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Near-Resonant Vibration → Vibration Energy Transfer Under Single-Collision Conditions *

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Vibration → vibration energy transfer in ground state polyatomics can be thought of as the simplest type of reaction involving only the rearrangement of energy distributions among vibrational modes and translational/rotational degrees of freedom. Details of the state-to-state pathways prior to a return to equilibrium are known only for the very low energy regime.[1] At energies near dissociation, statistical parameters concerning the efficiency of energy removal during a collision have been studied.[2] The work discussed here concerns energy transfer on a single collision basis subsequent to IR multiphoton absorption.

Interaction of an intense IR laser field with a polyatomic produces an energy distribution within the pumped mode and background states determined by both the peak power and fluence of the IR (CO_2) laser. In propynal, H—C≡C—CHO, it has been shown by IR-visible double resonance experiments under beam conditions,[3] that pumping ν_6 (944 cm^{-1}) <u>or</u> ν_{10} (980 cm^{-1}) causes an increase in vibrational populations at the $v = 1$ level of only the pumped mode with no leakage of energy into the nearby state(s). Vibrational populations are dependent on peak power and wavelength, but all rotational states appear to interact with the laser field to some degree independent of these parameters.

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DISCLAIMER

When single collisions are introduced under beam-gas conditions (Figure 1) subsequent to IR pumping of ν_6, the v = 1 populations increase (Figure 2) by an amount in excess of that due to the CO_2 laser alone as determined by the dye-laser probe. Such increases are dependent on the vibrational frequencies of the collider as shown in Figure 3 and Table I and occur only when the energy gap ΔE for pathways

$$P(6_{i>1}) + M \xrightarrow{k_{i1}} P(6_1) + M^{\dagger} \pm \Delta E \qquad (1)$$

is small (resonant V-V pathways). Energy transfer to nondriven modes probed with the dye laser does not occur except in one instance, indicating that resonant V-V processes within the pumped mode are the only pathways that are fast enough to be observed on a single collision time scale. This result agrees with results obtained under bulb conditions. However, no equilibration of ν_6 and ν_{10}, where $\Delta E \sim 40\ cm^{-1}$, is observed, contrary to expectation. An exception is found when ν_{10} is pumped and SiF_4 is the collider.

On the simplest level, the results of Table I can be analyzed from eq. 1 in terms of $\Delta v = 1$ or $\Delta v = 2$ transitions in propynal and $\Delta v = 1$ transitions in the collider. From the kinetics, it can be shown that the increase in the vibrational populations, normalized for number density in the molecular beam is equal to

$$\left[\sum_i \frac{k_{i1} N_i^o}{N_1^o} - k_{10} \right] Mt$$

where N_i^o and N_1^o are the laser-induced populations of levels v = i and v = 1; k_{10}, the rate constant for the pathway

$$P(6_1) + M \longrightarrow P(6_0) + M^{+} \pm \Delta E \quad ;$$

M, the pressure of added gas; and t, the real time of the observation. Results are shown in Figure 4a ($\Delta v = 1$ transition in propynal) and Figure 4b ($\Delta v = 2$), and Table III. Contrary to theory, $\Delta v = 2$ transitions occur on a similar time as $\Delta v = 1$ transisions. In both cases k_{i1} must be larger than gas kinetic. Since the spectroscopy impedes measurement of the ratio N_i^o/N_1^o in propynal, actual values for k_{i1} are not obtainable. Similar experiments concerning thiophosgene where spectroscopic complications are less important reveal more quantitative date on these energy transfer pathways.

REFERENCES

1. General reviews on vibrational energy flow can be found in G. W. Flynn, in Chemical and Biological Applications of Lasers, Vol. 1, edited by C. B. Moore (Academic Press, New York, 1974), p. 163; E. Weitz and G. W. Flynn, Ann. Rev. Phys. Chem., 25, 275 (1974); C. B. Moore, Acct. Chem. Rev., 2, 103 (1969); R. G. Gordon, W. Klemperer and J. I. Steinfeld, Ann. Rev. Chem., 19, 215 (1968).
2. D. C. Tardy and B. S. Rabinovitch, Chem. Rev., 77, 369 (1977).
3. D. M. Brenner, P. M. Curtis, and K. Brezinsky, Chem. Phys. Lett., 72, 202 (1980).

