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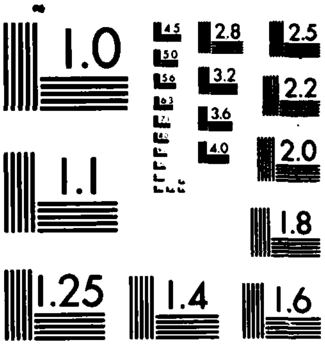

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FRAGMENTATION DYNAMICS OF SMALL MOLECULES UNDER NONLINEAR SHORT-PULSE UV EXCITATION IN THE GAS PHASE

December 1985

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Picosecond excitation and subnanosecond time resolution were used to distinguish prompt and delayed emission in the CN B bands from compounds XCN (X=Cl, CN, CH_3). The prompt component originates from unimolecular dissociation of excited valence states of ClCN and $(CN)_2$. From a detailed kinetic analysis of the dependence of CN B emission on initial pressure, the existence of a long-lived (ca. 24-136 ns) precursor (probably vibronically excited positive parent ions) has been postulated. Ion-molecule collisions appear essential for the delayed formation of CN B. The kinetic studies, in toto, have yielded a comprehensive mechanistic picture of the molecular processes subsequent to the impulse excitation and have emphasized the importance of ion-molecule collisional processes. [illegible]

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1. Summary of Progress

Various small organic molecules under nonlinear short-pulse UV excitation (25 ps, 266 nm) yield a variety of emissive diatomic fragments such as CN $B^2\Sigma^+$, C_2 $d^3\Pi g$, CH $C^2\Sigma^+$, CH $A^2\Delta$, NH $A^3\Pi$ etc. Two distinct formation channels have been observed for the emissive fragments: prompt and delayed. The prompt component is associated with unimolecular fragmentation from excited molecular states lying below the first ionization limit of the parent molecule. Absorption of further photons may compete with this unimolecular fragmentation channel and lead to the formation of excited parent ions distributed over different vibrational levels. We attribute the protracted formation process of emissive diatomics to the fragmentation of the excited parent ion following its collision with neutral parent molecules. A list of the various molecules, which yield different emissive fragments under nonlinear UV excitation, is displayed in Figure 1. The employment of short-pulse (25 ps) excitation with subnanosecond detection provides the time definition/resolution essential for exploring the temporal development of the emissive fragment population.

While two distinct CN B formation channels (prompt and delayed) have been identified for ClCN and C_2N_2, CH_3CN exhibits only the delayed channel of CN B production. The prompt component of CN B production is associated with unimolecular dissociation at the 2 hν (9.32 eV) level [1]. We have shown [2] that fragmentation attending ion-molecule collisions is the mechanistic process for the delayed CN B formation. In addition, at high pressures (> 7 Torr), there exists a persistent minor channel of CN B production which is attributed to the collisional transfer from CN A state.

A prompt CH C formation channel with an instrumentally-limited rate of growth has been recognized for ethane, ethylene, and acetylene. For methane, it has been inferred that CH C is formed via a metastable precursor, which may also be an ion.

2. Research Objective

The object of this research is to develop an overall picture of the molecular processes following initial energetic nonlinear UV excitation. This has been achieved through detailed temporal studies following picosecond gas phase photolysis of structurally related small molecules. The effect of intermolecular processes on precursor species is explored through the change of kinetics with pressure. The use of short-pulse excitation with a high photon fluence (10^{30} cm^2 s^{-1}) and subnanosecond detection of the emissive fragments have enabled us to study the nature and the kinetics of the species produced after initial nonlinear excitation. Such studies have provided kinetic information in the area of picosecond gas phase photolysis which was previously largely devoid of temporal information.

In our work with isotopically labeled CH_3CN, rapid bond reorganization and skeletal rearrangement within the highly excited intermediate were recognized [3]. Our results [2] from various XCN (X = Cl, CN and CH_3) compounds have been interpreted in terms of ion-molecule collisional fragmentation.

3. Status of the Research

We have studied the pressure dependence of CN B fragment formation [4] from ClCN and C_2N_2 as an extension of our earlier work on CH_3CN [3]. These studies have addressed the following issues: the role of ion-molecule reactions in the fragmentation process, the commonality of long-lived precursors in the nonlinear UV fragmentation of cyano compounds, and the competition between fragmentation at the 2 hν level and further excitation to states above the first ionization limit. We have also witnessed a persistent minor channel of CN B formation from CH_3CN at higher pressure.

It has been shown that the CN A state feeds this CN B population via collisional transfer.

3.a. The Effect of Collision upon CN A, B and X States

At low pressure (< 7 Torr) and low pulse energy (< 5 mJ), the nonlinear UV excitation of CH_3CN produces an emissive CN B population which exhibits a simple biexponential time profile with two distinct features: growth and decay. The CN B emission kinetics is well represented by a simple biexponential form incorporating a growth rate constant (k_1) and a decay rate constant (k_2):

$$I(t) = [k_1k_2/(k_1-k_2)][\exp(-k_2t)-\exp(-k_1t)] \text{-----} \quad (1)$$

The CN B time history exhibits a minor component of protracted emission, at a level of ca. 3 to 5% of the major peak. This minor secondary channel of CN B formation experiences a significant enhancement at high pressure (> 7 Torr) and at high pulse energy (> 5 mJ). This causes the resultant CN B waveform to depart strongly from any biexponential fit. The dependence of UV pulse energy on the CN B waveform is displayed in Figure 2; an examination of Figure 2 reveals that the waveforms exhibit an additional channel of CN B formation at higher pulse energies. This late term component of CN B becomes the major channel of formation at higher pressure (ca. 20 Torr) and higher pulse energies (ca. 6 mJ) as shown in Figure 3. A model curve with k_1 and k_2 values extrapolated from the pressure (< 10 Torr) plots in Ref. 5 has also been included in Figure 3. Obviously, the fast component can be attributed to the dominant low-pressure fragmentation channel (discussed below in Sect. 3.b) which is identified with the collisional ion-molecule reaction. The formation time of this channel is ca. 1.2 ns at 20 Torr. Consequently, the risetime of the waveforms in Figure 3 is essentially instrumentally-limited.

