

Pressure Effects in the Kinetics of cw Laser Induced Reactions

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Abstract. Rate constants k and translational temperatures T have been determined for the decompositions of ethyl acetate and perfluorocyclobutane at various pressures induced by a continuous (cw) CO₂ laser. Arrhenius plots give activation energies in good agreement with those reported for thermal rate constants k_t . The ratios k/k_t become progressively larger than unity with decreasing reactant pressure, indicative of laser induced non-thermalization, but the values of k/k_t appear to reach limiting values at low pressures, similar to effects reported elsewhere for CH₃CF₂Cl. Analysis of the data suggests important general features of vibrational-translational energy transfer in polyatomic compounds.

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Techniques are now available for accurate determinations of rate constants and translational temperatures in the beam region of a continuous (cw) infrared laser entering an absorbing gas [1–3]. One application is in thermal kinetic studies of systems complicated by wall (heterogeneous) reactions at high temperatures, since the laser can induce reactions far from container walls. However, at low reactant pressures the system is not entirely thermalized; laser pumping of vibrational levels successfully competes with the vibrational-translational (VT) deactivation rate to produce an effective vibrational temperature T_v above the translational temperature T [3]. This provides a new method for investigating molecular energy transfer.

VT transfer has been studied in the past by ultrasonic, infrared fluorescent decay, shock tube, and other techniques. In shock tubes the temperatures are in the same range as those produced by lasers, but the diagnostics are generally simpler for the quasi-steady-state condition involved in cw laser excitation. Only one quantitative study by the cw laser technique has been published to date [3]. In the simple unimolecular decomposition of CH₃CF₂Cl (via HCl elimination) the difference $T_v - T$ increased with decreasing reactant pressure but unexpectedly appeared to approach a

limiting value at the low end of the pressure range (~ 10 Torr). The purpose of the present report is to show that the effect just described occurs in other systems, suggesting that this is a general characteristic of VT transfer when $T_v - T$ becomes sufficiently large.

The data presented here are for the simple unimolecular decompositions of ethyl acetate and perfluorocyclobutane (*c*-C₄F₈). Ethyl acetate has vibrational modes of lower frequency than CH₃CF₂Cl, and it is generally recognized that VT transfer predominantly occurs through such modes [4]. The *c*-C₄F₈ was chosen because for various experimental reasons its reaction could be produced and measured at pressures somewhat lower than for CH₃CF₂Cl or ethyl acetate.

Experimental Details

Most of the experimental produces are described elsewhere [1–3]. The CO₂ laser frequencies used to drive the reactions of ethyl acetate and *c*-C₄F₈ were 1052 and 948 cm⁻¹, respectively. Reaction rates were obtained in real time by monitoring the growth of an absorption band of a product (C₂H₄ for ethyl acetate, C₂F₄ for *c*-C₄F₈) during laser irradiation. Rate constants were obtained [1] from the change in reaction rate R with respect to input beam power P , and calculations of dR/dP were facilitated by the empirical

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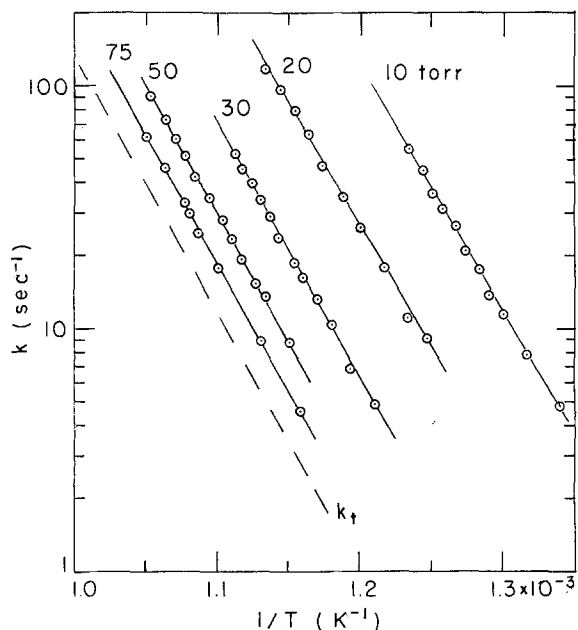


Fig. 1. Laser induced rate constant k vs. reciprocal translational temperature $1/T$ for ethyl acetate at various pressures. The dashed line is the thermal rate constant k_t .

observation that plots of $\log R$ vs. P^{-1} always gave straight lines within experimental error. Optical absorption coefficients were obtained from beam transmission measurements on short path length cells, extrapolated to zero path length. Translational temperatures were derived from interferometric effects on a He-Ne laser beam probe [2, 3]. The error in the average of a number of such measurements is estimated [2] as less than 1%, and the data presented here show a corresponding small degree of scatter.