Fig. 1. Cutaway drawing and schematic of experimental apparatus.

Fig. 2. Excitation spectra of the 6_1^0 band showing intensity changes due to (a) CO_2 laser excitation and (b) CO_2 laser excitation and subsequent collision-induced V-V energy transfer involving SiF_4 (3.5×10^{-4} torr). The excitation frequency is 951 cm^{-1} (P(12)) and the peak power is ∿12 MW/cm^2 (pulse duration 100 ns (FWHM)).

Fig. 3. Changes in population of the 6_1 level due to CO_2 laser excitation (ω = 951 cm^{-1}) (●) and subsequent collisions with added gases SiF_4 (▣), CH_3F (▲), CCl_4 (●), and CH_4 (□) when the peak power is (a) ∿10 MW/cm^2 (pulse duration 100 ns (FWHM)) and (b) ∿6 MW/cm^2 (100 ns (FWHM)). Changes in populations due to collisions are normalized to the room temperature 6_1^0 intensity in the presence of added gas.

Fig. 4. Plot of $\frac{N_1}{N_1^0} \cdot \frac{N_1^{RT}}{(N_1^{RT})}$, vs pressure (see text) for (a) $\Delta v = 1$ V-V energy transfer pathways and (b) $\Delta v = 2$ pathways were Δv refers to the quantum number change of the pumped mode ν_6.

□ SiF_4 ▲ CH_3F ● CF_4 △ NO □ CO

Table I: Collision-induced changes in populations of levels 6_1 and 10_1 following (3μ delay time) IR multiphoton pumping.

				Pumped Mode		Nondriven Modes	
Pumped Mode	Added Gas[a]	Peak Power (MW/cm^2)	t_p(ns)[b]	$\frac{N_1^o}{N_1^{RT}}$ x 100%[c]	$\frac{N_1}{(N_1^{RT})'}$ x 100%[d]	%$\Delta 6_1$	%$\Delta 10_1$
10	--	12	200	28.2±2.4			
	Ar	"	"		30.1±4.8		
	SiF_4	"	"		43.7±2.8	12.4±1.3	
	CH_3F	"	"		36.1±3.1	2.4±4.9	
6	--	12	200	59.2±4.8			
	Ar	"	"		58.1±3.2		1.8±1.5
	He	"	"		56.2±2.7		
	SiF_4	"	"		128.1±2.9		-1.2±2.3
	CH_3F	"	"		89.4±1.6		3.2±4.6
	CH_4	"	"		61.2±2.3		1.1±2.4
	CCl_4	"	"		56.8±3.1		
	CF_4	"	"		81.7±2.1		
	C_2H_6	"	"		46.0±3.6		2.1±4.8
	CO	"	"		98.9±2.6		5.6±3.2
	NO	"	"		95.9±4.2		
6	--	4.7	500	52.4±1.6			
	CO	"	"		51.7±2.9		
	NO	"	"		50.6±6.3		
	CH_3F	"	"		64.2±3.4		
6	--	5.4	200	52.3±2.5			
	SiF_4	"	"		69.1±2.4		
	CH_3F	"	"		62.3±6.1		

[a] Pressure for all entries is 5 x 10^{-4}

[b] Pulse duration, measured at baseline

[c] Population changes produced by IR laser in absence of added gas

[d] Population changes produced by IR laser in presence of added gas

Table II: Values for $\left[\frac{\sum_i k_{i1} N_i^o}{N_1^o} - \underline{k}_{10}\right]^t$ and intercept obtained by linear least squares fitting of experimental data.

