BNL-27999

V-V Energy Transfer From High Vibrational Levels of Propynal*

CONF-801201--1

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Abstract

Relative cross sections for energy transfer from high vibrational levels

$$C_3H_2O \xrightarrow{nh\nu} C_3H_2O \ (v > 1)$$

$$C_3H_2O \ (v > 1) + M \longrightarrow C_3H_2O \ (v=1) + M + \Delta E$$

have been measured directly for the first time using visible - IR double resonance in a molecular beam - gas experiment.

* Research carried out at Brookhaven National Laboratory under contract with the U. S. Department of Energy and supported by its Office of Basic Energy Sciences

DISCLAIMER

V-V Energy Transfer From High Vibrational Levels of Propynal

Vibrational energy transfer in polyatomics has been studied extensively by a number of techniques.[1] Microscopic detail on the mode-to-mode flow of energy at low levels of excitation (~ 1000 cm^{-1}) reveals certain propensity rules to be important. It is found, for example, that V-V energy transfer cross sections in the ground electronic state are generally small (less than gas kinetic) except in cases where the energy gap between the pumped and accepting modes is small (rates ~ gas kinetic). At very high energies (> 20,000 cm^{-1}) near dissociation, energy transfer observed on a macroscopic level becomes exceedingly rapid, but detail on the mode-to-mode pathways is lacking. At intermediate levels of excitation, intuition based on knowledge of the low and high energy regimes serves as the only guide for estimating rates of energy transfer.

Recently we reported[2] results on infrared multiphoton absorption in propynal in which changes in the vibrational populations of ν_6 (v=1,2) and ν_{10} (v=1,2) pumped under molecular beam or fast flow conditions were observed. By producing a vibrationally excited beam of propynal and allowing for subsequent collisions with added gas molecules, we have now been able to study V-V energy transfer processes which occur on a time scale $\geq$ gas kinetic and are described by the general equation

$$C_3H_2O\ (v > 1) + M \longrightarrow C_3H_2O\ (v=1) + M + \Delta E \qquad (1)$$

A molecular beam, defined by a skimmer and further collimated by two apertures, is pumped on axis with a CO_2 laser at a fluence of ~ 2.3 J/cm^2 (peak power 12 MW/cm^2) and a frequency of 951 cm^{-1}. Under these laser conditions the ν_6 mode (≡C-C-stretch) is populated with an average of 4-6 photons/molecule, measured by absorption under bulb conditions. The

scattering chamber is filled with an appropriate collision partner at pressures of .5 to 5 x 10^{-4} torr with the structure of the collider varied to determine the effect of relative vibrational frequencies on energy transfer. A tunable dye laser is used to probe the population of ν_6 (v=1) at a fixed delay with respect to the pump laser. The delay is also scanned at a fixed collider pressure from 50 ns to > 10 μs. In addition, non-driven modes below 1300 cm^{-1} are examined with the probe laser in the same manner that the pumped mode is examined.

The results are summarized below:

(1) On a single collision time scale, V-V energy transfer down the vibrational ladder only occurs within the pumped mode within the limits of detection and sensitivity. The v=1 level of ν_6 is observed to increase up to 100% of the level, produced by the CO_2 laser in the absence of collision partners. Time resolved studies from 50 to 400 ns after the CO_2 laser pulse show this not to be collision-related enhancement of IR laser pumping.

(2) V-T energy transfer does not occur when argon is the collision partner, i.e., there are no changes in ν_6 greater or less than those induced by the CO_2 laser and population of the nearby mode ν_{10} (ΔE = 35 cm^{-1}) is not observed.

(3) By varying the pulse duration at fixed CO_2 laser energy and hence the peak power, the initial population of ν_6 (v=1) is observed to change as well as the enhancement of ν_6 (v=1) due to collisional energy transfer. For example at a peak power of 12 MW/cm^2, the population of v=1 of ν_6 is enhanced by 30% when CO is the collision partner, but unchanged within experimental error, when the peak power is 5 MW/cm^2. This observation is further

confirmation that energy transfer from energy levels > v=1 is occurring.

(4) Enhancement in the v=1 level of ν_6 through collisions is efficient for molecules having vibrational frequencies around 900, 1050, and 2000 cm^{-1} as determined from the relative rate constants for equation 1. Molecules as CCl_4 or CH_4 appear to be inefficient energy transfer partners on a single collision time scale. The effective rate constants on which the relative rate constants are based are difficult to compare with other experiments because they are uncorrected for relative velocities of the collision partners. However, it is quite clear that these rates exceed gas kinetic rates and are due to long range interactions. The relative rates are both in agreement with and at odds with the propensity rules derived from low energy studies. Only collision partners for which ΔE in equation (1) is small are effective, although the actual number of quanta exchanged is not yet determined. That ν_6 (944 cm^{-1}) and ν_{10} (980 cm^{-1}) are not equilibrated is puzzling and suggests that other factors beside the energy gap (nuclear motion and symmetry, for example) are important. These factors and the absolute magnitudes of the cross-sections are currently under study.

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