단　　신

높이 여기된 플루오르메탄(CH₃F)의 진동이완 : 적외 다광자 여기법

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(1996. 5. 16 접수)

Vibrational Relaxation of Highly Excited Fluoromethane(CH₃F): Infrared Multiphoton Excitation

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(Received May 16, 1996)

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.[1] 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_{Vib} or E_{Trans}. In the past decades, techniques involving UV absorption (UVA)[2] and IR fluorescence (IRF)[3] have been used to measure the vibrational energy removal, while thermal lensing,[4] interferometry,[5] mercury tracer,[6] and optoacoustic techinique[7,8] have been employed for monitoring translational energy removal. In this report, we employed time-resolved optoacoustic technique (TROA) and limit ourselves to molecule in their ground electronic state, which on gas-phase collision converts vibrational to translational (V-T) energy.

The energy transfer (V-T) for a diatomic substrate and monatomic deactivator is well established.[1] However for polyatomics the V-T energy transfer at energies comparable to that needed for reaction has not been fully developed. For the case of low level of excitation, the energy transfer probability generally increases i) as lowest vibrational frequency decreased, ii) at the high excitation energy, and iii) with smaller mass collider. Hence, the energy transfer probabilities for polyatomics are greater than those for diatomics.[1] More detailed explanation for the different behavior of small and large molecules has been described elsewhere.[2,3,9] This work was intended to detect the rate coefficient of V-T energy transfer and to demonstrate the relaxation behavior of so-called medium-sized molecule (5 atoms) of CH₃F.

EXPERIMENTAL

The whole schematic diagram is shown in *Fig.* 1. The CH₃F substrate (PCR, research grade) mole fraction from 0.05% to 0.90% was used here. The use of this mole fraction range was to prevent self-relaxation between CH₃F molecules such as vibrational to vibrational (V-V) and/or V-T relaxation(s). A pulsed CO₂ laser (Tachisto model 215G), operating at 9.6 m (P(20)) for CH₃F with 1.2 0.1 mm beam radius, excites a cylinder (5 L) of substrate diluted with argon bath gas (Air Product 99.995%). For time-resolved optoacoustics(TROA),
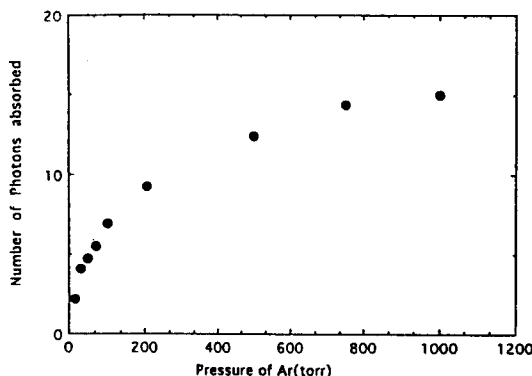
Fig. 1. Schematic diagram of experimental setup for TROA.

when the laser beam goes through the center of the cell, highly excited CH_3F was considered as an ensemble whose walls are both heat conducting, permeable to the passage of molecule. After equilibrium is reached, the entire ensemble is isolated from its surroundings (nonexcited gases). The highly excited CH_3F undergoes V-T energy transfer with argon gas as shown in Eq. 1.

$$CH_3F(E_{Vib}{}^*)+Ar(E_{Trans}) \xrightarrow[\text{monitor}]{\text{energy transfer}} CH_3F(E_{Vib})+Ar(E_{Trans}{}^*) \quad (1)$$
$$\text{excited}$$

When the excited CH_3F relaxes (V-T), it produces an acoustic wave and 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_-) to the condensation (I_+) wave is a known function of system parameters (laser beam radius) and the V-T relaxation time.[7,8]

$$P\tau_{V-T}=rP/v\varepsilon \quad (2)$$

where r is the radius of the cell and v is the speed

of the sound. ε is simply the ratio of the energy relaxation rate to the acoustic propagation rate. P is total pressure. τ_{V-T} is a relaxation time for V-T energy transfer. The observed peak height ratios (I_-/I_+) can be converted to $P\tau$ (relaxation time) by the theoretically generated curve.[7] A Gentec Joule meter (model 500-D) was used to determine the absorbed energy. The signal was amplified (Tektonic model AM-502 differential amplifier) and digitized using a Biomation transient recorder (model 805), and then the output was averaged upto 200 shots. Chart displayer (Honeywell 193) was used for obtaining a hardcopy of the signal.

