Vibrational to Translational (V-T) Energy Transfer of Highly Excited Pentafluorobenzene (C₆F₅H): Dependence on Deactivator Mass

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Intermolecular collisional energy transfer from vibrational to translational (V-T) plays a crucial role in many physical phenomena including chemical kinetics and transport properties. Studies have been carried out into ways of dissipation of the vibrational energy in gases and liquids, rules of conversion, and the distribution of energy between vibrational modes in polyatomic molecules. Depending upon the complexity of the collision partners, different degrees of freedom which act as energy sources and/or sinks may be involved in the transfer: translational (T), vibration (V), rotation (R), and electronic (E). A variety of experimental techniques have been developed to obtain energy transfer information; monitoring either E_{vb} or E_{trans}. In the past decades, techniques involving UV absorption (UVA) and IR fluorescence (IRF) have been used to measure the vibrational energy removal, while thermal lensing, interferometry, mercury tracer, and optoacoustic technique have been employed for translational energy removal. In this report, we limit ourselves to molecule in their ground electronic state, which on gas-phase collision converts vibrational to translational (V-T) energy.

The V-T energy transfer upon gas phase collisions for a diatomic substrate and monatomic deactivator at low levels of excitation is well established. However for polyatomics the V-T energy transfer at energies comparable to that needed for reaction has not been fully developed. In general for polyatomics at low levels of excitation the probability for energy transfer increases: i) as the lowest vibrational frequency decrease, ii) the excitation energy increases and iii) as the mass of the collider decreases. For polyatomic molecules at high levels of excitation (comparable to that for chemical reaction) the probabilities are larger than those reported for diatomics.

The categorization of large and small molecule, and high and low energy have been artificially introduced; a unified theory must connect these categories. A qualitative explanation for the different behavior has been presented. The purpose of this work is intended to detect the rate constant of V-T energy transfer between substrate and deactivator (eq. 1) by time-resolved optoacoustics (TROA). The substrate, C₆F₅H (PFB, Aldrich, 98.0%), with a series of bath gases (M: He, Ne, Ar, Kr) as deactivator was examined so that the
importance of bath gas mass could be evaluated, semi-quantitatively.

\[
PFB \left( E_{fb}^* \right) + M \left( E_{ram} \right) \xrightarrow{\text{energy transfer}} PFB \left( E_{vb} \right) + M \left( E_{trans}^* \right)
\]

**EXPERIMENTAL**

In the TROA technique a pulsed CO\(_2\) laser excites the PFB via multiphoton process which was expanded and diluted with the specified bath gas (Air Product: Ar, 99.995%; He, 99.995%; Ne, 99.99 \%; Kr, 99.995%). The excited PFB undergoes the V-T relaxation producing an acoustic wave, and it propagates radially from the excitation cylinder.

A piezoelectric transducer placed within the excitation cell is used to detect the nascent pressure wave. The ratio of the amplitude of the rarefaction (\(I_1\)) to the condensation (\(I_2\)) wave is a known function of system parameters (laser beam radius) and the V-T relaxation time (V-T). In describing the acoustic response of the medium it is convenient to define the dimensionless quantity

\[
\varepsilon = \frac{I_1}{I_2} = \frac{\rho v}{\eta T - \gamma}
\]

where \(r\) is the radius of the cell and \(v\) is the speed of the sound, \(\varepsilon\) is simply the ratio of the energy relaxation rate to the acoustic propagation rate.

The TROA is usually performed in a small cylindrical cell with a microphone mounted flush with the interior curved surface. A laser pulse aligned along the cylinder axis excites some fraction of the PFB in the cell. The relaxation of the molecules produces a pressure rise that is modulated by the natural acoustic frequencies of the cell. The rise time of the envelope of the resonant oscillators equals the time constant for energy relaxation in the medium.

A schematic diagram of experimental setup for TROA is shown in Fig. 1. Specific details for the apparatus and procedure used in these experiments are given below. A pulsed transversely excited atmospheric (TEA) CO\(_2\) laser (Tachisto model 215 G) tuned to 10.6 \(\mu\)m with a top hat intensity profile was used as the excitation source; its energy was determined with a Gentec Joule meter (model 500-D). An iris aperture (0.09–0.3 cm) was placed between the laser and cylindrical cell. The pressure wave was monitored with a piezoelectric transducer (International Transducer Corp. Model PK14-14) mounted \(~5\) cm from the center of the irradiated cylinder equipped with NaCl cell in entrance and exit windows. The signal was amplified (Tektronic model AM-502 differential amplifier) and captured to be digitized with a Biomation (model 805) transient recorder, and then averaged (\(~200\) shots with a repetition rate of 1 Hz) with an EG&G 4203 signal averager. The stored data was then transferred to a strip chart recorder for hardcopy (Honeywell). The observed peak height ratios were converted to \(P\), where \(P\) is total pressure, by the theoretically generated curve (the laser beam radius and the calculated sonic velocity).

**RESULTS AND DISCUSSION**

The substrate PFB and bath gases were prepared by the mole fraction ranging from 0.05% to
0.99% in advance and mixed for 45 min at 23°C. The mole fraction used here was due to large self-
relaxation between substrates (PFB*+PFB) such as vibrational to vibrational (V-V) and/or to trans-
lational (V-T) relaxation(s). The self-relaxation can be ruled out by employing the PFB mole frac-
tion less than 2%. For mole fraction larger than 2%, there was considerable increase in Pt value, 
indicating that the larger portion of vibrational energy stored in PFB dissipated to another modes 
of the PFB. Consequently, only the data for the highest dilution were used here to calculate the 
Pt values.

