Nearly collisionless sub-Doppler spectroscopy of molecular jets

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The theory of sub-Doppler spectra of molecules subjected to rotational and translational relaxation in the supersonic jet is developed in a weak collision approximation. The broad background of unknown origin (''the pedestal'') emerging beneath the resolved spectrum is attributed to a biline structure of all hyperfine components whose broad lines overlap. Such a composite structure is shown to appear neither at stationary nor at nonstationary saturation regimes, but only in the case of nearly collisionless molecular transit through the laser beam of finite width. The theory accounting for a single collision during transit explains the rise of the pedestal at shorter distances from the nozzle and higher backing pressure. [S1050-2947(97)09610-8]

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I. INTRODUCTION

Supersonic jets of I_2 in He or Ar carrier gases were used to measure high-resolution molecular spectra by means of sub-Doppler spectroscopy [1–3]. The molecular jet was crossed by two counterpropagating cw laser beams that saturate the resonant spectral components. The total fluorescence from the excited electronic state was measured as a function of the laser frequency. The well-resolved hyperfine structure of a few rovibrational lines was obtained in this way when the interaction region is far from the nozzle. However, at closer distances a broad pedestal appears underneath the narrow hyperfine features of a single rotational line [3] (Fig. 1). This may be nothing but the envelope of the unresolved hyperfine structure provided that all hyperfine components consist of two lines, one narrow and the other broad, with a width larger than the hyperfine splitting.

An important observation concerning the pedestal was made in Ref. [3]. The effect is more pronounced the shorter the distance x from the nozzle to the intersection region. At a short distance ($x \sim 2$ mm) from the nozzle of diameter $D = 0.25$ mm the pedestal develops with increasing backing pressure and totally dominates the spectrum at pressures higher than 300 torr (Fig. 2). However, for a slightly larger distance from the nozzle a more complex, nonmonotonic pressure dependence of the relative intensity of the narrow resonances to the intensity of the pedestal was found. The aim of this work is to understand the origin of the broad lines composing the pedestal and to explain the distance and pressure dependence of the phenomenon.

For this goal we first have to extend the theory of sub-Doppler spectroscopy made for atoms in a bulk (Sec. II) to molecules in a supersonic jet. As the rotational relaxation of molecules dominates over the decay of the excited state, we must account for the rotational relaxation time within the simplest solvable model (Sec. III), which determines the shape of the sub-Doppler spectral components when natural decay is negligible.

The particles crossing the laser beam in a bulk of gas undergo many collisions that, being weak, constitute a continuous diffusion in the velocity (spectral) space. The stationary broadening of sub-Doppler lines is attributed to a diffusional extension of a hole burned in the velocity distribution along the light beam [4]. The light from a single-mode ring dye laser saturates the molecular transition whose frequency is properly Doppler shifted into resonance. The saturation spreads from the resonant to closely detuned frequencies by spectral diffusion induced by the velocity changing collisions. The width of the dip determines the pressure broaden-