It has been suggested that the CN A state (lifetime 3-7 μs) [6] may account [7] for a slowly decaying population of CN B. Parallel production of CN A and CN B during the VUV photolysis of the cyano compounds has been previously reported [7,8]. Collisionally-induced internal conversion is thought to occur between near isoenergetic levels [9]:

$$\mathrm{CN}\ (A)_{v'\geq 10,k'} + M \rightarrow \mathrm{CN}(B)_{v\geq 0,k} \text{---------------} \quad (2)$$

Thus we initiated a careful search for the low level CN A emission around 600-900 nm. A detailed examination of the A state risetime was not feasible due to a poor signal/noise ratio. The A state is not the precursor of the low-pressure B state formation process, since we failed to observe any rapidly decaying A state population which could be correlated with the formation of the B state population. However, we observed a concomitance of the late term CN B emission and that of the CN A (10,5) emission (ca. 630 nm). This implies that the B and A emission have a common decay time. Communication between A and B states with/without the intervention of vibrational levels of the X state can successfully account for this observation. Thus our studies have provided the first direct temporal observation of the communication between A and B states. The 2 hν level (214 kcal/mole) represents the lowest quantum-order process for the production of CN A (v' = 0-10), since the thermodynamic threshold for its production lies in the range of 147-196 kcal/mole. Our findings are not altogether isolated; Duric et. al. [10] and Katayama et. al. [11] have recognized communication among low-lying electronic and vibrational states of CN. This may play an important role in the decomposition behavior of cyano propellant flames.

3.b. Fragmentation of the Cyano Compounds under Nonlinear UV Excitation: Ion-molecule Collisional Channels

The most striking result of the nonlinear UV excitation of cyano compounds is the delayed onset of CN B formation. In addition, a prompt component of CN B emission is observed for ClCN and C_2N_2. Figure 4 illustrates this point.

The prompt component is associated with fragmentation [1] from parent valence states at 2 hν level. A comparison of CN B waveforms for $v' = 0$ and $v' = 5$ for ClCN and C_2N_2 confirms this hypothesis. Figure 5 illustrates the effect of vibrational level upon the nature of CN B waveforms for ClCN and C_2N_2. It is evident from Figure 5 that ClCN exhibits a prompt component of CN B formation for both $v' = 0$ and $v' = 5$ levels; both fragmentation channels are accessible at 2 hν. However, for C_2N_2 the prompt component of CN B is much stronger for $v' = 0$ than for $v' = 5$; that latter channel is not energetically favorable at 2 hν.

The delayed CN B formation process for CH_3CN, ClCN, and C_2N_2 is characterized by similar risetime values. This observation implies a commonality of fragmentation mechanism. We postulate that the delayed channel of CN B formation is associated with ion-molecule collisional processes [2]. The population kinetics have been explored by spectral and temporal analysis of emission waveforms with several specific refinements: isotopic labelling, analysis of waveforms vs. pressure, vs. pulse energy, vs. vibrational quantum number v', and vs. energy threshold of CN B $v' = 0$, 5 levels according to the parent (ClCN and C_2N_2 - see above). The CN B waveforms from ClCN and C_2N_2 are strongly dependent upon the parent pressure. This is illustrated in Figure 6 for ClCN. These waveforms have been parameterized with a kinetic model [1] which includes rate constants k_1 and k_2 (analogous to those for CH_3CN) and $D = R_{\phi 1}$, where R is the ratio of parent population which initially enter the delayed and prompt channels and ϕ_1 is the efficiency of the CN B production from metastable precursors. R may be a function of pulse energy, because of the differing quantum orders of excitation associated with each channel. However, for a fixed pulse energy we may assume that R has a constant value. The model does not consider collisionally-assisted excitations. The emission rate S(t) is then expressed as a sum of terms for the prompt and delayed components:

$$S(t) = k_2\phi_2\exp(-k_2t) + R\phi_1\phi_2k_1k_2\frac{[\exp(-k_2t)-\exp(-k_1t)]}{(k_1-k_2)}\text{--------}(3)$$

where ϕ_2 is the radiative efficiency of the CN B (considering quenching). ϕ_1 may be expressed as

$$D/R = \phi_1 = (\phi_{1U} + \phi_{1Q}P_r)/(1 + P_r)\text{---------}\ (4)$$

where ϕ_{1U} and ϕ_{1Q} represent the efficiency of CN B production through unimolecular and collisionally-assisted processes, respectively, and P_r (the reduced pressure) = P/P_0. By definition, $P_0k_{1U} = k_{1Q}$ where k_{1U} and k_{1Q} represent the collisionless and collisional removal rate constants of the precursor, respectively. It is evident from Figure 6 that our kinetic treatment provides a satisfactory explanation of the pressure dependence of the CN B waveforms. A study of the pressure dependence of k_1 and k_2 can give valuable information regarding the nature of the precursor and the quenching behavior of the CN B state. The zero pressure lifetime (τ_{1U}) of the precursor is given by

$$\tau_{1U} = 1/k_{1U}\text{----------------------}\ (5)$$

where k_{1U} represents the zero pressure value of k_1. The collision-free lifetime, τ_{2u}, of the CN B state can be similarly obtained from the zero pressure value of k_2, k_{2u}.

Figure 7 shows the linear plots of k_1 and k_2 with pressure. The intercept of the k_2 plot yields a zero pressure lifetime of 60 ns which is in good agreement with the literature value for the CN B radiative lifetime [12]. The intercept of the k_1-pressure plot yields a precursor lifetime for ClCN of 133 ns. This compares favorably with the literature value of 170 ns for the lifetime of the $\tilde{B}\ ^2\Pi$ state of $ClCN^+$ measured by Maier et. al. [13]. It should be noted that our measurement represents an average over the vibrational states produced under our experimental conditions. A smaller τ_{1U} value may be consistent with a $\tilde{B}$ state having a high degree of vibrational excitation [13]. Also, our experimental value is in reasonable agreement with that of Braitbart et. al. [14]. The slope of the k_1-plot gives a collisional removal rate constant of the precursor, $k_{1Q} = 1.8 \times 10^{-9}$ $cm^3\ s^{-1}$. This rate constant, which is an order of magnitude larger than that typical of neutral-neutral collisions, compares favorably with the computed [15] value of the ion-molecule rate constant (see below). The current work may represent the first direct temporal examination of ion-molecule rates. Rate parameters of all three parent species are assembled in Table 1.

A linear relationship of $D(1 + P_r)$ vs. P_r is predicted by eqn. 4. Indeed, Figure 8 exhibits such a linear plot. ϕ_{1U} appears to be small; it is quite likely that it may be zero: That is, there is no unimolecular mechanism for for production of delayed CN B; it is solely collisonal. Our earlier work [3] on the isotopically labelled CH_3CN satisfactorily accommodates the above hypothesis: the delayed formation of CN B is associated exclusively with a collisionally-mediated fragmentation process. For isotopically-labeled CH_3CN, the relative amounts of CN B produced from fragmentation channels in which the atoms originate both in common and in distinct parents were not perceptibly different at 2 Torr and at 5 Torr. If k_{1U} had a nonzero value of efficiency, ϕ_{1U}, it should have been expressed at 2 Torr, since $P_o = 1{\cdot}2$ Torr for CH_3CN.