The relaxations of vibrationally excited PFB with \( \langle n \rangle \), where \( \langle n \rangle \) is the number of photon 
absorbed per PFB molecule, ranged from 2 to 23 by He, Ne, Ar and Kr deactivators were moni-
tored. Two methods were employed to increase the range of \( \langle n \rangle \). Firstly \( \langle n \rangle \) was increased by raising 
the bath gas pressure. Since PFB, like many other molecules, exhibits rotational hole filling (the rota-
tional level of the pumped mode initially depleted by the laser is rapidly repopulated via collisional 
energy redistribution), increasing the pressure of the bath gases at constant laser fluence has the 
effect of increasing the value of \( \langle n \rangle \). Secondly it is based on the red shift in the frequency of the 
pumped mode after the initial photon is absorbed. This allowed us to increase \( \langle n \rangle \) by tuning the la-
er to the red of the pumped mode. This is based on the assumption that redistribution of energy 
among the rotational levels of the initially excited state occurs rapidly as compared to vibrational re-
relaxation of that state. An explanation of the \( \langle n \rangle \) dependences of \( \mathbf{E}/\lambda_n \) for all bath gases indicate 
that the relaxation rate constant \( (P_t)^{-1} \) is not energy dependent, representing the exponential decay 
of the excited PFB. Similar observation was seen with perfluoroalkane series.\(^8\) For a given fluence 
the absorption was independent of deactivator pressure (10~800 torr) as shown in Fig. 2. Efforts 
were made to obtain very low \( \langle n \rangle \) region, but the region of \( \langle n \rangle \) less than 7 was never obtained 
owing to the low lying quasicontinuum states. This pressure independence indicates that the V-T 
energy relaxation for PFB/bath gases system is first-order. This is characteristic of a unimodal 
distribution, i.e. the energy distribution is not bi-
modal. It is generally assumed that a Poisson distri-
bution is formed.\(^16\) The high density of internal 
eigenstates for PFB also supports the idea that most 
absorbing molecules are initially in the quasi-continuum. Hence, Letokhov's expectation\(^11\) 
that an excitation bottleneck is absent for this la-
arge molecules seems to be demonstrated. In con-
trast to this, the multiphoton excitation of SF\(_6\), 
SiF\(_4\), CH\(_3\)Br,\(^16\) CH\(_3\)Cl,\(^16\) CF\(_3\)Cl,\(^16\) CF\(_3\)HCl,\(^16\) and CF\(_3\)\(^13\) 
appears to generate a bimodal distribution at low 
average energies. The Pt values of multiphoton-
excited 1,1,2-trifluoroethane (C\(_3\)F\(_2\)H)\(^11\) was repro-
duced and was in semiquantitative agreement with 
reported value using IRF. For a fluence of 2 J/cm\(^2\) 
and argon/C\(_3\)F\(_2\)H\(_3\) dilution>40/1, IRF data give 4.0 
\( \pm 0.8 \) \( \mu \text{sec-torr} \) while with TROA it was 2.6\( \pm 0.6 \) 
\( \mu \text{sec-torr} \). This difference is probably attributable 
to what is monitored (vibrational energy removal 
in IRF and translational energy of bath gas in 
TROA). In the case of TROA, the increase in trans-
lational energy is probed while with IRF the relax-
ation of the vibrational energy of the substrate 
is observed. If only V-T is allowed, then these 
energy will give comparable Pt values. The Pt va-
value for PFB/Ar is also comparable with that of 
Gordon's result (22.2\( \pm 1.4 \) \( \mu \text{sec-torr} \))\(^9\) and Hg tra-
cer (19.0\( \pm 5.0 \) \( \mu \text{sec-torr} \)).\(^16\)

The average Pt (\( \mu \text{sec-torr} \)) is 14.9\( \pm 2.2 \), 21.5\( \pm 
2.8 \), 25.2\( \pm 2.5 \), 28.6\( \pm 3.1 \) for PFB with He, Ne, Ar

\[ \text{Fig. 2. Plot of number of photons absorbed by substrate (C}_3\text{F}_2\text{H} \text{ vs. pressure of bath gas.} \]
and Kr, respectively. These bath gases only possess a transla
tional degree of freedom. Average \( P_t \) values increased as the bath gases in-
creased. PFB/He showed a fastest relaxation process with a smallest value of \( P_t \). The Total pressures were changed from 10~40 torr with base pressure of PFB as 0.2 torr. As illustrated in Fig. 3, for hard sphere collisions, there is a monotonic increase in \( P_t \) from helium to krypton. Theoretically, \( P_t \) is a function of the encounter rate, interaction potential, impulsiveness of the collision, and the internal characteristics of the PFB and bath gases. Thus, the encounter rate should depend upon the reduced mass of the colliders. Information on the relative importance of the interaction potential and mass to the \( P_t \) value can be determined by comparing the bath gases. If the \( P_t \) for energy transfer was related solely to the duration of the encounter then helium due to its highest relative velocity would be the most efficient, i.e. an impulsive collision; this is not the case. Nevertheless, due to the lowly lying vibrational modes for PFB impulsive encounters may play an important role in the mechanism for V-T energy transfer in these systems. The maximum in the \( P_t \)-mass plot (not shown) at largest bath gas mass may be attributed to impulsive collisions with a match of the bath gas to the mass of a pseudo atom in the PFB.

In summary the results of the TRQ experiments indicate that the observed \( P_t \) for PFB are independent of excitation energy. The relaxation rate constant \((P_t)^{-1}\) is found to be sensitive to the mass of the bath gases. Due to the low vibrational frequency modes of and high density of states of PFB, impulsive collisions and no bottleneck seem appropriate.

REFERENCES
