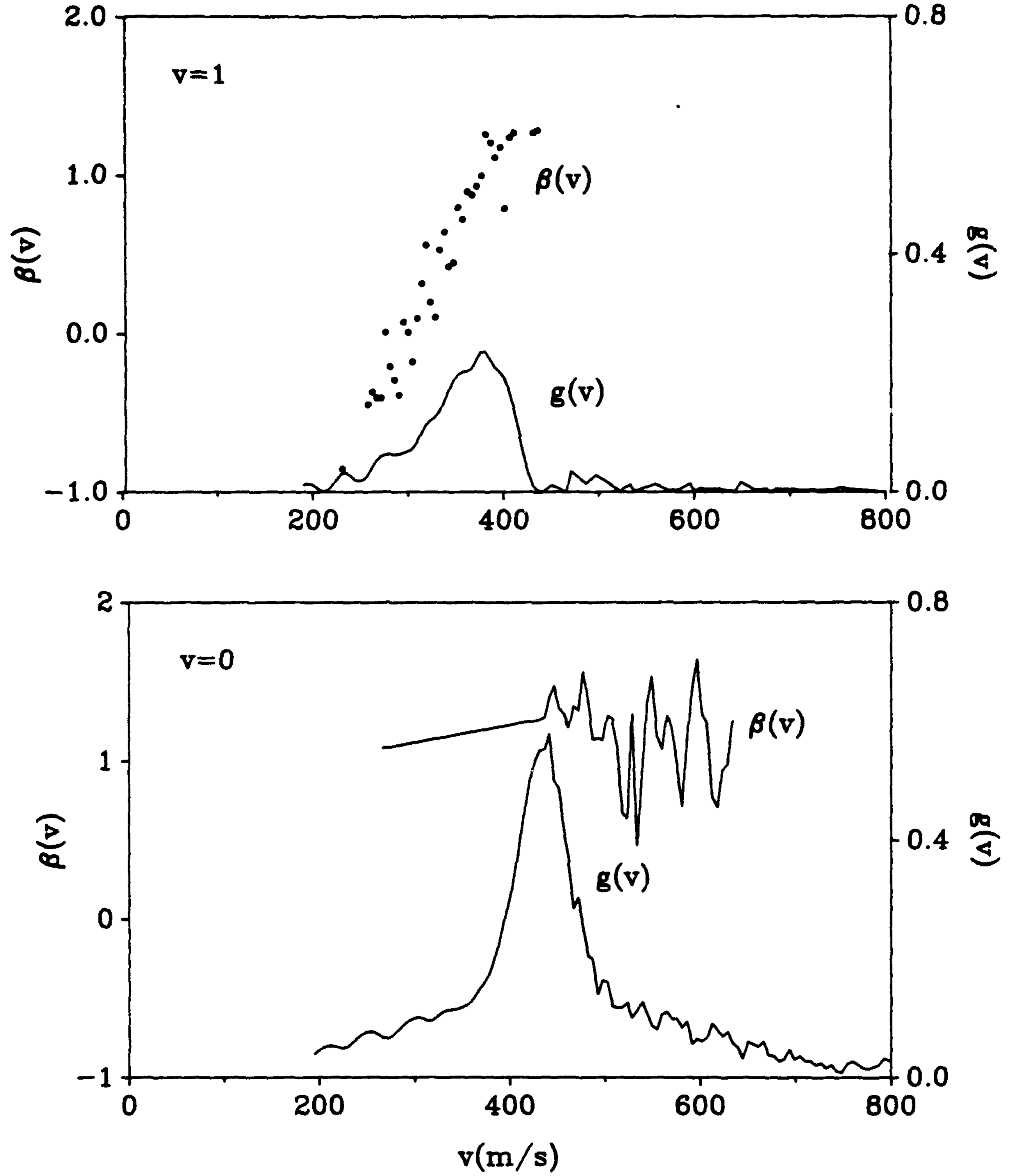
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β(v)
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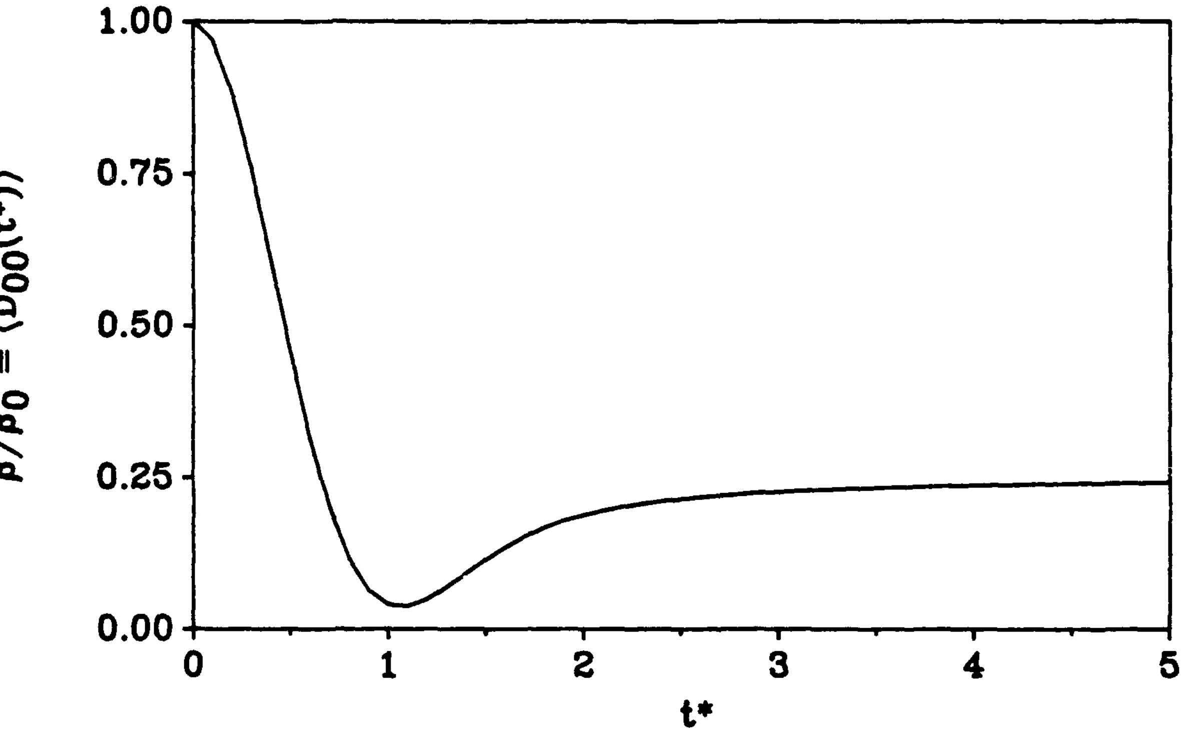
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2
3
4
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$\beta/\beta_0 = \langle D^2_{00}(t^*) \rangle$
t*