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Observation of anomalous light-induced drift

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In a two-component gas consisting of light-absorbing particles immersed in a buffer gas, velocity-selective excitation combined with a state-dependent kinetic collision frequency results in light-induced drift. Standard theory predicts that the drift velocity as a function of frequency detuning should have a dispersion-curve-like behavior. This was indeed found experimentally for the molecular species studied so far. We report a dramatic deviation from this behavior for C_2H_4, excited into its ν_7 vibrational mode by a CO_2 laser, with Kr as a buffer gas. The extent of the deviation is found to depend strongly upon the rotational sublevels involved. A possible explanation in terms of a three-level model is attempted but found to be unlikely.

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Velocity-selective excitation of light-absorbing particles immersed in a buffer gas can result in demixing of the gas when the kinetic collision frequencies for ground- and excited-state particles differ. This phenomenon, predicted by Gel'mukhanov and Shalagin [1], is called light-induced drift (LID). The LID effect has been observed for both atomic [2] and molecular [3] systems. In the latter case the experiments have concentrated on isotrope separation (e.g., in CH_3F [3] and in NH_3 [4]). An extensive study on LID of vibrationally excited CH_3F molecules immersed in noble gases has also been reported [5]. From these data, information about the intermolecular potential for vibrationally excited CH_3F molecules was deduced on the basis of combination rules [6]. In some case also broadband (thermal) light sources can be applied for velocity-selective excitation, and thus LID may explain unusual isotopic abundances in astrophysical systems [7].

In the simplified case of a two-level system with δ-peak excitation of the velocity group around v_{xL} (where **x** is directed along the **k** vector of the laser light), the drift velocity can be written as [8]

$$v_d = -\frac{\Delta\nu}{\nu}\frac{n_e}{n_a}v_{xL} . \tag{1}$$

Here $\Delta\nu/\nu = (\nu_e^b - \nu_g^b)/\nu_g^b$ is the relative difference in kinetic collision frequency of the absorbing particles with respect to the buffer gas b upon excitation, n_e is the number density of excited molecules which are still in the selected velocity class v_{xL}, and n_a is the total number density of absorbing particles. For small absorption, constant laser intensity, and in the absence of homogeneous line broadening, the fraction of excited particles (which is proportional to the absorbed laser power) follows the Maxwell velocity distribution:

$$\frac{n_e}{n_a} \propto \exp\left[-\left(\frac{v_{xL}}{v_0}\right)^2\right], \tag{2}$$

where $v_0 = (2k_BT/m)^{1/2}$. If (2) is substituted into (1), one finds that the drift velocity is proportional to the frequency derivative of the absorption profile, if $\Delta\nu/\nu$ is velocity independent (the frequency detuning Ω is related to the selected velocity v_{xL} by $\Omega = kv_{xL}$). It was shown by Bakarev and Folin [9,10] that this relation holds even for nonzero homogeneous line broadening. In this case the LID profile is also broadened, in such a way that it is still the derivative of the absorption profile. Indeed, this relation should be valid for two-level systems in general, provided that the following conditions are met. First, the velocity dependence of the relative difference in kinetic collision frequency, $\Delta\nu/\nu$, can be neglected. Second, the absorption of laser light by the gas can be considered linear in the intensity of the radiation field. Third, at least one of the three following situations must apply: (a) the laser intensity is well below the saturation intensity of the transition, (b) the rate for spontaneous decay is much larger than the rate for the elastic and the inelastic collision processes, or (c) the frequency detuning with respect to absorption line center is large. Furthermore, Bakarev and Folin have experimentally investigated their relation in isotope separation experiments on CH_3F and found good agreement [10].

The molecular systems studied so far were found to obey the Bakarev-Folin relation within the experimental accuracy. In this paper, we report a dramatic violation of this description, even to the extent that four peaks and three nodes are observed as a function of detuning. This system is rovibrationally excited C_2H_4 (ethylene) immersed in Kr.