The total number of molecules excited should vary linearly with pressure. Figure 9 displays such a linear plot for ClCN. A similar plot was obtained for

CH_3CN. These observations provide additional support for the kinetic model and suggest that collisionally-assisted excitation is not important to CN B formation channels.

The long-lived precursors, which are identified with excited states of the complete parent ions, should be influenced by the application of an electric field. The E-field should accelerate ions and increase the number of collisions with parent neutrals. However, the cross-sections (σ) for such reactions are controlled by polarization forces and $\sigma = \text{const}/g$ where g is the relative velocity between collision partners. Hence, kN (the ion-molecule collision rate) should be independent of g as expressed in the following relationship:

$$\text{Rate} = kN = \sigma g N \text{ ------------------ } (6)$$

where N is the concentration of parent neutrals. Thus the application of an electric field is not expected to produce any effect on the collisional removal rate of the precursor. Figure 10 illustrates such a null effect of the electric field on the CN B kinetics for ClCN. k_{1Q} values can be calculated according to the AADO/AQO (electrostatic) theory [15]. The calculated values of k_{1Q} are presented in Table 1 along with their experimentally measured values. The favorable agreement between these large experimental and computed values supports the ion-molecule picture rather well.

The mechanism for the production of CN B from ClCN via an ion-molecule reaction can then be represented as follows:

$$\mathrm{ClCN} \xrightarrow{4h\nu} \mathrm{ClCN^+}\ (\tilde{B}\ {}^2\Pi)$$

$$\mathrm{ClCN^+}\ (\tilde{B}\ {}^2\Pi) \xrightarrow{k_{1U}} \mathrm{ClCN}\ (\tilde{A}\ {}^2\Sigma,\ \tilde{X}\ {}^2\Pi)$$

$$\mathrm{ClCN^+}\ (\tilde{B}\ {}^2\Pi) + \mathrm{ClCN} \xrightarrow{k_{1Q}} \mathrm{CN}\ B\ {}^2\Sigma^+ + \mathrm{Cl_2CN^+}$$

This scheme is consistent with the long-lived precursor (ca. 133 ns). Indeed, Yergey and Franklin [16] have observed production of Cl_2CN^+ in the reaction of $ClCN^+$ with ClCN. Further, the above scheme is consistent with 4 hν as the lowest quantum order process for the collisional production of CN B (unimolecular dissociation of $ClCN^+$ to yield CN B is not allowed at 4 hν on energetic grounds). Superexcited states may account for large k_{1Q} values and the null effect of the electric field on kinetics. However, the large values of the precursor collision-free lifetime (24 - 136 ns) are not consistent with super excited species. Our kinetic observations do not support dissociative recombination as the mechanistic process for the delayed production of CN B. Also, distinct values of τ_{1U} for different parents rule out the possibility of a common fragment precursor ion, such as CN^+.

In summary, following nonlinear UV excitation of simple cyano compounds we have observed delayed channels of CN B production. Our findings lead us to infer that these formation channels originate through ion-molecule collisions. In our preferred interpretation, the precursors to the delayed channels are vibronically excited positive ions of the parent molecular formula: for CH_3CN, skeletal rearrangement is likely and H-migration is quite possible. For the simpler case of ClCN, we have identified a collisional channel of lowest quantum order.

In survey work, we have recognized a number of other parent molecules which give rise to delayed components of diatomic emission. We suggest that chemiluminescent ion-molecule reactions may be the underlying general mechanism. Kinetic studies of this kind will shed light on the overall picture of molecular processes, especially collisional channels, following energetic electronic excitation. Similar processes are significant, e.g., in mass spectroscopy, in cometary chemistry, where fragmentation can be observed under conditions favoring ion-molecule collisions.

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4. Publications

a. Delayed Formation of Emissive CN and C_2 Fragments Following Short Pulse UV Excitation of Isotopically Labeled CH_3CN. B.B. Craig, W.L. Faust and R.G. Weiss, in "Lasers as Reactants and Probes in Chemistry", W.M. Jackson and A.B. Harvey, Eds., Howard University Press, Washington, D.C., 1985, p. 29.

b. Fragmentation Dynamics of Nitriles under Nonlinear UV Excitation. B.B. Craig, S. Chattopadhyay and W.L. Faust, in "Photophysics and Photochemistry above 6 eV", F. Lahmani, Ed., Elsevier, Amsterdam, 1985, p. 531.

c. Fragmentation of Cyano Compounds under Nonlinear UV Excitation: Delayed CN $B^2\Sigma^+$ Chemiluminescence through Ion-Molecule Collisions. W.L. Faust, B.B. Craig, S. Chattopadhyay and R.G. Weiss, submitted to J. Phys. Chem.

d. Fragmentation Dynamics of Small Molecules under Nonlinear Short-Pulse UV Excitation in the Gas Phase. W.L. Faust, B.B. Craig, S. Chattopadhyay and R.G. Weiss, Final Technical Report, Grant AFOSR-84-0019.

5. Professional Personnel

Dr. Richard G. Weiss - Principal Investigator
Dr. Swapan Chattopadhyay - Postdoctoral Researcher
Dr. Bruce B. Craig - Employee, Naval Research Laboratory
Dr. Walter L. Faust - Employee, Naval Research Laboratory

6. Meeting Presentations

a. Fragmentation Dynamics of Nitriles under Nonlinear UV Excitation. B.B. Craig, S. Chattopadhyay and W.L. Faust, Conference on Photophysics and Photochemistry above 6 eV, Bombannes, France, Sept. 17-21, 1984.

b. Collisional Fragmentation of Highly Excited XCN, W.L. Faust, B.B. Craig, S. Chattopadhyay, and R.G. Weiss, XIIth International Conference on Photochemistry, Tokyo, Aug. 4-6, 1985.

Table 1

Rate Parmeters for the Parent Species

and the Calculated Values of k_{1Q}

Parent	k_{1U} (10^6 s^{-1})	k_{2U} (10^6 s^{-1})	τ_{1U} (ns)	τ_{2U} (ns)	k_{2Q} (10^{-10} cm^3 s^{-1})	k_{1Q} (10^{-9} cm^3 s^{-1})	k_{1Q} (calculated) (10^{-9} cm^3 s^{-1})
ClCN	7.5	16.5	133	61	0.76	1.80	2.45
C_2N_2	7.4	16.6	136	60	0.03	0.89	1.12
CH_3CN	41.7	17.3	24	58	2.2	1.70	3.89

Figure Captions

1. A representative list of the small molecules which yield diatomic emissive fragments under our conditions of nonlinear uV excitation.