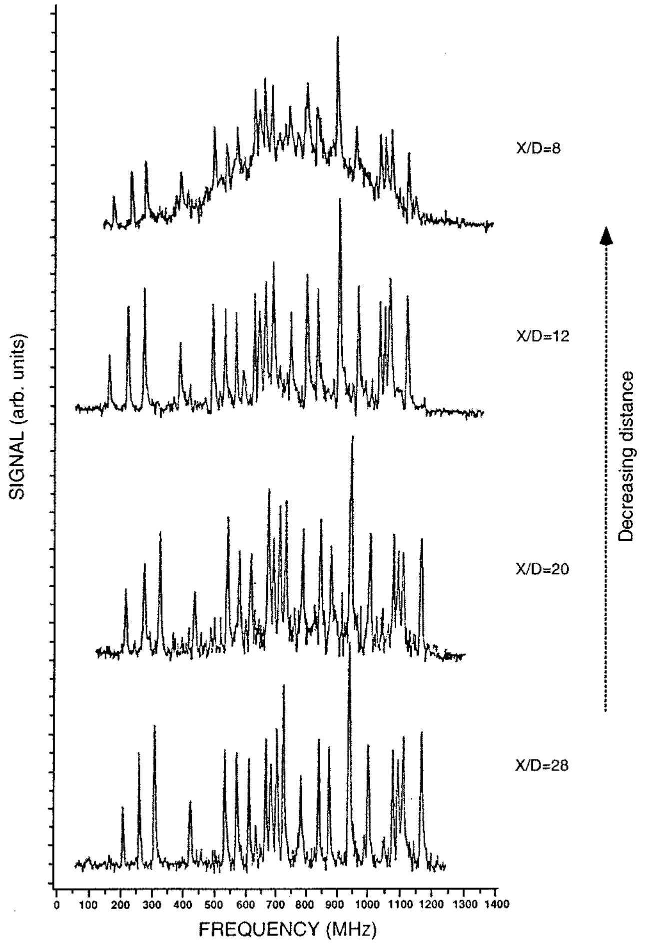

FIG. 1. Hyperfine line shapes of $^{127}I_2$, $R15$ rotation, for several distances X from the nozzle related to its diameter D. The spectra have been taken at the same He pressure, of 150 torr, and are represented at the same scale.

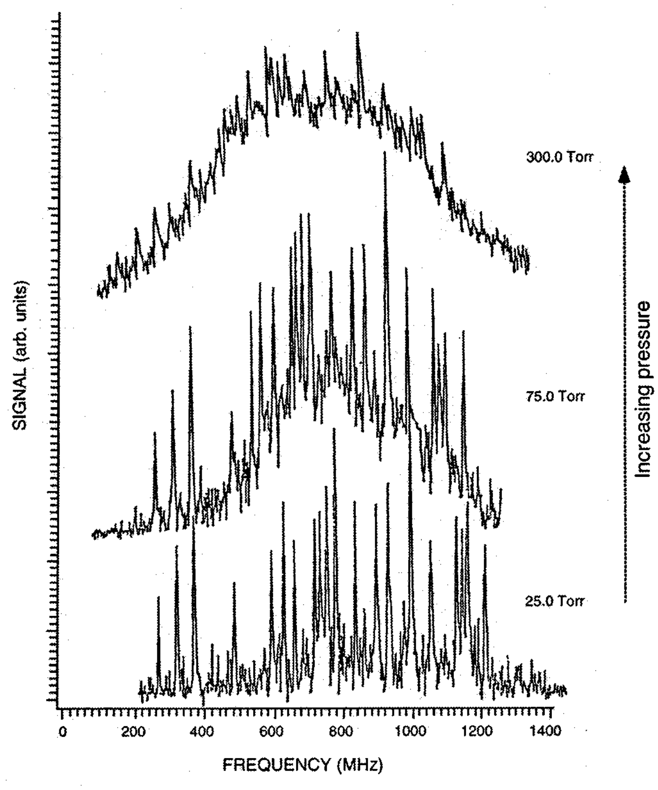

FIG. 2. Recorded hf line shapes of $R15$ rotation of $^{127}I_2$ expanded in various stagnation pressures of He, probed at a reduced distance, $X/D=8$. The recording sensitivity for the top spectrum was twice as small.

ing and thus restricts the spectral resolution of the sub-Doppler spectroscopy. It was commonly accepted that the number of collisions during transit time is sufficiently large that the stationary profile of the dip has shaped almost immediately.

The situation is essentially different if the transit of molecules through the laser beam is limited in time and the particle density is rather low. In a molecular jet the density of a gas decreases with distance from the nozzle as well as the frequency of collisions and related diffusion coefficient. As a result the stationary regime of saturation may be unattainable during too short a transit time τ. Then the saturation is nonstationary and τ determines the final width of the hole expanding during transit (Sec. IV). Since this width is smaller than the stationary one, the spectrum is better resolved, but each of its components is still a single line, not a composite one, which is necessary to explain the origin of a pedestal.