Ethylene is an asymmetric top molecule, whose rotational states are described by the rotational quantum numbers (J,K_a,K_c) where J is the rotational quantum number and K_a,K_c denote its projection along the C=C axis and the axis perpendicular to the plane of the (nonvibrating) molecule, respectively. The quantum number K_c can only take the values $J-K_a$ and $J+1-K_a$. Since ethylene is a nearly prolate symmetric top molecule, its rotational energy can be approximated by $E_{\rm rot}(J,K_a,K_c) \approx \beta J(J+1) + (A-\beta)(K_a^2+w)$ where $\beta = \frac{1}{2}(B+C) \approx 0.91\ {\rm cm}^{-1}$, $(A-\beta) \approx 3.95\ {\rm cm}^{-1}$ [11], and w is a small correction which is only important when $K_a = 1$ (see, e.g., Ref. [12] for further details). The molecule, which has D_{2h} symmetry, can be excited with a CO_2 laser into its ν_7 vibrational mode (an out-of-plane bending

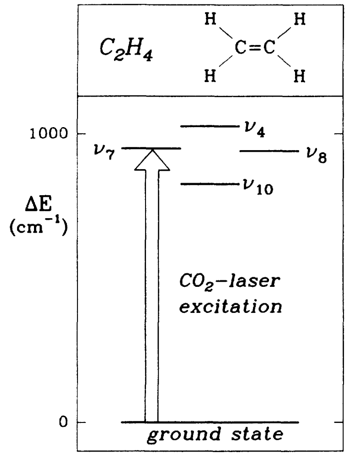

FIG. 1. Level scheme of the lowest vibrational modes of the planar molecule C_2H_4, which has D_{2h} symmetry. The ν_7, ν_4, and ν_{10} mode have ungerade inversion symmetry and the ν_8 mode has gerade inversion symmetry.

mode). This mode is strongly coupled through Coriolis interaction with the neighboring vibrational modes ν_{10} (an in-plane bending mode) and ν_4 (an out-of-plane rocking mode), both having ungerade inversion symmetry like the ν_7 mode [11]. Probably also the ν_8 mode (an out-of-plane rocking mode, which has gerade inversion symmetry) plays an important role. The position of the modes is shown in Fig. 1.

Molecular-beam experiments by Dam, Stolte, and Reuss [13] have shown that vibrational relaxation in (pure) ethylene from the ν_7 to the ν_{10} mode is very fast. This deexcitation channel may also populate the ν_4 and ν_8 mode, but this could not be studied with the detection method used in Ref. [13]. The rate for deexcitation was measured to be at least of the order of the kinetic collision rate [14]. It was also concluded from the data that the surplus of vibrational energy is mainly converted into kinetic energy [13].

The setup for experiments on LID will only be described briefly; further details can be found in Ref. [5]. The gas was contained in a closed stainless steel capillary with an internal diameter of 2 mm and a length of 30 cm. The light-induced difference in gas composition between the ends of the cell was monitored by two thermistors in the self-heat mode. Since the thermal conduction of the gas depends on its composition, the differential signal of the thermistors is proportional to the concentration difference Δx_a along the tube, where x_a is the mole fraction $n_a/(n_a+n_b)$ and n_b is the number density of the buffer gas. The relation between the drift velocity and the concentration difference can be derived from the condition that the net flux vanishes in the stationary state, viz., the LID flux is balanced by the diffusion flux:

$$n_a v_d = (n_a+n_b) D_{ab} \nabla_x x_a \tag{3}$$

where $\nabla_x x_a$ denotes the $\mathbf{x}$ component of ∇x_a and D_{ab} is the binary diffusion coefficient of absorbing particles in the buffer gas. Integration of (3) along the tube yields the relation between $\Delta x_a \equiv x_{a,\text{exit}} - x_{a,\text{entrance}}$ and v_d.

Excitation of the gas was brought about by a tunable cw CO_2 laser with a tuning range of 260 MHz. The laser frequency could be shifted by an additional 90 MHz using an extracavity acousto-optic modulator. In the experiment the laser was slowly scanned through the absorption profile while the resulting concentration difference Δx_a and the absorbed laser power ΔP_L (from which n_e is determined) were recorded on a computer, on which further data analysis was performed.