2. Energy dependent CN B Waveforms at higher pressures. Representative CN B emission waveforms recorded at 388.3 nm, 10 ns/div. Averages of 64 laser pulses, from 7 torr of CH_3CN. (a) Average pulse energy 1.0 mJ. (b) 1.8 mJ. (c) 4.0 mJ and (d) 5.6 mJ.

3. CN B emission waveform at 388.3 nm, 20 ns/div. Average of 32 laser pulses, 20 Torr of CH_3CN, average pulse energy 6.0 mJ. A model curve is also included, with risetime 1.2 ns and decay time 8 ns. These parameters are extrapolated from pressure plots in Ref. 3.

4. CN B violet band emission monitored at 388.3 nm from ClCN, C_2N_2 and CH_3CN.

5. The effect of vibrational level on the nature of CN B waveforms for ClCN and C_2N_2.

6. Representative signal-averaged CN B waveforms for ClCN 2.5 - 3.5 mJ. Typical model curves are included.

7. For ClCN, the pressure dependence of the removal rates: k_1, for precursors to CN B; and k_2, for CN B itself.

8. The linear plot of $D(1 + P_r)$ vs. P_r for fixed pulse energy (3 mJ).

9. For ClCN, the total number of molecules, M_{tot}, excited into the prompt and delayed CN B channels.

10. Demonstration of a null effect of an electric field of 400 V/cm upon CN B waveforms from ClCN, 0.8 Torr.

For Nonlinear UV Excitation of Simple Organics,

DELAYED DIATOMIC CHEMILUMINESENCE

is <u>prevalent</u> and <u>prominent</u>.

$$CH_3CN \longrightarrow \left\{ \begin{array}{ll} CN\ B^2\Sigma^+ & \text{delayed} \\ C_2\ d^3\Pi_g & \text{delayed} \\ NH\ A^3\Pi & \text{delayed} \\ CH\ A^2\Delta & \text{delayed} \\ CH\ C^2\Sigma^+ & \text{delayed} \end{array} \right.$$

$$C\ell CN \longrightarrow \left\{ \begin{array}{ll} CN\ B^2\Sigma^+ & \text{delayed + prompt} \\ C_2\ d^3\Pi g & \text{delayed (weak)} \\ CC\ell\ {}^2\Delta & \text{delayed (weak)} \end{array} \right.$$

$$C_2N_2 \longrightarrow \left\{ \begin{array}{ll} CN\ B^2\Sigma^+ & \text{delayed + prompt} \\ C_2\ d^3\Pi g & \text{delayed} \end{array} \right.$$

$$HCN \longrightarrow CN\ B^2\Sigma^+ \quad \text{delayed}$$

$$CH_2\ CO \longrightarrow C_2\ d^3\Pi g \quad \text{delayed + prompt}$$

$$CH_3\ NO_2 \longrightarrow CN\ B^2\Sigma^+ \quad \text{prompt}$$

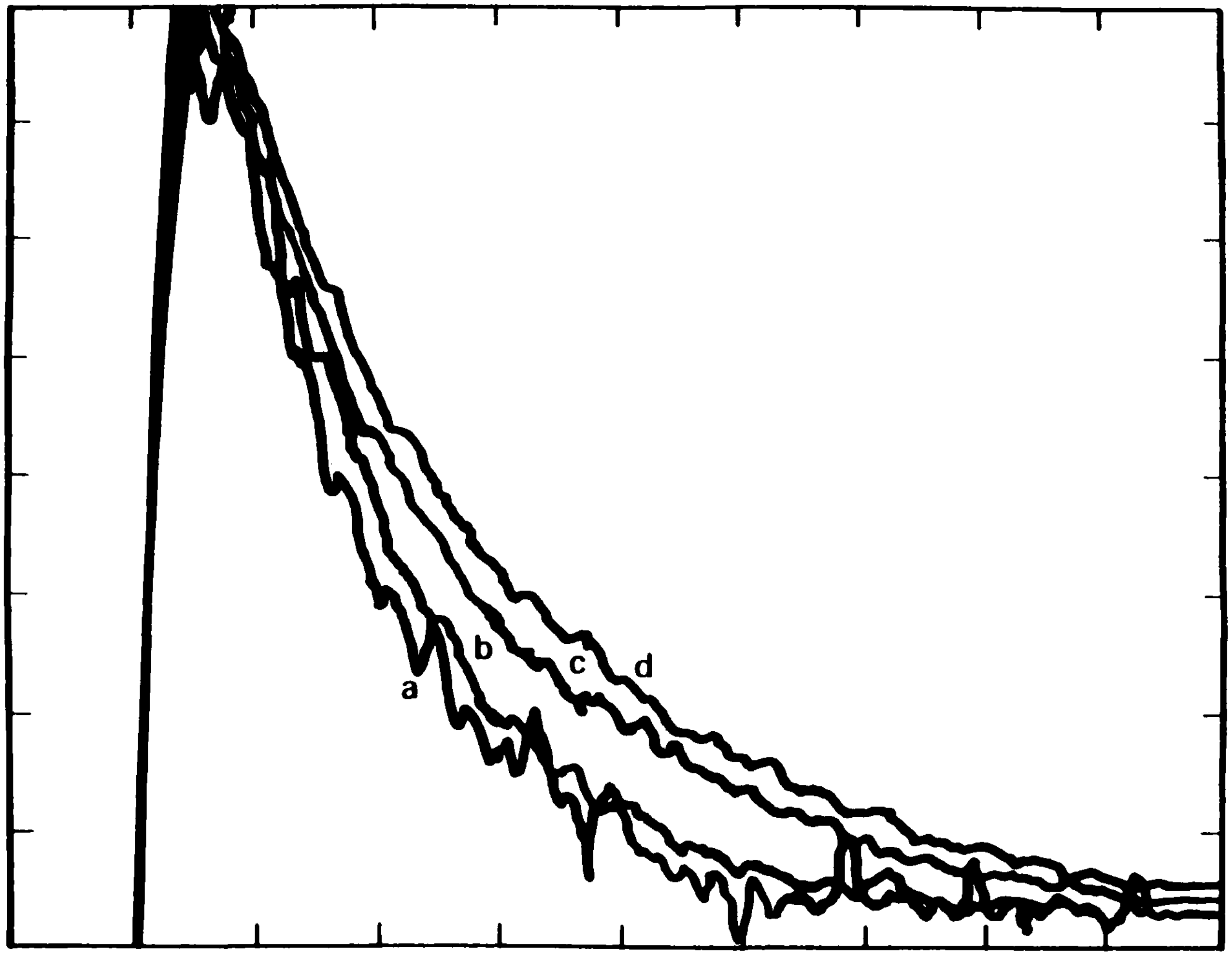
$$CO \longrightarrow C_2\ d^3\Pi g \quad \text{delayed} \left\{ \begin{array}{l} \text{fast} \\ \underline{\underline{\text{slow}}} \end{array} \right\} \text{complex}$$

$$\text{Also, simple hydrocarbons} \longrightarrow C_2\ d^3\Pi_g \quad \text{delayed + fast}$$