The best resolution in jets is achieved for the largest distances where one may expect a collisionless transit of the molecules through a laser beam. As long as collisions are excluded, the pedestal may not emerge and the line broadening should be determined by the width of the laser light employed in a sub-Doppler technique. However, the situation is more complex for shorter distances and higher pressure. The pedestal arises at the bottom of the multicomponent spectrum, making the resolution of the method worse. If the pedestal is actually an envelope of unresolved broad components of hyperfine lines they are not of a diffusional nature. On the other hand, the diffusional description of velocity relaxation is not universal and cannot be extended to times less than or comparable to the free path time. To take this limit into consideration we used the linearized Boltzmann equation, which describes the ‘‘spectral diffusion’’ as a random walk in the velocity space due to collisions. Only then the shape of the spectral component was found to be comprised of two lines (Sec. V). One is the narrow Lorentzian corresponding to molecules that pass the light beam without collisions, while the other one is much broader and its intensity is proportional to the probability of collision during transit.

With these results we were able to explain some of the above-mentioned peculiarities of the effect. The ratio of the line intensities (broad to narrow) decreases with the distance from the nozzle and depends on the density of the carrier atoms determined by the backing pressure (Sec. VI). This dependence is different for short and longer distances because the average velocity of particles in a jet increases with adiabatic gas expansion and affects significantly the transit time (Sec. VII).

II. LIGHT-INDUCED TRANSITION RATE

If the light is a linearly polarized monochromatic wave,

$$E_x=E_0\cos(\omega t),$$

then the transition rate according to the quantum mechanical golden rule is

$$W=\frac{\pi|D_{01}|^2E_0^2}{2\hbar^2}\,\delta(\omega-\omega_0), \tag{2.1}$$

where D_{01} is the matrix element of the dipole operator $\hat{D}_x$ of the optical transition with a frequency ω_0. Since the latter is close to ω only the resonant component of the light $(E_0/2)\exp(i\omega t)$ is taken into account in Eq. (2.1). The density of the electromagnetic energy is connected with a photon current I: $cE_0^2/4\pi=\hbar\omega I$. Taking this into account one may rewrite Eq. (2.1) as follows:

$$W=BI\delta(\omega-\omega_0), \tag{2.2}$$

where $B=2\pi^2|D_{01}|^2\hbar\omega/c$ is the Einstein coefficient.

Taking into account the finite width of the resonance, Eq. (2.2) may be replaced by the following:

$$W=BIg(\omega-\omega_0)=BI\int_{-\infty}^{\infty}K(t)e^{-i(\omega-\omega_0)t}dt. \tag{2.3}$$

In the simplest case of homogeneous broadening $K(t)=\exp(-\Gamma|t|)$ and

$$g(\omega-\omega_0)=\frac{1}{\pi}\frac{\Gamma}{\Gamma^2+(\omega-\omega_0)^2}. \tag{2.4}$$

If this broadening is light induced then Γ is actually the width of the laser spectrum.

When there are two counterpropagating waves of the same frequency the total field is

$$E=\frac{E_+}{2}\,e^{i(\omega t-kr-\omega_0 t+\alpha)}+\frac{E_-}{2}\,e^{i(\omega t+kr-\omega_0 t+\alpha')}. \quad (2.5)$$

During the free path $r=vt$ and the molecule moving with a fixed velocity v is exposed to the simultaneous action of two light beams, Doppler shifted at frequencies $\omega\pm kv$. If their phases are uncorrelated and random the stationary rates of light-induced transitions are additive:

$$W=B[I_+g(\Delta-kv)+I_-g(\Delta+kv)], \quad (2.6)$$

where I_+ and I_- are light intensities and $\Delta=\omega-\omega_0$.