The results for three rovibrational transitions within the ν_7 fundamental are shown in Fig. 2. For the (6,2,5) $\rightarrow \nu_7(6,1,5)$ transition and the (3,2,1) $\rightarrow \nu_7(4,3,1)$ transition (i.e., left and right panels of Fig. 2), the observed concentration difference shows an LID-like behavior, in which the former has $\Delta v/v > 0$ and the latter has $\Delta v/v < 0$. A closer examination, however, does show a significant deviation from the derivative of the absorption profile (this curve is dashed in the same plot with the magnitude chosen to match the experiment). Furthermore, these two transitions show the first observation of two different directions of the drift velocity (i.e., two different signs of $\Delta v/v$) for rovibrational excitation of one and the same vibrational mode. Calculation of $\Delta v/v$ from the maximum concentration difference, $\Delta x_{a,m}$, yields $+1.0\%$ for the (6,2,5)$\rightarrow \nu_7(6,1,5)$ and -3.0% for the (3,2,1) $\rightarrow \nu_7(4,3,1)$ transition, which is rather large for rovibrationally excited molecules immersed in noble gases (typically 0.5% [5]). The results are summarized in Table I.

The most dramatic violation of the Bakarev-Folin relation is shown in the middle panel of Fig. 2 for the (4,1,3)$\rightarrow \nu_7(5,0,5)$ transition: A double-peaked structure at either side of the absorption maximum is observed for the concentration difference as a function of frequency detuning. The magnitude of this anomalous signal at the extrema is approximately a factor of 3 smaller than for the (6,2,5)$\rightarrow \nu_7(6,1,5)$ transition.

Various cross checks were performed to rule out spurious thermal and pressure effects as a cause of this anoma-

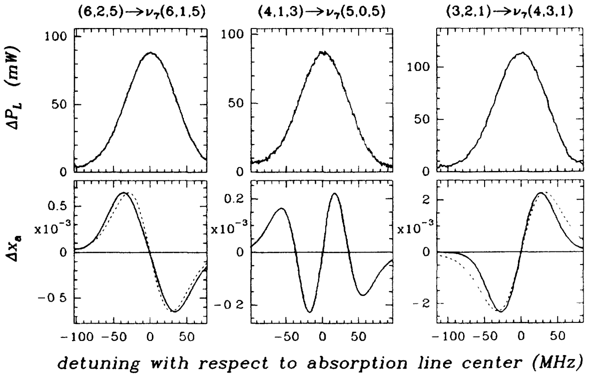

FIG. 2. Experimental results for absorbed laser power (ΔP_L) and the resulting concentration difference (Δx_a) as a function of detuning with respect to the absorption line center. All experiments were performed in a 10-90 mixture of C_2H_4-Kr at a total pressure of 133 Pa. The laser power entering the cell was about 700 mW. Further details can be found in Table I. Note the different scales for the concentration differences of the transitions studied.

TABLE I. Results for the rovibrational transitions studied for a 10-90 mixture of C_2H_4-Kr. All experiments were performed at 275 K at a total pressure of 133 Pa. The mismatch denotes the C_2H_4 transition frequency minus the CO_2 laser frequency. The absorbed laser power at line center is given by ΔP_m. The homogeneous linewidth divided by the Doppler width, Γ/kv_0, is found from the absorption profile. The sign and value of the maximum effect at positive detuning is indicated by $\Delta x_{a,m}$, where x is the mole fraction. Note that $\Delta x_{a,m} < 0$ for $\Delta\nu/\nu > 0$ [see Eqs. (1) and (3)].

Ground state	Excited ν_7 level	CO_2 laser line	Mismatch (MHz)	ΔP_m (mW)	Γ/kv_0	$\Delta x_{a,m}$ (units of 10^{-3})
(6,2,5)	(6,1,5)	10*P*(26)	+106 [19]	88.2	0.22	−0.648
(4,1,3)	(5,0,5)	10*P*(10)	−98 [19]	86.8	0.29	+0.224[a]
(3,2,1)	(4,3,1)	10*R*(22)	+111 [19]	113.8	0.33	+2.30

[a] The largest extremum at positive detuning (cf. middle panel of Fig. 2).

lous behavior. In order to exclude thermal effects—e.g., by thermal diffusion—the temperature difference between the ends of the cell was monitored while the laser was scanned through the Doppler profile. It was found that this difference was small (< 10 mK) and *even* in detuning, in contrast to the observed concentration difference which is *odd.* Pressure effects, measured in parallel with the concentration difference [5], were found to have a dispersionlike shape and an amplitude of ≈ 1 mPa, thereby causing only negligible corrections. In addition, the buffer-gas pressure was varied between 50 and 190 Pa (and thus the homogeneous linewidth between $\Gamma/kv_0 = 0.25$ and 0.5) at a fixed partial pressure of 13 Pa C_2H_4. The position of the extrema and their magnitude ratio was found to change less than 10%. Similar insignificant variations were observed when the laser power was varied between 0.4 and 1.4 W.