Results and Discussion

Arrhenius plots of the laser-induced rate constant k vs. reciprocal translational temperature $1/T$ for the ethyl acetate and $c\text{-C}_4\text{F}_8$ reactions at various pressures are shown in Figs. 1 and 2. The dashed lines in the figures represent tabulated "preferred" Arrhenius expressions derived from standard pyrolysis [5]. With k_t denoting the thermal value of rate constant and R the gas constant in kcal/mole, these expressions are $\log k_t = 12.59 - 48.0/(2.303RT)$ for ethyl acetate and $\log k_t = 16.0 - 74.3/(2.303RT)$ for $c\text{-C}_4\text{F}_8$.

We note that the slopes of all data plots in Figs. 1 and 2 correspond to activation energies that are within 1% of the tabulated thermal values. The ratios k/k_t are independent of T and become progressively larger than unity as reactant pressure is reduced. Exactly the same behavior was observed [3] in the unimolecular decomposition of $\text{CH}_3\text{CF}_2\text{Cl}$ and was attributed to an effective vibrational temperature T_v which exceeds the translational temperature T , where T_v is defined as the

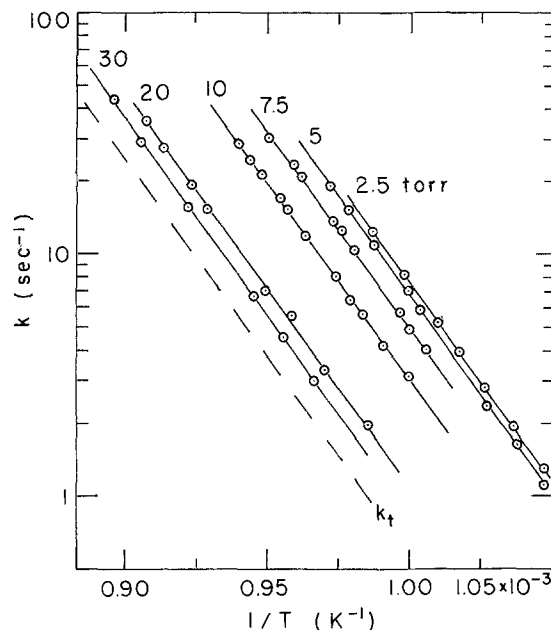


Fig. 2. Laser induced rate constant k vs. reciprocal translational temperature $1/T$ for perfluorocyclobutane at various pressures. The dashed line is the thermal rate constant k_t .

temperature required in the Arrhenius expression to provide the observed value of k . To characterize the departure from thermalization, we choose the quantity $1/T - 1/T_v$ which is proportional to $\log(k/k_t)$ and therefore depends on pressure but not on T .

Figure 3 shows the variation of $1/T - 1/T_v$ with reactant pressure for ethyl acetate and $c\text{-C}_4\text{F}_8$; also included are data for $\text{CH}_3\text{CF}_2\text{Cl}$ from [3]. $\text{CH}_3\text{CF}_2\text{Cl}$ exhibits the largest departure from thermalization, but even at 10 Torr the vibrational temperature exceeds the translational temperature by only 20%, which roughly corresponds to 70% of the energy of one infrared laser photon.

The significant feature of Fig. 3 is the tendency in each compound for $1/T - 1/T_v$, or the departure from thermalization, to saturate at low pressure. Phenomenologically, this is not what one might expect for the steady-state balance of rates of excitation (by photon absorption) and deexcitation (by VT transfer). Absorption varies as the first power of molecular density while VT transfer, a collisional process, is proportional to density squared. Accordingly, with decreasing pressure the degree of nonthermalization should continue to increase and should not saturate. Therefore, the behavior of the data suggests that the VT transfer probability per collision grows rapidly as $1/T - 1/T_v$ increases.