<u>HYPOTHESIS</u>:

Ion-Molecule Reactions ⟶ Chemiluminescence

Figure 1



Energy-Dependent Waveforms at Higher Pressures

Figure 2

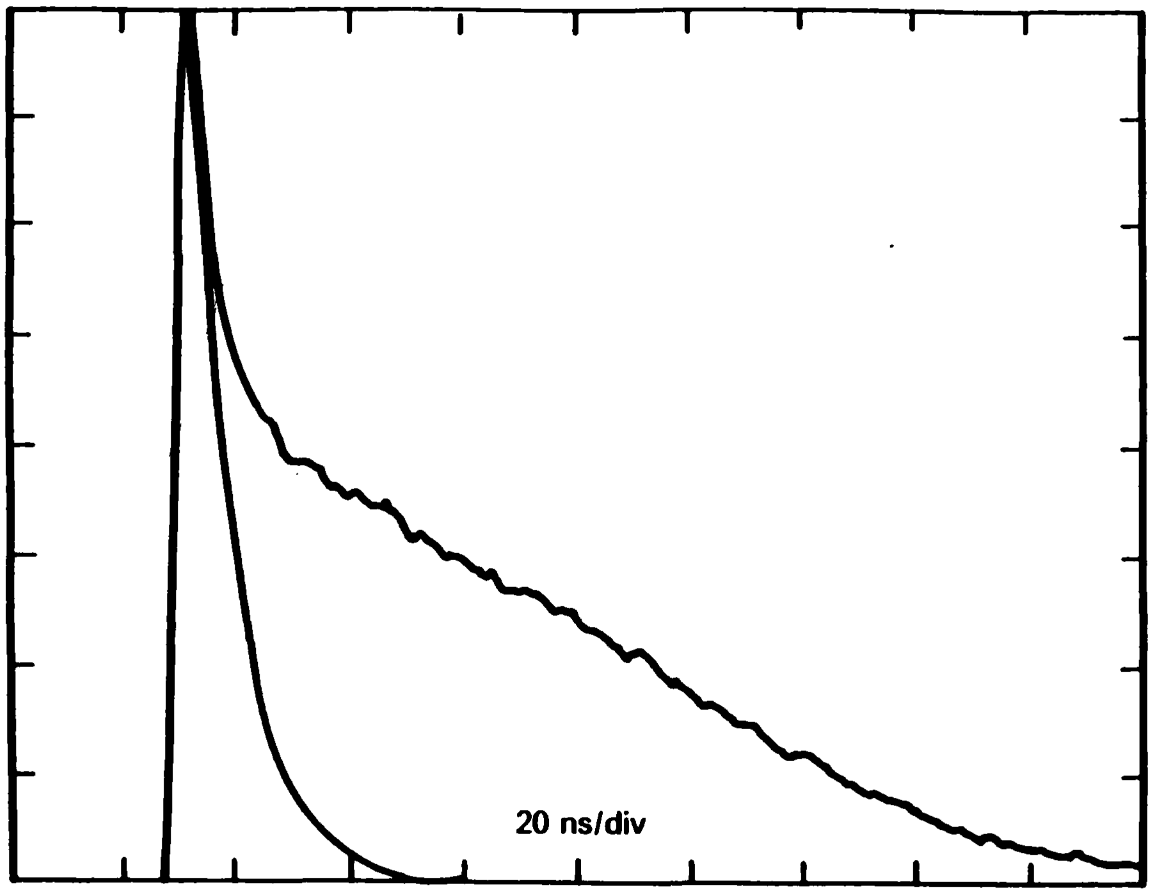
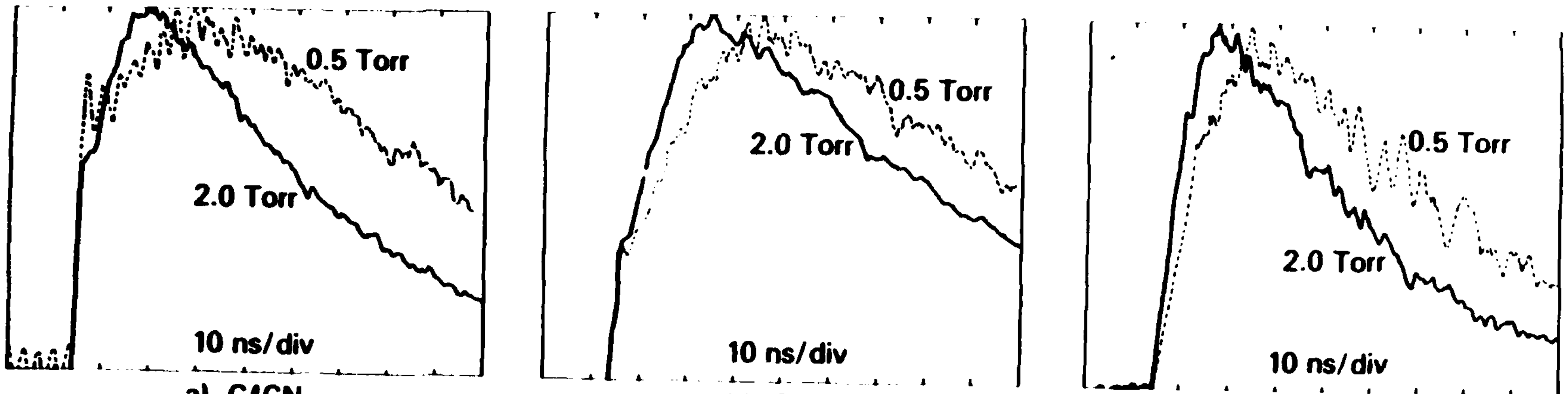
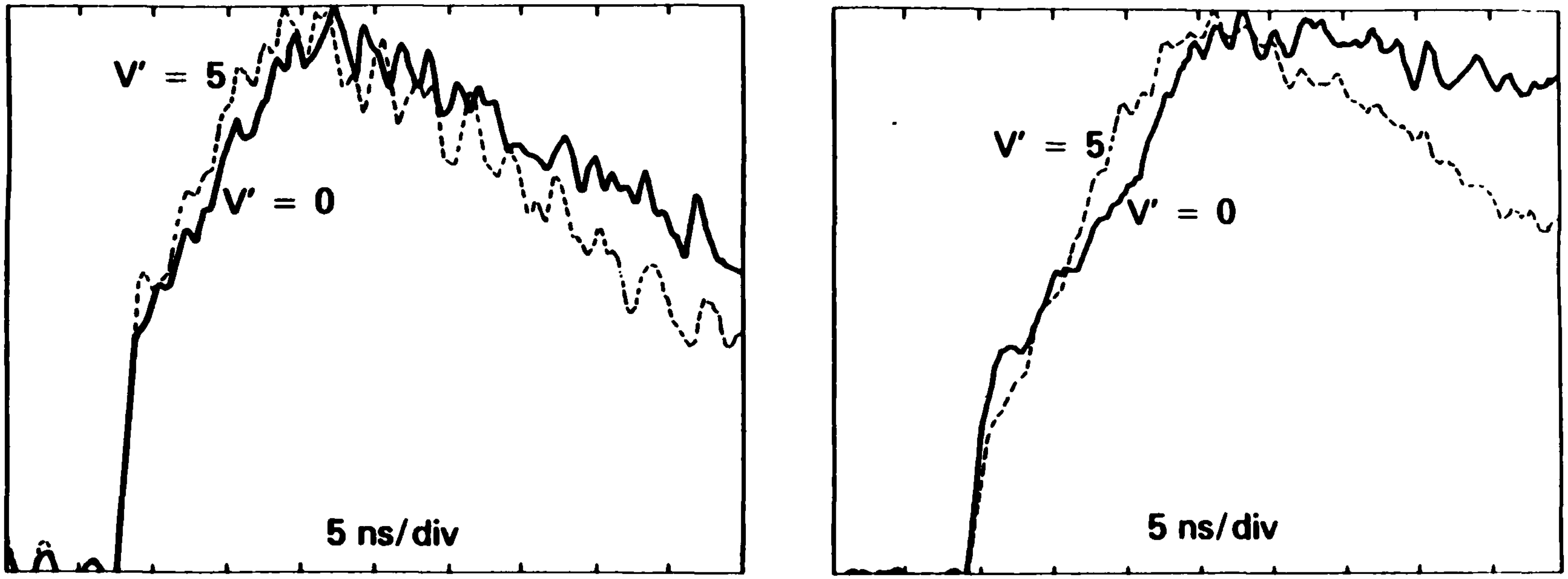