It is obvious from the above that the anomalous LID results observed for the C_2H_4-Kr mixtures can no longer be described with the theoretical model of Refs. [5,15] for a two-level system with velocity-independent transport collision cross sections. For an explanation, one may either take more levels into account or allow $\Delta\nu/\nu$ to be velocity dependent.

In view of the fast relaxation from the ν_7 to the ν_{10} mode in pure C_2H_4 discussed above, we will attempt to explain the observed anomalous behavior using a three-level approach with velocity-independent ν's. Let us first simplify the three-level analysis by recalling that the observed behavior is found to be essentially independent of total pressure (and thus of homogeneous linewidth) and buffer-gas concentration. Consequently, an explanation of the basic features of the experimental results can be restricted to the idealized situation of δ-peak excitation and infinite dilution of the absorbing particles in the buffer gas. The three-level model employed consists of a ground state (g), an excited state (e), and an intermediate level (i). We assume that e and g are coupled through δ-peak laser excitation and that i is coupled with e through rapid deexcitation with rate γ caused by an interaction with the buffer gas. In this context, rapid means that γ is at least on the order of the kinetic collision frequency, which implies that the deexcitation takes place mainly in small-angle scattering collisions. The level scheme is shown in Fig. 3. An expression for the concentration difference along the tube can now be derived analogous to the procedure described in Ref. [5].

Under stationary conditions, the equations for the distributions of the molecules over the velocity $\mathbf{v}$ are

$$\mathbf{v}\cdot\nabla n_e(\mathbf{v}) = S_e^b(\mathbf{v}) + n_a p(v_{xL}) - \gamma(v_{xL}) n_e(\mathbf{v}) \,, \tag{4}$$

$$\mathbf{v}\cdot\nabla n_i(\mathbf{v}) = S_i^b(\mathbf{v}) + \gamma(v_{xL}) n_e'(\mathbf{v}) \,, \tag{5}$$

$$\mathbf{v}\cdot\nabla n_g(\mathbf{v}) = S_g^b(\mathbf{v}) - n_a p(v_{xL}) \,, \tag{6}$$

where $S_j^b(\mathbf{v})$ is the collision integral for molecules in state j colliding with the buffer gas b. The total number density of absorbing particles $n_a = n_g + n_e + n_i$, where $n_j = \int d\mathbf{v} \times n_j(\mathbf{v})$. The velocity-dependent excitation probability per unit time, $p(v_{xL})$, is assumed to be a δ peak. Then the non-Maxwellian part of the excited-state velocity distribution $n_e(\mathbf{v})$ is sharply peaked. Furthermore, we assume that the distribution of the particles deexciting into the i level has a nonzero average velocity, which is *not* necessarily equal to v_{xL}. This term is indicated by $n_e'(\mathbf{v})$. Thus we allow an anisotropic internal to kinetic- ($I \rightarrow T$) energy transfer upon deexcitation, such that the velocity is increased in a preferential direction (this is discussed for a two-level system in Ref. [16]). The deexcitation rate $\gamma(v_{xL})$ can still be velocity dependent, but in view of the assumed δ-peak excitation, it can be treated as a constant for fixed detuning. We will therefore use the shorthand notation $\gamma(v_{xL}) \equiv \gamma$.

The concentration difference along the tube can be calculated by multiplying Eqs. (4)–(6) by $\mathbf{v}$, adding the equations and integrating over velocity space, which yields

$$\int d\mathbf{v}\,\mathbf{v}[\mathbf{v}\cdot\nabla n_a(\mathbf{v})] = \int d\mathbf{v}\,\mathbf{v}[S_g^b(\mathbf{v}) + S_e^b(\mathbf{v}) + S_i^b(\mathbf{v}) + \gamma n_e'(\mathbf{v}) - \gamma n_e(\mathbf{v})] \,. \tag{7}$$

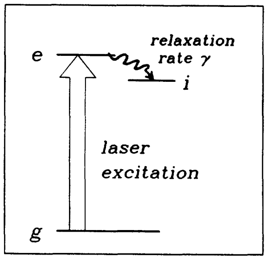

FIG. 3. Three-level model for description of LID in C_2H_4-Kr mixtures. The ground state (g) and the excited state (e) are coupled through laser excitation, and the excited and intermediate states (i) are coupled through fast relaxation with rate γ caused by interaction with the buffer gas.

