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Trapped Metastable Vibrational Energy Distributions in Laser Pumped Molecules

Sir:

Although certain molecules[1] (e.g., CO_2, N_2O, and SO_2) are known to require many thousands of collisions to transfer energy between vibrational modes, such an occurrence is in fact a rarity. Indeed, for the kinds of molecules and pressure regimes used in many laser decomposition experiments,[2,3] complete intermode energy equilibration involving the *entire* vibrational manifold is expected to occur within a laser pulse-width.[4,5] Thus the achievement of mode specific or bond specific laser driven chemical reactions under such conditions is expected to be difficult. Nevertheless, for at least some laser pumped molecules, intermode relaxation processes can lead *naturally* to localization of energy in a small number of vibrational modes. Such distributions require thousands of collisions to reach equilibrium with the translational and rotational degrees of freedom. Thus the normal energy distribution characterized by a single temperature that is expected for a gas heated by a Bunsen burner does not necessarily apply to a laser pumped gas. Pulsed laser heating leads automatically to a substantial separation of vibrational and translational temperatures which lasts for a time of the order of the overall vibration–translation/rotation (V–T/R) relaxation time. In addition, the intermode energy equilibration processes which occur either during or shortly after the laser pulse almost always require the exchange of a *small* amount of energy with the translational degrees of freedom. Under such conditions the energy distribution in the vibrational modes cannot be described by a single temperature.[6,7] Nevertheless, once the dominant kinetic processes which couple the various vibrational modes are known, the vibrational temperatures of all the modes are well defined in the harmonic oscillator limit.[8] These features can lead to a highly localized metastable vibrational energy distribution as illustrated below for CH_3F, one of the few molecules for which vibrational energy transfer pathways have been reasonably well established.[9-13]

The laser excitation and subsequent dominant vibrational equilibration pathways coupling the fundamental modes of CH_3F are as follows:[9-14]

Characteristic time	Reaction	
τ_p	$CH_3F(0) + h\nu_3 \rightarrow CH_3F(\nu_3)$	(1)
τ_{VV}	$CH_3F(\nu_3) + CH_3F \rightleftarrows CH_3F(\nu_6) + CH_3F - 133\ cm^{-1}$	(2)
	$CH_3F(\nu_6) + CH_3F \rightleftarrows CH_3F(\nu_2, \nu_5) + CH_3F - 284\ cm^{-1}$	(3)
	$2CH_3F(\nu_2, \nu_5) \rightleftarrows CH_3F(2\nu_2, 2\nu_5) + CH_3F(0)$	(4)
	$CH_3F(2\nu_2, 2\nu_5) + CH_3F \rightleftarrows CH_3F(\nu_1, \nu_4) + CH_3F - 60\ cm^{-1}$	(5)
τ_{VT}	$CH_3F(\nu_3) + CH_3F \rightarrow CH_3F(0) + CH_3F + 1049\ cm^{-1}$	(6)

The typical laser pulse width τ_p is about 10^{-6} s while the four vibration–vibration (V–V) intermode equilibration processes (2–5) can be considered to reach steady state in about 75 gas kinetic collisions (7×10^{-6} s at 1 Torr).[10,14] However, the V–T/R process (eq 6), which restores an energy distribution characteristic of Bunsen burner heating, typically takes 15 000 gas kinetic collisions (1.4×10^{-3} s at 1 Torr) under low level laser excitation conditions.[11] Thus the highly specialized conditions which exist in laser pumped CH_3F at vibrational steady-state after a time τ_{VV} persist for a time τ_{VT} which is at least three orders of magnitude longer than τ_{VV}.

The steady-state equilibrium constant for process 2 in the time domain $\tau_{VV} < t < \tau_{VT}$ leads to the following relationship[6,7,12]

$$K_{eq} = e^{-133/kT'} = \frac{e^{-E_{\nu6}/kT_{\nu6}}}{e^{-E_{\nu3}/kT_{\nu3}}} \tag{7}$$

with T_{ν_i} defined by

$$N_{\nu_i} = N_0 g_{\nu_i} e^{-E_{\nu i}/kT_{\nu i}} \tag{8}$$

E_{ν_i}, T_{ν_i}, g_{ν_i}, N_{ν_i} are the energy, vibrational temperature, degeneracy, and population of level ν_i, respectively; n_0 is the ground state population, and k is Boltzmann's constant (cm^{-1}/K). T' is the steady state translational/rotational temperature which is less than the ambient temperature T since the intermode equilibration pathway for CH_3F requires a loss of translational energy.[15] Equation 7 merely illustrates that the equilibrium constant at steady-state is defined by the bath temperature T' whereas the vibrational state populations are defined by their respective vibrational temperatures or energies. Equation 7 gives immediately the result:

$$\frac{E_{\nu3}}{T_{\nu3}} - \frac{E_{\nu6}}{T_{\nu6}} = \frac{-133}{T'} \tag{9}$$