Analogous behavior has been noted in certain shock-tube experiments on diatomic molecules [6-9] and in the relaxation of SF_6 following excitation by a TEA CO_2 laser [10]. In these pulse-type experiments the VT

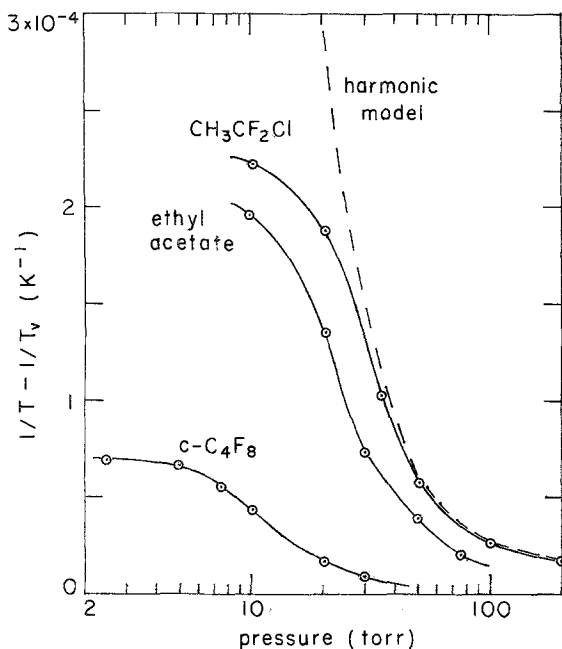


Fig. 3. Laser induced deviation from thermalization, represented by $1/T - 1/T_v$, as a function of reactant pressure for three compounds

relaxation time decreased markedly with increasing difference between vibrational and translational temperatures. To account for the shock tube results, Losev et al. [9] developed a model for the net rate of VT transfer from an anharmonic vibrational mode. The same model was applied [10] to the SF_6 data by assuming for simplicity, as others [11] have done, that VT transfer in polyatomics occurs predominantly through a single low frequency vibrational mode.

In a similar fashion we find that the model provides a good fit to the present results. From available spectroscopic data [12–14] the low-lying vibrational mode frequencies of $\text{CH}_3\text{CF}_2\text{Cl}$, ethyl acetate and $c\text{-C}_4\text{F}_8$, respectively, were taken as 272, 146, and 86 cm^{-1} . Other model parameters were chosen on the basis of best fit and the values used seem quite reasonable. In particular, the anharmonicity factors, expressed as the fractional decrease in the separation between successive vibrational levels, were taken as 0.04, 0.05, and 0.08 for the compounds in the above order. Also, the quantity representing the average number of collisions required for one VT deactivation between the first excited and ground states, often designated as Z_{01} in the literature, was chosen to have the respective values 65, 58, and 39. For the frequencies of the low-lying modes involved here, these values of Z_{01} are entirely consistent with those reported for other polyatomics [4, 15]. The resultant calculations from the model are exhibited by the solid curves in Fig. 3.

Despite the excellent fits to the data, we emphasize that the model itself should not be taken too seriously since

several gross approximations are involved. These include the use of the Landau-Teller form for calculating the effect of anharmonicity on VT transition probabilities [9] and the neglect of contributions to the overall VT transfer rate from the large number of closely spaced excited vibrational states of other modes in polyatomics (often called the quasi-continuum). Nevertheless, the model has some instructional value. When anharmonicity is removed, the model produces results exemplified by the dashed curve in Fig. 3. Such "harmonic model" curves do *not* saturate at low pressure and therefore are quantitatively incapable of matching the data. Thus, the saturation effects exhibited by the data are mimicked by an oversimplified model whose key feature is a progressive decrease in the energy separation of higher lying vibrational levels. In turn, this suggests the importance of the vibrational quasi-continuum in polyatomics in determining the overall VT transfer rate at elevated vibrational temperatures.

In the treatment of our data, we have ignored corrections to account for the fact that unimolecular reactions depart from simple first-order kinetics at low pressures. From RRKM calculations and available experimental data it can be estimated that for the compounds and pressure ranges used here, the corrections would modify the shape of the curves in Fig. 3 only slightly and therefore would not obviate the saturation effects as indicated.

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