Laser-induced diffusion by collisional redirection of molecules

N. M. Lawandy, W. S. Rabinovich, and R. P. Willner
Division of Engineering, Brown University, Providence, Rhode Island 02912
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We describe a new mechanism for generating macroscopic fluxes in polyatomics absorbing infrared radiation. The mechanism is based on the recoil kinematics which accompany the vibrational-translational relaxation of stretch-type modes. A five-level model is analytically solved, and expressions for the resultant flux are given. The excitation of the ν_3 asymmetric stretch of C_2H_2 in a Kr buffer gas is discussed, and flux magnitudes due to this mechanism are given.

INTRODUCTION

The phenomenon of laser-generated macroscopic flows in rarefied gases has been known since 1979.[1] This previously studied effect relies on the scattering-cross-section change which accompanies optical excitation. In 1981 a more detailed theory for two-level systems was developed.[2] More recently, models for laser-induced diffusion (LID) in polyatomic systems have appeared.[3,4]

The rate-equation model proposed in Ref. 4 indicated that a new mechanism for LID could exist in polyatomic systems. This effect, which we discuss in this paper is based on the dynamics associated with the relaxation of stretch-type modes. This mechanism is possible when vibrationally excited molecules (1) require collinear trajectories to relax and (2) collide with buffer gases massive enough to result in a velocity direction change accompanying the release of a vibrational quantum into translation. We will present a rate-equation-model solution for the flux generated and the criteria for observing this mechanism in real systems. The magnitudes of the LID fluxes for two-model systems (C_2H_2:Kr and CH_3F:He, CH_3F:Kr, and CH_3F:CCl_4) are also calculated. The C_2H_2:Kr system is expected to result in fluxes dominated by the collisional redirection mechanism while the CH_3F systems exhibit primarily cross-section-change effects.

THEORY

In a collision between a vibrationally excited (active) gas molecule and a buffer-gas molecule vibrational-

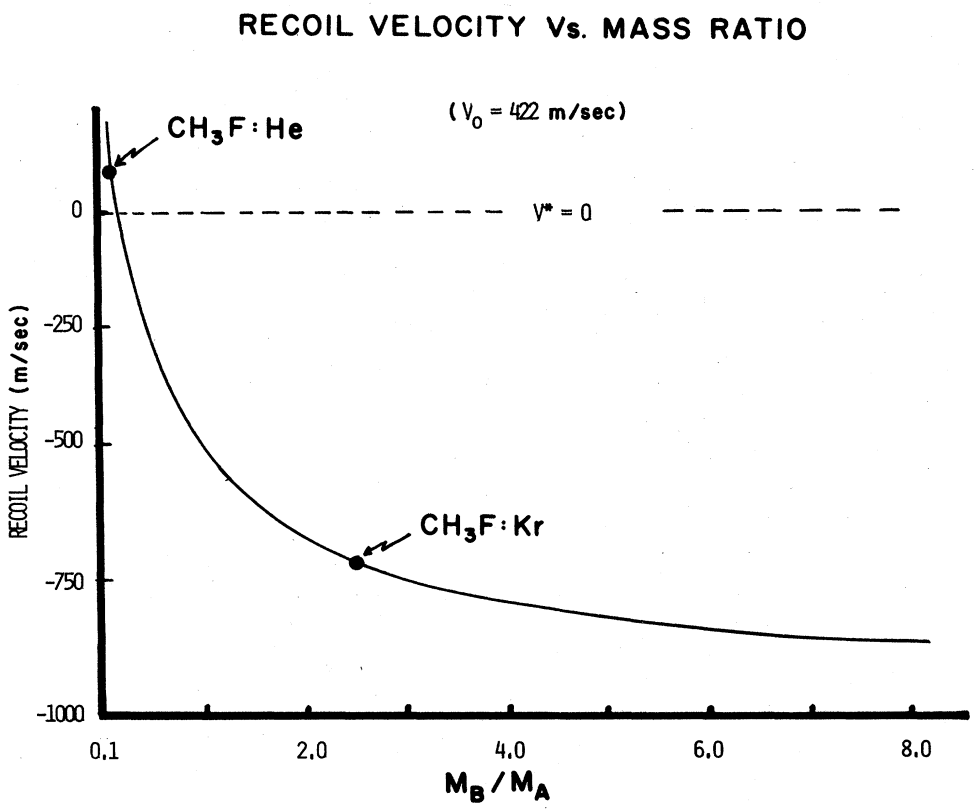

FIG. 1. Recoil velocity versus mass ratio.