Added Gas	$\left[\frac{\sum_i k_{i1} N_i^o}{N_1^o} - \underline{k}_{10}\right]^t \times 10^{-8}$ ($S^{-1}torr^{-1}$)	intercept	r^2 [a]
SiF_4	8.43±1.81	1.06	0.92
CH_3F	3.40±0.61	1.05	0.90
CF_4	1.84±0.71	1.13	0.89
CO	4.99±0.57	0.96	0.99
NO	4.62±0.44	1.10	0.96

[a] Correlation coefficient

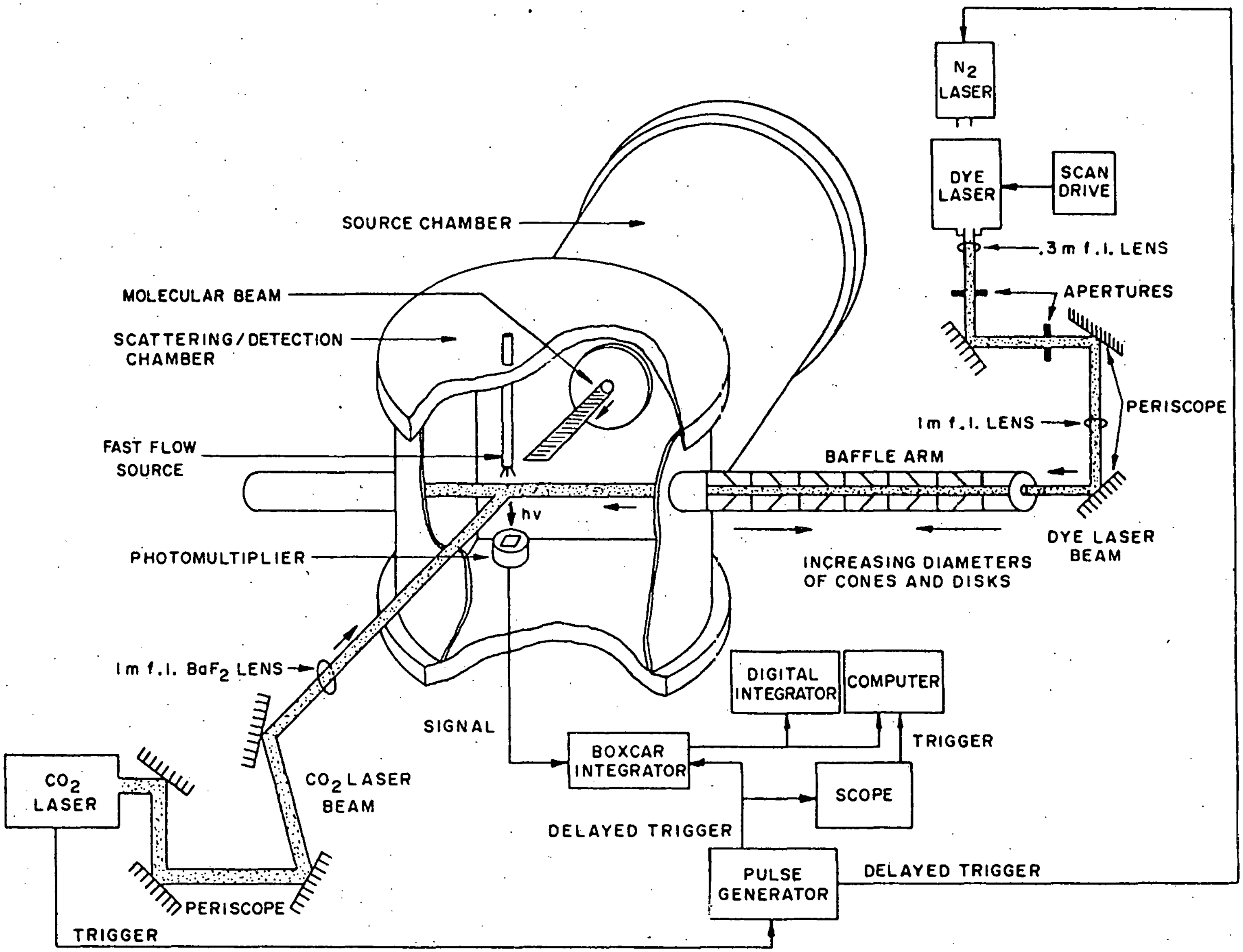

N$_2$ LASER
DYE LASER
SCAN DRIVE
.3 m f.l. LENS
APERTURES
PERISCOPE
1 m f.l. LENS
SOURCE CHAMBER
MOLECULAR BEAM
SCATTERING/DETECTION CHAMBER
FAST FLOW SOURCE
BAFFLE ARM
hv
PHOTOMULTIPLIER
DYE LASER BEAM
INCREASING DIAMETERS OF CONES AND DISKS
1 m f.l. BaF$_2$ LENS
SIGNAL
DIGITAL INTEGRATOR
COMPUTER
TRIGGER
BOXCAR INTEGRATOR
CO$_2$ LASER
CO$_2$ LASER BEAM
SCOPE
DELAYED TRIGGER
PULSE GENERATOR
DELAYED TRIGGER
PERISCOPE
TRIGGER