A few different techniques may be used for sub-Doppler spectroscopy provided that the homogeneous broadening is much smaller than the Doppler one:

$$\Gamma\leqslant\Delta_D=k\overline{v}, \quad (2.7)$$

where $\overline{v}=\sqrt{2kT/m}$ is the average velocity of the particle with a mass m. In one method [4] only one wave is actually strong while the other served as a weak probe field. In this case the narrow hole around $\Delta=0$ is recovered from the Doppler contour if one uses to measure the difference between the absorption coefficients of the probe wave with and without a strong field. However, this scenario is not possible if the total fluorescence intensity is measured as a function of Δ. When only one wave saturates the resonant transition the total luminescence spectrum has always the Doppler shape. The detection of the sub-Doppler resolution spectra can be achieved when two laser beams in a counterpropagating configuration are used. The intermodulated fluorescence sub-Doppler technique [5] has been considered throughout this work.

III. ROTATIONAL RELAXATION

An important distinction between atomic and molecular sub-Doppler spectroscopy lies in the fact that the rotational energy reservoir participates in optical saturation of molecules. The pumping light is resonant only to one of the rovibrational transitions: between sublevel j_0 of the ground state and j_1 of the excited state. Changing their population, the light switches on the collisional relaxation that tends to restore the equilibrium in the rotational reservoir. In general, this is a very complicated process described by the set of kinetic equations for the populations of rotational sublevels, n_j:

$$\dot n_i=-\frac{n_i}{\tau_{ii}}+\sum_{j\neq i}\frac{n_j}{\tau_{ji}}, \quad (3.1)$$

where $1/\tau_{ji}$ are the rates of collision-induced rotational transitions.

We will denote the populations of the radiatively coupled sublevels by n_0 and n_1. All the rotational sublevels of the excited state were empty before pumping and all of them (except for one) remain almost empty during and after saturation due to a fast decay with the rate γ. Therefore the relaxation of the peculiar sublevel 1 can be described by the very simple equation

$$\dot n_1=-\frac{n_1}{\tau_{11}}-\gamma n_1=\frac{n_1}{T}. \quad (3.2)$$

In the case of the ground state the situation is similar. All the sublevels of the ground state were initially populated with the equilibrium statistical weight g_i [that is, $n_i(0)=g_iN$, where N is the total number of particles] and distributed over v with equilibrium density

$$\varphi(v)=\frac{\exp(-v^2/\overline{v^2})}{\sqrt{\pi}\overline{v}}=k\,\frac{\exp(-\omega^2/\Delta_D^2)}{\sqrt{\pi}\Delta_D}=k\varphi(\omega), \quad (3.3)$$

where $\omega=kv$. The pumping changes significantly only the population of the resonant sublevel n_0 while keeping the population of all other sublevels almost unchanged. If so, the restoration of the equilibrium in a lower optical state is approximately described by the equation

$$\dot n_0=-\frac{n_0}{\tau_{00}}+\sum_{j\neq 0}\frac{g_jN\varphi(v)}{\tau_{j0}}. \quad (3.4)$$

Taking into account the detailed balance relation [6]

$$-\frac{g_i}{\tau_{ii}}+\sum_{j\neq i}\frac{g_j}{\tau_{ji}}=0,$$

Eq. (3.4) can be expressed as

$$\dot n_0=-\frac{n_0}{\tau_{00}}+\frac{g_0N\varphi(v)}{\tau_{00}}. \quad (3.5)$$

The optical transition occurs between rotational states j and $j\pm1$ whose relaxation times may not differ significantly. Hence we may suppose for simplicity that $\tau_{00}=\tau_{11}=\tau_E$, where τ_E is the relaxation time of the rotational reservoir as a whole [6]. The latter is only a rough estimation of the real relaxation times and should be better considered as a fitting parameter of the model.