Figure 3

CN violet Band Emission from CℓCN, C_2N_2, and CH_3CN



a) CℓCN b) C_2N_2 c) CH_3CN

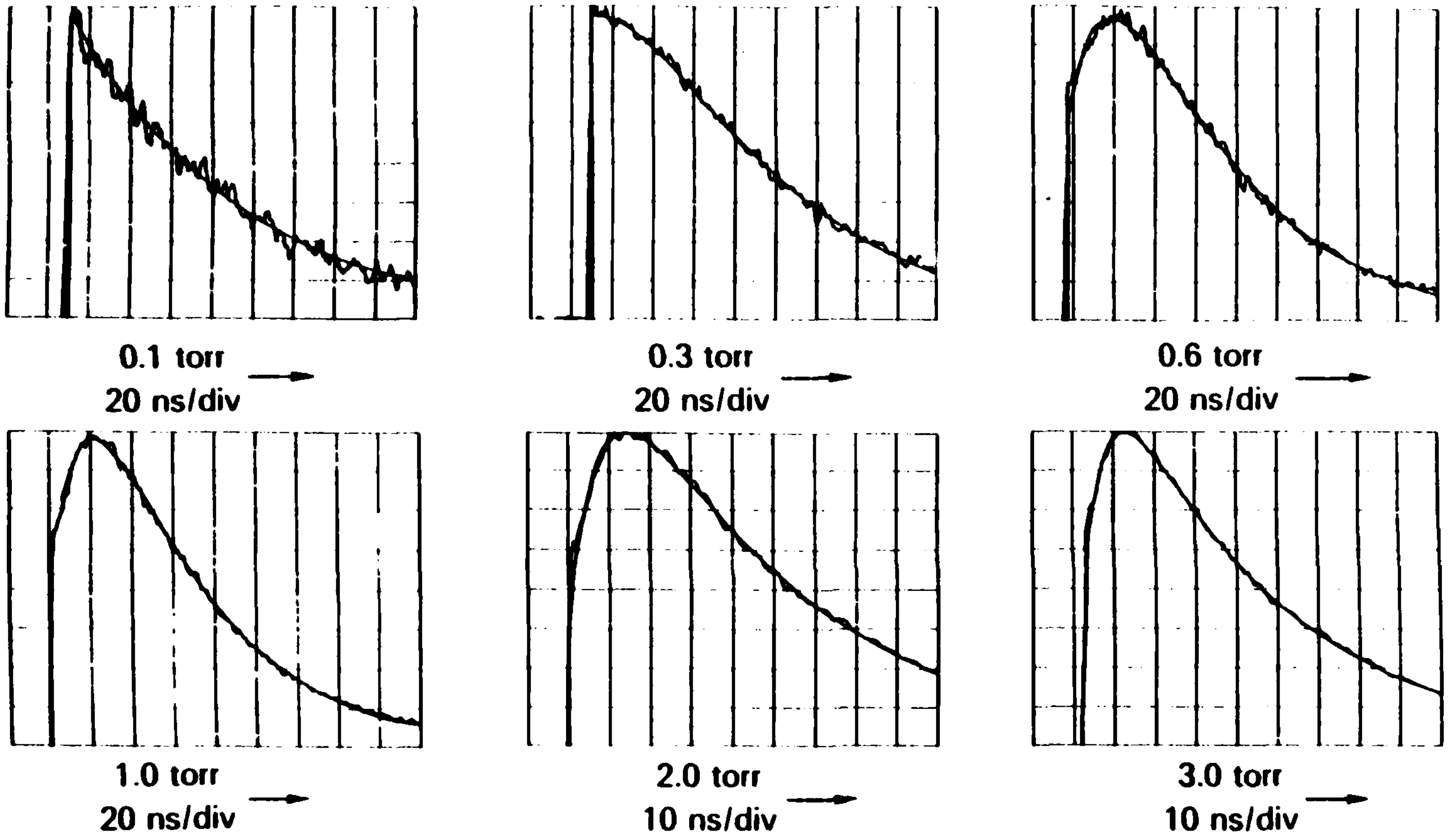


a)CℓCN

b) C_2N_2

Figure 5

Pressure Dependent Waveforms of Emission, CN Violet Bands from CℓCN


0.1 torr →
20 ns/div

0.3 torr →
20 ns/div

0.6 torr →
20 ns/div

1.0 torr →
20 ns/div

2.0 torr →
10 ns/div

3.0 torr →
10 ns/div

Figure 6

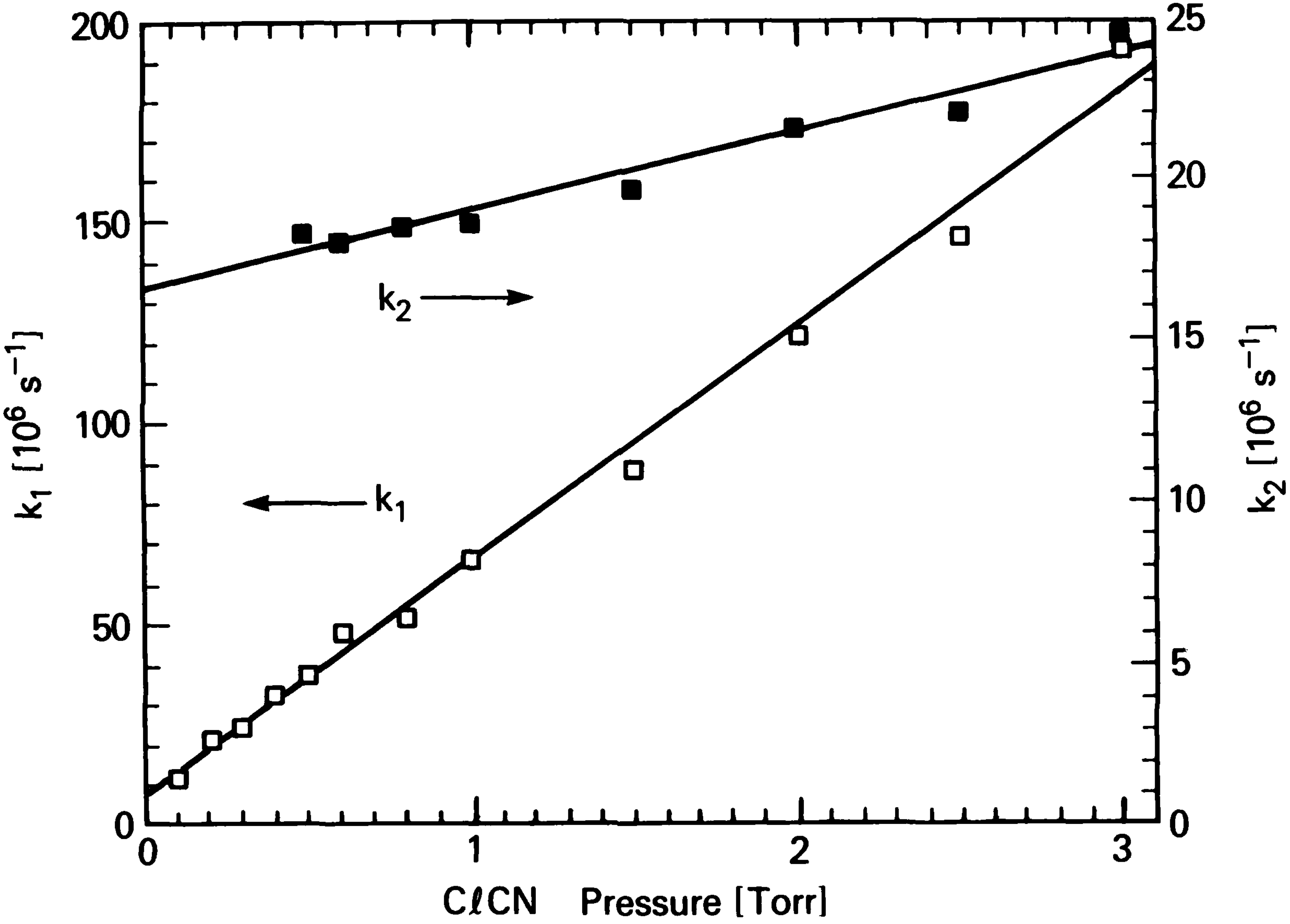

200
150
100
50
0
25
20
15
10
5
0
0
1
2
3
k_1 [10^6 s^{-1}]
k_2 [10^6 s^{-1}]
k_2 →
← k_1
CℓCN Pressure [Torr]