Fig 1

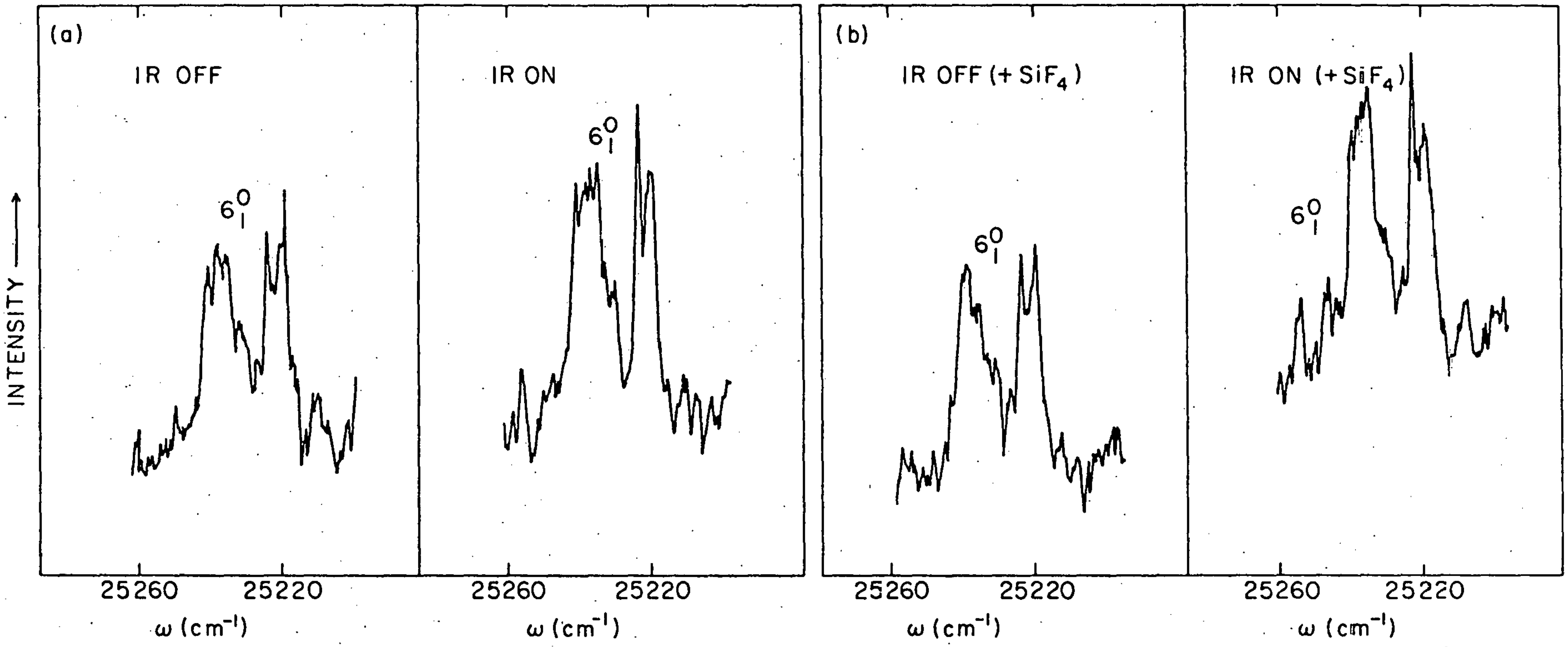

(a)
IR OFF
6^0_1
IR ON
6^0_1
(b)
IR OFF (+ SiF_4)
6^0_1
IR ON (+ SiF_4)
6^0_1
INTENSITY →
25260
25220
ω (cm^{-1})
25260
25220
ω (cm^{-1})
25260
25220
ω (cm^{-1})
25260
25220
ω (cm^{-1})