RESULTS AND DISCUSSION

The relaxation of vibrationally excited CH_3F with the average energy absorbed per CH_3F molecule(n) ranging from 2 to 12 by Ar bath gas was monitored. For given fluence of 0.8 J/cm^2 (fluence was varied using CaF_2 flats between the laser and iris aperture), the n was revealed as a function of Ar pressure as shown in *Fig.* 2. Constant composition mixture of CH_3F and Ar was irradiated as a function of total pressure for a given photon fluence. The average number of photons calculated from the amount of energy absorbed increased with Ar pressure and leveled off at approximately 1000 torr. This behavior is characteristic of a bimodal energy distribution. Using time-resolved optoacoustic technique(TROA), Beck and Gordon have reported the similar relaxation pattern of CH_3Cl and CH_3Br by argon.[10] However those investigations were limited to low excitation energy below 9000 cm^{-1}, hence approximate bottleneck region was not measured in those case so that absolute comparison was not made. In case of CH_3F, it reached high excitation energy over 13,000 cm^{-1} by adjusting pressure of argon bath gas. Aslo it can be compared with lowest vibrational frequency differences between C-F, C-Cl, and C-Br in terms of initial energy distribution. The initial energy distribution is made up of those molecules in which energy remains in the absorbing mode (9.6 μm) and those in which the energy is distribu-

Fig. 2. Plot of number of photons absorbed by substrate (CH_3F) vs. pressure of bath gas.

Fig. 3. Plot of P (sec-torr) vs. number of photons absorbed by substrate (CH_3F).

ted between all vibrational modes. At sufficient excitation energy the bimodal distribution becomes a cannonical distribution; likewise sufficient pressure provide a mechanism for collisionally assisted relaxation.

The $P\tau$ value for CH_3F/Ar system was found to be dependent significantly on n. Plot of $P\tau$ vs. number of photon absorbed is shown in Fig. 3. At low excitation energy $(2<n<9)$ the relaxation time $P\tau$ decreased as n increased, indicating non-exponential decay of the excited CH_3F. This result suggests that for energies $n>9$ the average amount of energy transferred per collision is linear with the average internal energy. The $P\tau$ value (780 sec-torr) was not changed upon variation of n at high excitation energy $(n>9)$ as shown in Fig. 3. This observation means that the bottleneck between discrete level and quaisicontinuum level obviously exist at approximately 9000 cm^{-1}, since $P\tau$ values started to be saturated at this energy. Generally for upto 4 atomic molecules, excitation occurs via resonantly enhanced multiphoton steps and little population of excited states is achieved due to lack of resonances (discrete region dominates).[9] As one progress to larger molecules, the quasicontinuum gradually reaches down to lower excitation energies, for the largest, heaviest species, like C_6F_5H[8] and perfluorinated alkane,[11] most molecule in a thermal ensemble at room temperature are already in the quasicontinuum. The bottleneck effect leads to a bimodal distribution. Such
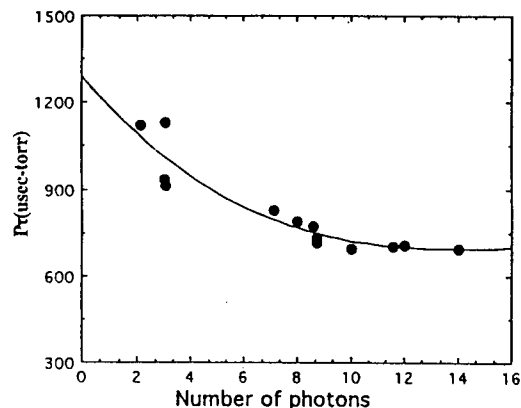
behavior can often be seen in the medium-sized polyatomic molecules such as CF_2Cl_2 (69 sec-torr),[12] CF_2HCl (87 sec-torr),[12] SF_6 (210 sec-torr),[7] and SiF_4 (19 sec-torr)[8] by TROA method. The $P\tau$ of CH_3F at comparable energy is 746 esc-torr. The deactivation of the excited CH_3F by Ar results from a combination of relaxation processes occurring through the two lowest vibrational levels, $v=1$ of both the v_3 (1048 cm^{-1}) and v_6 (1195 cm^{-1}) modes.[13] However, vmin for CF_2Cl_2 is 261 cm^{-1}, which indicate very low doorway vibrational frequency for energy relaxing. The larger vmin (lowest vibrational frequency) for the hydrogen containing methanes may account for the order of magnitude increase in $P\tau$ compared to CF_2Cl_2.

Comparison was made for CH_3F/Ar system for IRF[13] and TROA. A great deviation in $P\tau$ values was seen depending on the methods employed. Although IRF is especially powerful in probing the initial equilibration among the various vibrational modes by fast V-V transfer, measurement of the relaxation from the excited vibrational manifold to the ground state by this technique gives less detailed information. It just gives an average time for the conversion of vibrational into rotational and/or translational energy. Hence, the P value of IRF for CH_3F/Ar system gave a 1695 sec-torr, which is greatly different from that of TROA (746 sec-torr) even at comparable high excitation energy. The explanation for the difference in relaxa-

tion time or rate constants measured is that different relaxation processes are probed by two methods. Both methods should exhibit comparable relaxation times if the underlying physical process is simply a direct transfer of vibrational energy into translation.

In summary, vibrational (low and high energy) excited CH$_3$F created by multiphoton excitation with a CO$_2$ laser; the average energies were measured in the range of 2,000 to 13,000 cm^{-1}. Vibrational to translational relaxation time for the deactivation of the CH$_3$F by the argon bath gas was determined by monitoring the translational energy uptake via TROA.

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