Figure 7

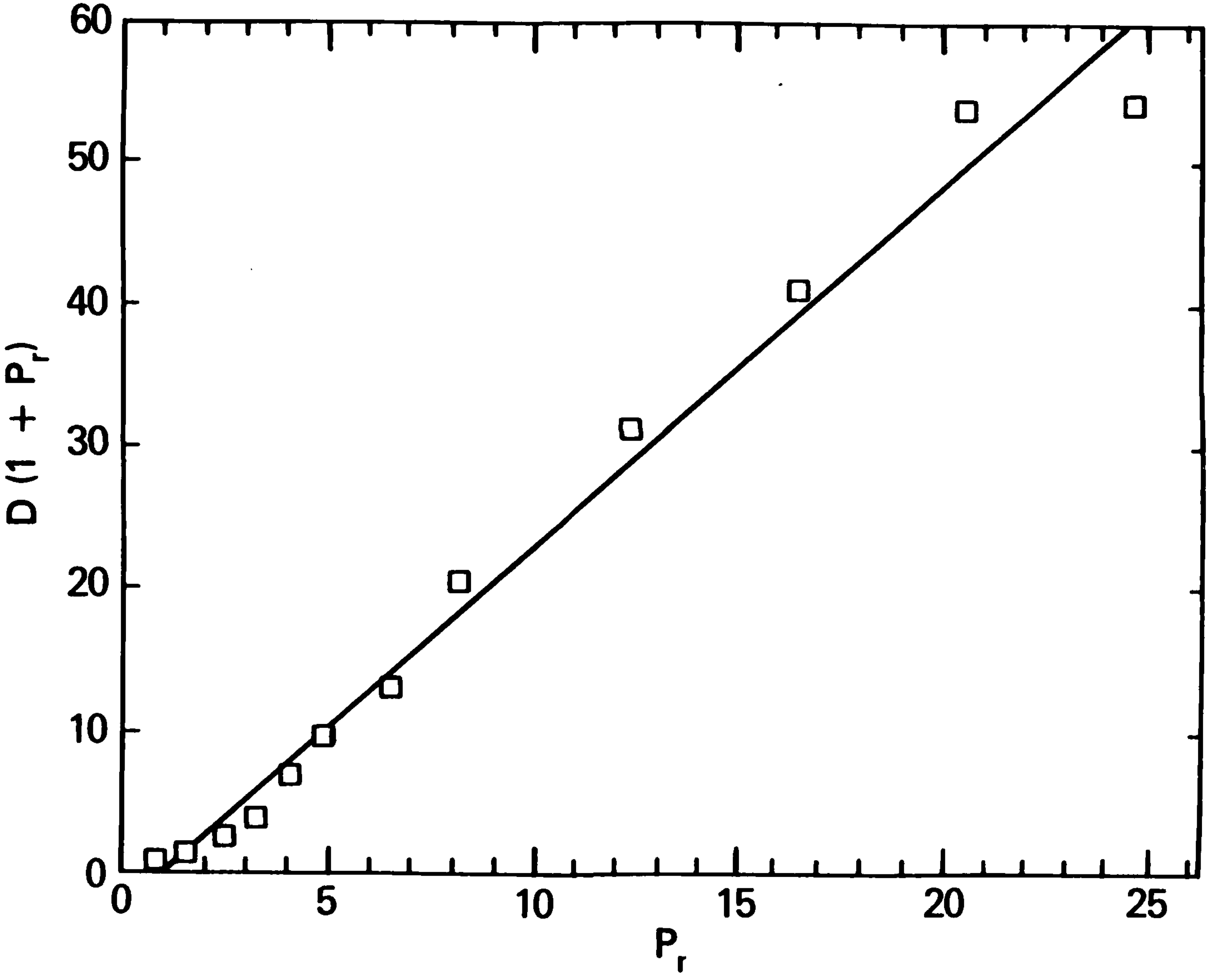


Figure 8

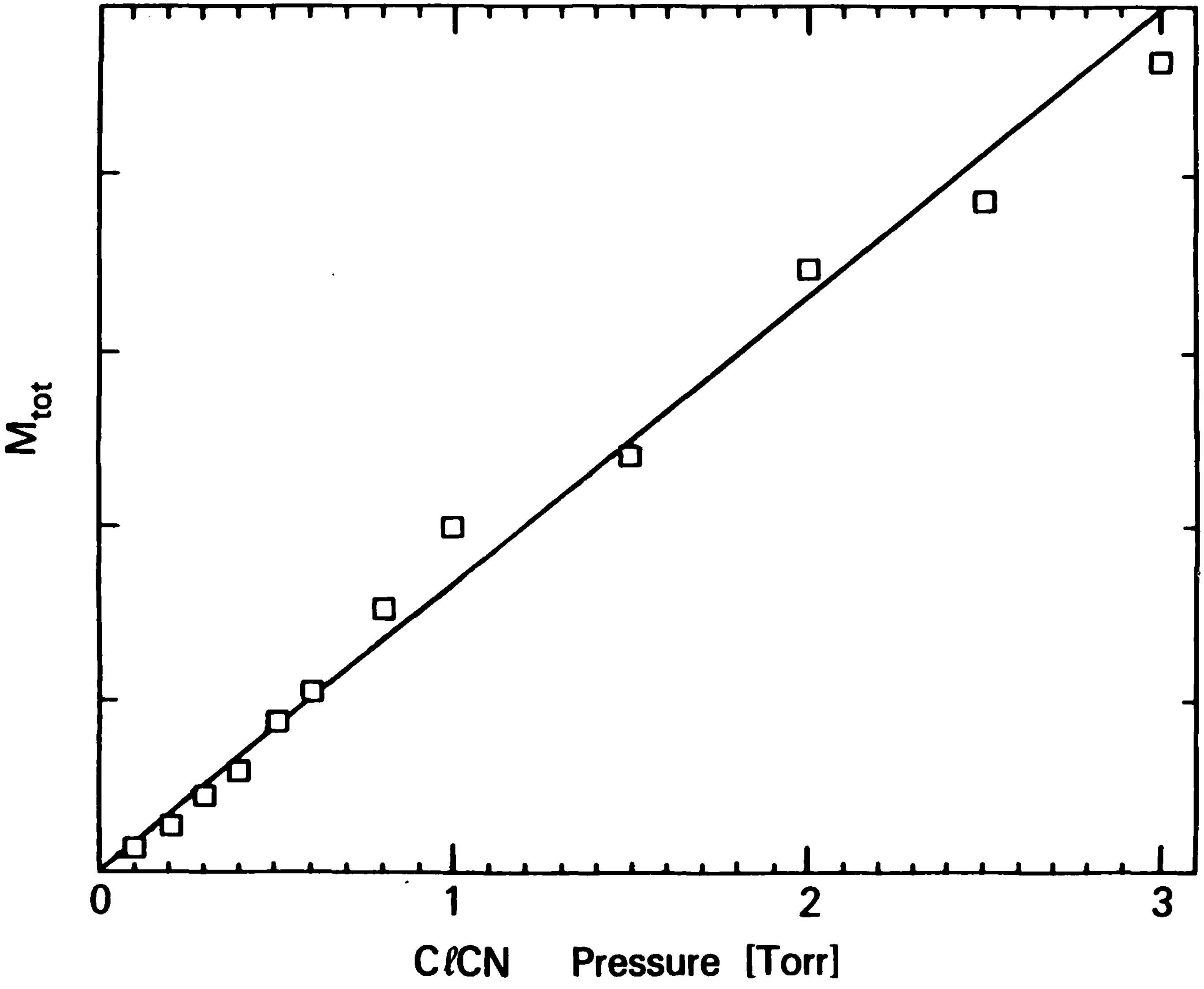


Figure 9