Fig 2

Fig 3

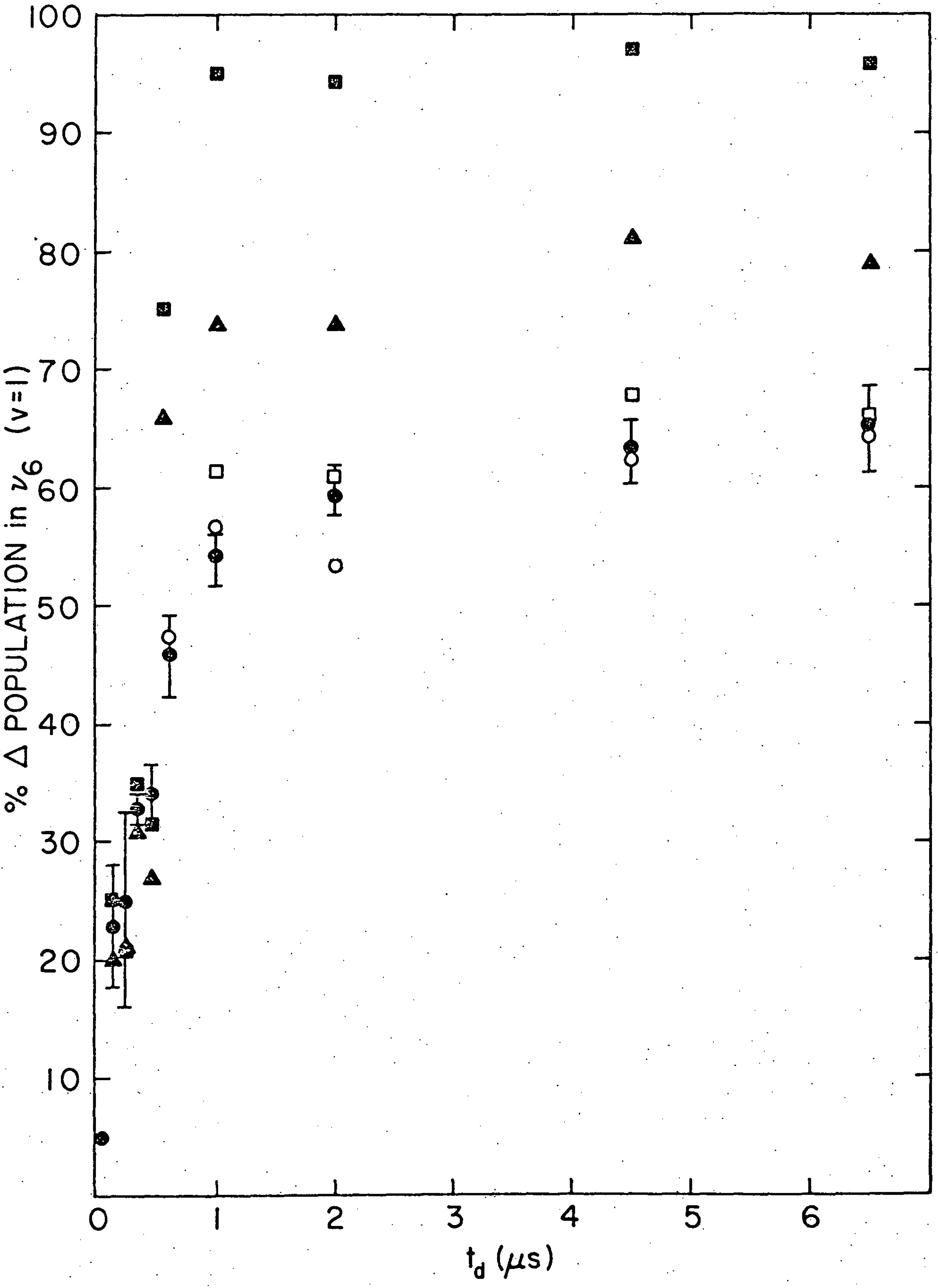
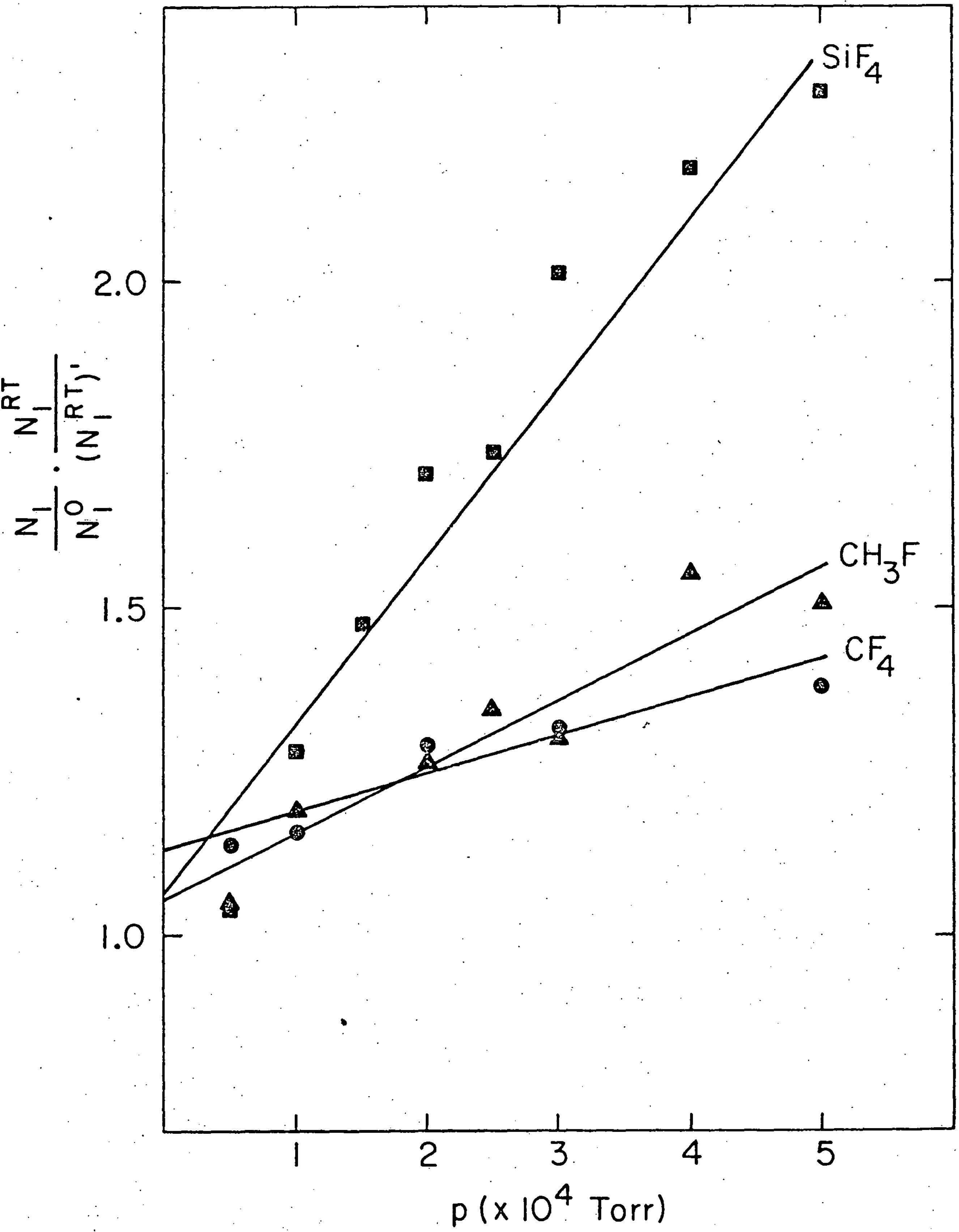

100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
% Δ POPULATION in ν_6 (v=1)
t_d (μs)

Fig 4a



SiF$_4$
CH$_3$F
CF$_4$
$\frac{N_1}{N_1^0} \cdot \frac{N_1^{RT}}{(N_1^{RT})'}$
2.0
1.5
1.0
1
2
3
4
5
p (x 10^4 Torr)

Fig 4b