In order to simplify the right-hand side of Eq. (7), we introduce kinetic collision frequencies, ν_j^b, for particles j with the buffer gas, which can be defined as [17]

$$\int d\mathbf{v}\,\mathbf{v}S_j^b(\mathbf{v}) = -\nu_j^b n_j(\mathbf{u}_j-\mathbf{u}_b)\,, \tag{8}$$

where $\mathbf{u}_j$ is the average velocity of the particles in level j and $\mathbf{u}_b$ is that of the buffer gas. In the stationary state in a closed tube, the net fluxes vanish. Thus $\mathbf{u}_b=0$ and $n_g\mathbf{u}_g+n_e\mathbf{u}_e+n_i\mathbf{u}_i=0$. Simplification of the left-hand side of Eq. (7) is also possible, since the molecular LID effect is small. Thus, $n_a(\mathbf{v})$ can be approximated by a Maxwellian and the left-hand side of Eq. (7) becomes (see, e.g., Ref. [5])

$$\int d\mathbf{v}\,\mathbf{v}[\mathbf{v}\cdot\nabla n_a(\mathbf{v})] = \nu_a^b D_{ab}(n_a+n_b)\nabla x_a\,, \tag{9}$$

with $D_{ab}=v_0^2/2\nu_a^b$. The concentration gradient along a closed tube for a three-level system is now found by substituting (8) and (9) in (7):

$$\begin{aligned} D_{ab}(n_a+n_b)\nabla x_a = &-\left[\frac{\nu_e^b-\nu_g^b}{\nu_a^b}\mathbf{u}_e-\frac{\gamma}{\nu_a^b}(\mathbf{u}_i-\mathbf{u}_e)\right]n_e \\ &-\left[\frac{\nu_i^b-\nu_g^b}{\nu_a^b}\mathbf{u}_i\right]n_i\,, \end{aligned} \tag{10}$$

where we used that $\int d\mathbf{v}\,\mathbf{v}n_e'(\mathbf{v})=n_e\mathbf{u}_i$ and similarly for $n_e(\mathbf{v})$. It is seen from Eq. (10) that ∇x_a is now determined by two contributions. Their weight depends on the ratio between n_e and n_i, for which one finds $n_i/n_e=\gamma/\nu_e^b$ from a simple rate equations model. For $\gamma \ll \nu_e^b$ only the first term in the right-hand side of Eq. (10) survives and the "normal" LID result of the two-level system is retrieved [see, e.g., Eq. (9) of Ref. [5]]. For $\gamma \gg \nu_e^b$, only the last term survives and normal LID will also result.

In order to observe a switch in sign of Δx_a as a function of detuning like for the $(4,1,3)\rightarrow \nu_7(5,0,5)$ transition (see middle panel Fig. 2), the two contributions in Eq. (10) must have opposite signs and their ratio has to change with detuning. For the deexcitation process the following situations can be distinguished: First, isotropic $I\rightarrow T$ transfer combined with a velocity independent γ. Then both $\mathbf{u}_e$ and $\mathbf{u}_i$ are equal to v_{xL} and the ratio between the two terms in Eq. (10) is independent of detuning. Therefore, the concentration difference Δx_a exhibits a normal dispersion-curve-like behavior. Additional broadening upon deexcitation does not give any velocity dependence since only the average velocity $\mathbf{u}_i$ enters in Eq. (10). Second, isotropic $I\rightarrow T$ transfer combined with a velocity-dependent deexcitation rate. Then the ratio of the two contributions obviously changes with detuning. In principal, this can give rise to double peak structures like those observed for the $(4,1,3)\rightarrow \nu_7(5,0,5)$ transition. Third, anisotropic $I\rightarrow T$ transfer. For this situation the concentration difference Δx_a will deviate from the Bakarev-Folin relation if $\mathbf{u}_i$ is not proportional to v_{xL}.

Thus, although a three-level model can in principle describe the observed anomalous LID results, such a hypothesis seems unlikely: It requires that the two contributions of Eq. (10) have opposite signs, in combination with either a velocity-dependent deexcitation rate or anisotropic scattering in the deexcitation process. In addition, the strong dependence of the rotational sublevels involved is not easily explained in this model. It seems likely, therefore, that a comprehensive description is required which fully accounts for the role of the internal states in the collision process [18]. Further experiments to clarify this behavior are in progress.

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