With these simplifications the saturation kinetics is described by the following equations

$$\dot n_1=-W(n_1-n_0)-\left(\gamma+\frac{1}{\tau_E}\right)n_1+\hat L n_1, \quad (3.6a)$$

$$\dot n_0=W(n_1-n_0)-\frac{n_0}{\tau_E}+\frac{g_0N\varphi(v)}{\tau_E}+\hat L n_0, \quad (3.6b)$$

where $\hat L$ is an operator of the random walk in the velocity space induced by the velocity changing instantaneous collisions. For further simplicity we assume here that $\hat L$ is the same for both excited and ground states. In the weak collision approximation (case A in Ref. [4]) the velocity migration may be considered as a continuous diffusion in the velocity space governed by the operator

$$\hat L=\nu\,\frac{\partial}{\partial v}\left(v+\frac{\overline{v^2}}{2}\,\frac{\partial}{v}\right). \quad (3.7)$$

This approximation implies that the mean velocity displacement due to a single collision δ is smaller than the characteristic width of W in the velocity space [7,8]:

$$\delta \leqslant \Gamma / k. \tag{3.8}$$

In the weak collision approximation the velocity relaxation rate ν is always smaller than the frequency of collisions $1/\tau_0$, but in view of Eq. (3.8) this inequality is even stronger [9–11]:

$$\nu = \frac{1}{\tau_0}\left(\frac{2\delta^2}{\overline{v^2}}\right) \leqslant \frac{1}{\tau_0}\left(\frac{2\Gamma^2}{\Delta_D^2}\right) < \frac{1}{\tau_0}.$$

In the alternative, strong collision approximation (case B in Ref. [4]) the equilibrium is restored in each collision, so that $\nu = 1/\tau_0$ and $\hat{L}$ becomes a more simple hopping operator that makes analytically tractable a large range of complex nonlinear problems [12,13]. However, this is the only advantage of this approximation, which is less reliable as a model of velocity relaxation [14,15] and will not be considered here; nor will we consider the combination of cases A and B which may not be justified microscopically.

Equation (3.6a) may be integrated over v to obtain

$$\dot{\overline{n}}_1 = \int W(v) y(v,t) dv - \frac{1}{T}\overline{n_1},$$

where $\overline{n} = \int n(v,t) dv$, $1/T = \gamma + 1/\tau_E$, and $y = n_1 - n_0$. The first term in the right-hand side (rhs) of this equation is the rate of pumping of the upper state. The total number of molecules excited at time τ during transit through the laser light beam is

$$Q = \int_0^{\tau} dt \int_{-\infty}^{+\infty} W(v) y(v,t) dv. \tag{3.9}$$

Neglecting the intersystem conversion and vibrational relaxation we conclude that each of them emits a photon from either this or other rotational states populated in the course of collision redistribution. All the emitted photons are assumed to be detected although they have slightly different frequencies. Hence, the relevant parameter that is measured and has to be calculated is Q.

At moderate pressures, $\gamma \ll 1/\tau_E$ and the set of equations (3.6) may be reduced to a single one:

$$\dot{y} = -2Wy + \hat{L}y - \frac{1}{\tau_E} y + \frac{g_0}{\tau_E} N\varphi. \tag{3.10}$$

Equations (3.9) and (3.10) with W defined in Eq. (2.6) provide the exhaustive mathematical formulation of the problem. Rotational relaxation plays here a role similar to the natural decay of the excited state in atomic spectroscopy.

Following the approach in Ref. [7] let us introduce a variable n defined by the relationship

$$y(v,t) = Ng_0\left[n(v,t) e^{-t/\tau_E} + \frac{1}{\tau_E}\int_0^t n(v,t') e^{-t'/\tau_E} dt' \right]. \tag{3.11}$$

To find y we have to solve now a much simpler equation for n:

$$\dot{n} = -2W(v)n + \hat{L}n, \tag{3.12}$$

with the initial condition $n(v,0) = \varphi(v)$. It is remarkable that this equation is widely used in the theory of irreversible electron transfer from the parabolic energy level. The case of interest $(\Delta \approx 0)$ corresponds to the so-called activationless reaction first considered in Ref. [16] and later on [17–19]. In Ref. [16] the problem was solved for the Lorentzian shape of $W(v)$ similar to Eq. (2.4), though it may be essentially simplified by substitution of $\delta(v - v_0)$ for $W(v)$ [20,21]. The same equation governs the energy diffusion accompanied by the nonadiabatic reaction above level crossing, but the shape of $W(E)$ is essentially different [22–24].