translational relaxation may take place releasing as much as 20 kT ($T=300$ K) into translation. Furthermore, if the mode excited is a stretch mode such as the ν_3 mode of CH_3F or C_2H_2, the transition probability strongly favors a collinear trajectory.

The resultant speed of the active gas molecule, in a collinear collision, can be determined simply, through kinematics. Figure 1 shows the recoil velocity of CH_3F moving initially at 300 K thermal velocity for a range of buffer molecule masses. This calculation is based on the relaxation of the ν_3 mode of CH_3F which releases 0.13 eV. As can be seen, the buffer molecules that are heavier than CH_3F result in high velocity recoil. Krypton, for instance, results in a recoil at approximately twice the initial speed.

An asymmetry in the velocity distribution of the ground and excited states of the active gas molecule is created by selectively exciting a particular velocity group of the gas at some velocity V. The relaxation to the superfast velocity reversed state creates a bump at the superfast velocity V^* in the ground-state distribution. This velocity asymmetry creates a flux in a direction opposite to that of the pump laser detuning.

Our model utilizes a five-level scheme which assumes that molecules rotationally equilibrate at a rate greater than or equal to the velocity equilibration rate. This assumption is justified from the kinetics point of view for polar species which interact via dipolar R^{-3} or R^{-6} long-range interactions and have small rotational constants as compared to kT. Furthermore, this constraint puts a *lower* limit on the LID flux generated as it fixes the rotational fraction at the equilibrium value. In equilibrium there is no net flux since the velocity distribution of the gas is symmetric. Flux is generated from the velocity groups of interest, V and V^*, only when the populations of these levels are different from their thermally equilibrated values. For this reason we split the populations of the V and V^* velocity group into two classes: thermally equilibrated population and the "differential" population present only when there is pumping. This differential population may be negative or positive as pumping may reduce or increase the occupation of a given velocity group relative to its equilibrium value.

The levels in our model are labeled by $|g\rangle$, $|e\rangle$, $|g^*\rangle$, $|E\rangle$, and $|G\rangle$ and have the following physical correspondences in the active species: $|g\rangle$ contains the differential population in the ground state V velocity group. $|e\rangle$ contains the differential population in the excited state V velocity group. $|g^*\rangle$ contains the differential population in the ground state V^* velocity group. $|G\rangle$ contains all equilibrated molecules in the ground state for all velocity groups. $|E\rangle$ contains all equilibrated molecules in the excited state for all velocity groups.

The model also utilizes the following rates and quantities: W_p, optical transition rate for $|g\rangle$ and $|e\rangle$; W_e, velocity equilibration rate between $|e\rangle$ and $|E\rangle$; W_g, velocity equilibration rate between $|g\rangle$ and $|G\rangle$; Γ, vibrational-translational rate for the $|E\rangle$ ensemble; $\eta\Gamma^*$, vibrational-translational rate for the transition from $|e\rangle \rightarrow |g^*\rangle$ (fraction with molecular axis oriented along the laser-beam axis); W^*, velocity equilibrium rate between $|g^*\rangle$ and $|G\rangle$; f, the fractional occupation of the vibrational-velocity group.

RATE EQUATION MODEL FOR LID

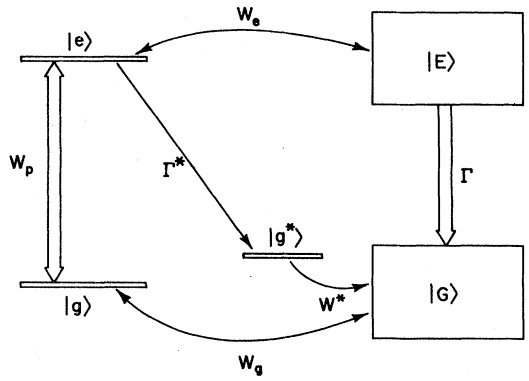

FIG. 2. Rate-equation model for LID.