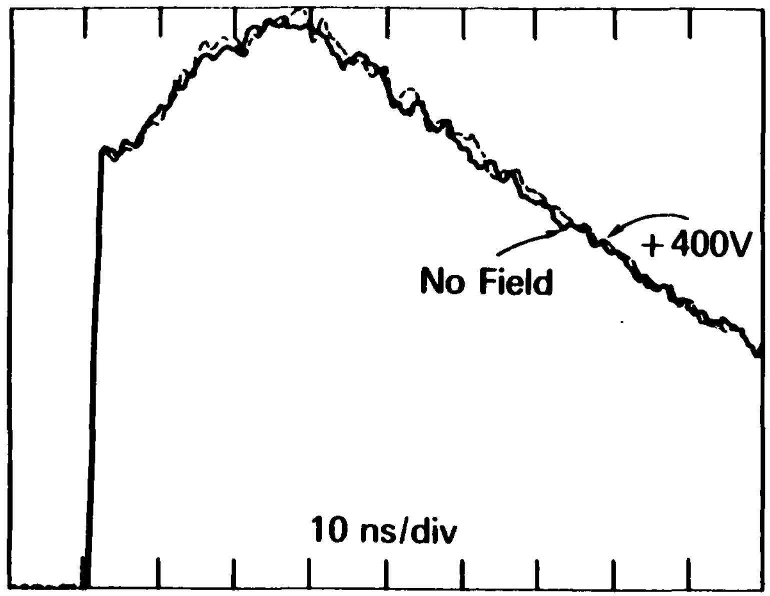


Figure 10

END

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