IV. SPECTRAL DIFFUSION

The general solution of Eq. (3.12) is

$$n(v,t) = \varphi(v) - 2\int_0^t dt' \int G(v,v',t-t') \times W(v') n(v',t') dv', \tag{4.1}$$

where $G(v,v',t-t')$ is the Green function that obeys the equation

$$\dot{G} = \hat{L}G, \tag{4.2}$$

with the initial condition $G(v,v',0) = \delta(v - v')$.

In the vicinity of $\Delta = 0$, $\hat{L}$ may be simplified to a one-dimensional free space diffusional operator

$$\hat{L} = D\frac{\partial^2}{\partial v^2}, \quad \text{where} \quad D = \nu\frac{\overline{v^2}}{2} \tag{4.3}$$

is a diffusion coefficient in velocity space. Such a simplification is valid if the maximum (stationary) width of a dip in velocity space, $v_r = \sqrt{D\tau_E} \ll \overline{v}$ [4,5,11]. Then the well-known expression for the Green function is obtained:

$$G = \frac{1}{\sqrt{4\pi D(t-t')}} e^{-(v-v')^2/4D(t-t')},$$

which is valid for

$$t \geqslant \tau_0, \tag{4.4}$$

when the diffusional description of the velocity (spectral) exchange is appropriate.

Further simplifications are possible if the rate

$$W(v) = B[I_+\delta(\Delta/k - v) + I_-\delta(\Delta/k + v)]/k \tag{4.5}$$

is used instead of that defined in Eq. (2.6). This is possible from the time when the increasing width of the dip exceeds the homogeneous width of the resonance: $\sqrt{2Dt} \gg \Gamma$. Due to the inequality (3.8) this condition is actually stronger than Eq. (4.4):

$$t \geqslant \frac{\Gamma^2}{\nu \Delta_D^2} = \frac{\tau_0}{2}\left(\frac{\Gamma}{k\delta}\right)^2 . \tag{4.6}$$

Inserting Eq. (4.5) into Eq. (4.1) we obtain

$$\begin{aligned} n(v,t) = \varphi(v) - 2B\int_0^t dt'[&I_+ G(v-\Delta/k)n(\Delta/k) \\ &+ I_- G(v+\Delta/k)n(-\Delta/k)]/k. \end{aligned} \tag{4.7}$$

The zero-order approximation with respect to $I_\pm$ is $n(\pm\Delta/k)=\varphi(\Delta/k)$. Making an iteration one can find from Eq. (4.7),

$$\begin{aligned} n(v,t) = \varphi(v) - 2B\varphi(\Delta/k)[&I_+ J(v-\Delta/k)/k \\ &+ I_- J(v+\Delta/k)/k], \end{aligned} \tag{4.8}$$

where

$$J(v) = \int_0^t G(v,t')dt' = \frac{|v|}{4\sqrt{\pi D}} \int_{v^2/4Dt}^{\infty} \frac{e^{-x}}{x^{3/2}}\, dx. \tag{4.9}$$

Inserting n from Eq. (4.8) into Eq. (3.11) one can easily find $y(v,t)$, which is all that we need to obtain the nonstationary fluorescence spectrum from Eqs. (3.9) and (4.5):

$$Q = B\left[I_+ \int_0^\tau y(\Delta,t)dt + I_- \int_0^\tau y(-\Delta,t)dt \right], \tag{4.10}$$

where $y(v)=ky(\omega)$, if $\omega=kv$.