The rates for W_g, W_e, and W^* are estimated from the linear approximation for a relaxing Boltzmann gas, given by Morse.[5] The rate Γ is taken from the experiments of various groups.[6–8] Γ^* is calculated from the known value of Γ and the Schwartz-Slawsky-Herzfeld- (SSH-) theory velocity-dependent rate.[9] The rate equation model is illustrated in Fig. 2. The rate equations which arise from the model are the following:

$$\begin{aligned}
&\dot{\rho}_e = W_p[\rho_g - \rho_e + f(\rho_G - \rho_E)] \\
&\quad -\eta\Gamma^*\rho_e - (1+f)W_e\rho_e + f\Gamma\rho_E \ , \ \dot{\rho}_E = w_e\rho_e - \Gamma\rho_E \\
&\dot{\rho}_g = W_p[\rho_e - \rho_g + f(\rho_E - \rho_G)] - (1+f)W_g\rho_g \\
&\quad -f\Gamma\rho_E - fW^*\rho_g^* \ , \ \dot{\rho}_g^* = -W^*\rho_g^* + \eta\Gamma^*\rho_e \qquad (1) \\
&\dot{\rho}_G = \Gamma\rho_E + \rho_g w_g + \rho_g^* w^* \ , \ \rho_e + \rho_g + \rho_G + \rho_E + \rho_g^* = \rho_{\text{tot}} \ .
\end{aligned}$$

LID FLUX MAGNITUDES

	FLUX (m^{-1} sec^{-1}) COMBINED	CROSS-SECTION	T(K)	P_{buff} (Torr)
CH_3F:He	3.23×10^{17}	2.37×10^{17}	300	35
CH_3F:Kr	9.86×10^{13}	7.78×10^{13}	200	2.2
CH_3F:CCl_4	10.41×10^{12}	10.22×10^{12}	300	1.2
C_2H_2:Kr	2.5×10^{11}	~0	200	0.5

CH_3F PARAMETERS	C_2H_2 PARAMETERS
$\delta\nu = -44$ MHz	$\delta\nu = -50$ MHz
$I_0 = 5$ W/cm^2	$I_0 = 5$ W/cm^2
$\Delta\nu_h = 20$ MHz	$\Delta\nu_h = 8$ MHz

FIG. 3. LID flux magnitude.

With the above model we may define a laser-induced flux $\vec{J}_{\rm LID}$ by $\vec{J}_{\rm LID}=(\rho_e+\rho_g)\vec{V}+\rho_g^*\vec{V}^*$.

Using the steady-state values calculated for ρ_e, ρ_g, and ρ_g^* we find a flux for our rate-equation system given by

$$\vec{J}\,\text{LID}=\frac{NW_p\Gamma f[W^*(W_g-W_e-\eta\Gamma^*)\vec{V}+\eta\Gamma^*W_g\vec{V}^*]}{\{W^*[(f-1)W_p-(1+f)W_g](\eta\Gamma^*-\Gamma)+W_g(\Gamma\eta\Gamma^*f(W_p-W^*)-W^*W_ef(\Gamma-2W_p)+W^*\Gamma(1+f)W_p)\}}\ . \quad (2)$$

A cross-section-change type flux can be incorporated into our model by making the rates W_e and W_g different. It can also be seen in the flux expression that the Γ^* relaxation mechanism acts to create an effective cross-section difference between the ground and excited states.