This analysis can easily be performed on the remaining V–V processes to yield equations relating the six mode fundamental temperatures with each other and the translational temperature. The remaining vibrational state temperatures are linear combinations of the mode fundamental temperatures in the harmonic oscillator approximation. In addition, the requirement of conservation of particles and total energy at steady state leads to a relation between the fundamental temperatures and the initial experimental conditions. The distribution of fundamental temperatures can thus be obtained in terms of the input laser energy by combining the temperature and conservation equations and solving iteratively on a computer.[16] Since the steady-state vibrational energy expressions are functions of the vibrational temperatures and under most conditions the translational/rotational energy can be expressed by its equipartition limit, $3kT'$, the entire steady-state energy distribution can be calculated for laser pumped CH_3F. These calculations are valid in the time range $\tau_{VV} < t < \tau_{VT}$ ignoring

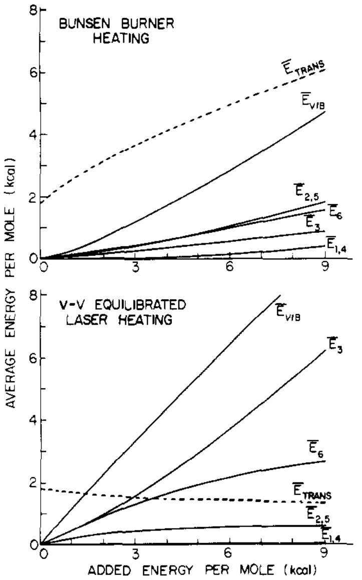

Figure 1. (Upper) Plot of the average energy in the translational, rotational, and vibrational degrees of freedom of CH_3F vs. added energy. A Boltzmann equilibrium at a single temperature and harmonic oscillator states are assumed. $\overline{E}_{TRANS}$ is the sum of the translational and rotational energies, $\overline{E}_{VIB}$ is the total average vibrational energy, and $\overline{E}_i$ is the mean vibrational energy of mode i. (Lower) Plot of the average energy distribution in CH_3F vs. laser input energy for a system at vibration-vibration equilibrium obeying the energy transfer mechanism of eq 1-5; 3 kcal per mole is equivalent to 1 laser photon absorbed per molecule. The calculated curves neglect vibration-translation/rotation relaxation.

anharmonic effects and radiative cooling via spontaneous emission.[17]

Figure 1 presents a comparison of the Boltzmann equilibrium energy distribution in CH_3F with the laser induced steady-state distribution for the input energy range equivalent to 0-9 kcal/mol (0-3 photons absorbed per molecule). The upper plot represents the case where the added energy is divided among the various degrees of freedom according to the equilibrium equipartition, Boltzmann description. Compared to any particular vibrational mode the translational and rotational degrees of freedom receive the majority of the added energy. Yet the energies of the vibrational degrees of freedom do not change greatly their absolute or relative values compared to ambient conditions. The lower plot representing the pulsed laser heated, V-V equilibrated case differs substantially from the Bunsen burner-like expectations. Here the translational/rotational energy is slowly decreasing with increasing input energy reflecting the fact that the relaxation pathway is translationally endothermic. The rate of increase of vibrational energy, on the other hand, is markedly different for each mode. The C-H stretches ν_1,ν_4 receive practically no excitation while the C-F stretch ν_3 is overwhelmingly enhanced compared to the remaining vibrational modes, particularly at excitation levels greater than 4.5 kcal/mol (1.5 photons per molecule). Therefore CH_3F in this high exctation regime will trap most of the input laser energy in the ν_3 mode for a period lasting for thousands of gas kinetic collisions. The overall features of the distinctive laser induced energy distribution of Figure 1 have also been observed experimentally.[18] Similar results have been obtained independently for laser pumped CCl_3F[19] using the CH_3F model[18] and an assumed energy transfer path with constant translational temperature.

The assumption of a vibrational steady state in which the molecular modes are equilibrated with each other but not with the translational and rotational degrees of freedom is not the only model nor the only effect which can lead to vibrational energy localization.[20] Nevertheless, the effects which are described here for CH_3F are quite general. Any laser pumped polyatomic molecule which undergoes nonresonant mode-to-mode equilibration processes much faster than the overall V-T/R relaxation can exhibit highly localized metastable vibrational energy distributions.

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Kinetic Energy Release as a Transition State Probe

Sir:

A central problem in chemistry is that of increasing our knowledge of transition states. There are clear advantages in using a molecular beam in studies of this problem, so that information, which might otherwise be lost due to collisions following the collapse of a transition state (as in solution experiments), can be conserved. The molecular beam approach can be employed using conventional magnetic sector mass spectrometers. In appropriate experiments, the unimolecular dissociations of ions are observed some 10^8 vibrations after their formation; reactions taking place so long after the ion formation ensure that there is little excess energy present in the transition state. Thus, in such experiments primary deuterium isotope effects are often large, and span the range found in solution experiments.[1] The most important advantage of the method is that if a dissociation involves a reverse activation energy, then the fraction of the reverse activation energy which appears as mutual repulsion of the products (the kinetic energy release) can be directly measured.[2]

Kinetic energy release profiles must contain useful information about transition state structures and geometries. For example, we have previously shown that symmetry-forbidden 1,2-eliminations of H_2 occur with relatively large releases of