RESULTS

Our model predicts a relatively small effect from the redirective flux when $\eta\Gamma^*<W_e-W_g$, where η is an orientation average for the molecules with their axis aligned along the direction of laser propagation. In this regime LID is almost entirely due to cross-section change between the ground and excited state. The detuning from the active molecule's line center at which the most LID flux is observed is shifted by the presence of a redirective flux. When, however, the long-range part of the intermolecular potential dominates the *momentum* transfer cross section, the cross-section change between ground and excited states will be negligible and $W_e=W_g$. In addition the dominant contributions must come from the dispersion term since the permanent dipole term can result in sizable changes with vibrational excitation.[10] With these considerations in mind we are led to the choice of nonpolar, high polarizability buffer gases, and active gases with $kT/\epsilon\ll 1$ (ϵ is the Lennard-Jones potential-well depth) as good candidates for showing LID due primarily to redirective collisions. The C_2H_2:Kr system meets these criteria while CH_3F:Kr does not. Based on these considerations we would expect that the largest flux contributions for the C_2H_2:Kr system excited to the asymmetric stretch would come from redirection. Figure 3 shows the relative flux magnitudes for the systems discussed. Figure 4 shows the expected flux as a function of laser detuning in the C_2H_2:Kr system.

CONCLUSION

We have shown that a collinear collision between an active gas molecule and a buffer-gas molecule can cause the active molecule to recoil at substantial speed. This can result in a laser-induced flux. A five-level scheme can be used to model this effect and show that flux is produced both by the molecules in the superfast velocity state and by an *effective* cross-section change caused by the vibrational-translational relaxation mechanism. The model also allows for the standard cross-section-change type flux.

We predict that the magnitude of the redirective flux will be smaller than that of the cross-section-change flux

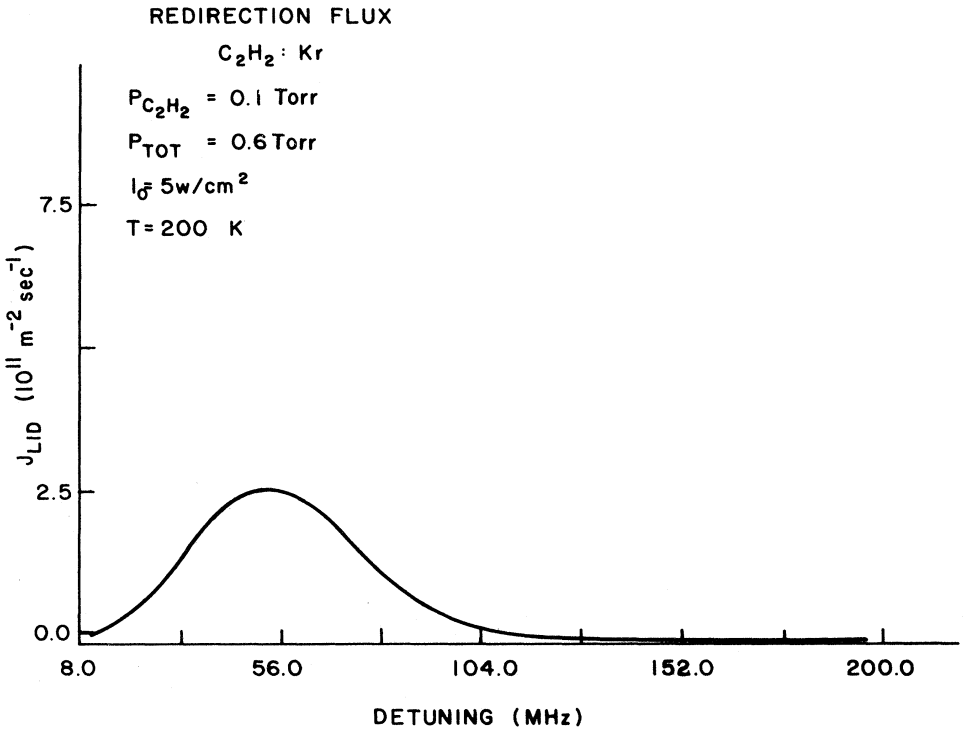

FIG. 4. Redirection flux.

when the cross-section change between ground and excited states is not negligible. There are systems, however, where this change is negligible and in these we expect collisional redirection to be the dominant flux-producing mechanism.

ACKNOWLEDGMENT

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