Let us first consider the stationary solution similar to those discussed everywhere [4,5]. It is clear from Eq. (3.11) that for sufficiently long $t \gg \tau_E$ $y(v,t)$ approaches the stationary value

$$y_s(v) = \frac{Ng_0}{\tau_E}\, \tilde{n}(v, 1/\tau_E), \tag{4.11}$$

where

$$\tilde{n}(v,p) = \int_0^\infty n(v,t')e^{-pt'}dt'.$$

Taking the Laplace transform of Eq. (4.8) we obtain

$$\begin{aligned} \tilde{n}(v,1/\tau_E) = \tau_E\{\varphi(v) - 2B\varphi(\Delta/k)[&I_+ \tilde{G}(v-\Delta/k) \\ &+ I_- \tilde{G}(v+\Delta/k)]/k\}, \end{aligned} \tag{4.12}$$

where

$$\tilde{G}(v) = \int_0^\infty \frac{e^{-(t/\tau_E + v^2/4Dt)}}{\sqrt{4\pi D t}}\, dt.$$

Performing integration by the saddle-point method we obtain

$$\tilde{G}(v) = \frac{\tau_E e^{-|v|/\sqrt{D\tau_E}}}{2\sqrt{D\tau_E}} = \tau_E k E(\omega), \tag{4.13}$$

where

$$E(v-v') = \frac{\exp(-|v-v'|/v_r)}{2v_r} = kE(\omega-\omega').$$

Inserting Eq. (4.13) into Eq. (4.12) we find

$$\begin{aligned} \tilde{n}(v,1/\tau_E) = k\tau_E\{\varphi(\omega) - 2B\varphi(\Delta)\tau_E[&I_+ E(\omega-\Delta) \\ &+ I_- E(\omega+\Delta)]\}. \end{aligned} \tag{4.14}$$

Substitution of this expression into Eq. (4.11) transforms it to the following:

$$y_s(\omega) = g_0 N \varphi(\Delta)\{1 - 2B\tau_E[I_+ E(\omega-\Delta) + I_- E(\omega+\Delta)]\}. \tag{4.15}$$

To estimate the stationary luminescence spectra Q_s we should start from a definition that follows from Eqs. (3.9) and (4.5):

$$\begin{aligned} Q_s &= \tau\int W(\omega) y_s(\omega) d\omega \\ &= B\tau \int d\omega [I_+ \delta(\Delta-\omega) + I_- \delta(\Delta+\omega)] y_s(\omega). \end{aligned} \tag{4.16}$$

Inserting here Eqs. (4.15) and (3.3) we obtain

$$\begin{aligned} Q_s(\Delta) = g_0 NB\tau \frac{\exp(-\Delta^2/\Delta_D^2)}{\sqrt{\pi}\Delta_D} \Bigg[&I_+ + I_- - B\tau_E \frac{I_+^2 + I_-^2}{\Delta_0} \\ &- 2B\tau_E I_+ I_- \frac{e^{-2|\Delta|/\Delta_0}}{\Delta_0} \Bigg]. \end{aligned} \tag{4.17}$$

Only the last interference term in this expression is Δ dependent and therefore presents the sub-Doppler structure, which has an exponential shape of $E(2\Delta)$.

Using the simplification (4.3) we actually assumed that the laser band is narrower than a dip that in its turn is narrower than the Doppler contour [11]:

$$\Gamma \leqslant kv_r = \Delta_0 \leqslant \Delta_D . \tag{4.18}$$

According to these inequalities the exponential structure of the last term in Eq. (4.17) is much narrower than the Gaussian background with a width Δ_D. The latter is of no interest for us because it coincides with the Doppler contour. Therefore we consider this structure as a single line of exponential shape with a width $\Delta_0 = k\sqrt{D\tau_E}$. This width is determined by the mean square displacement of the frequency in the course of spectral diffusion during time τ_E.

The main restriction of the above results is the condition imposed by Eq. (4.6), which requires a small resonance width Γ and can be rewritten as

$$\nu\tau_E \geqslant \frac{2\Gamma^2}{\Delta_D^2}. \tag{4.19}$$

Even being less than 1, due to a weak collision approximation, the parameter $\nu\tau_E$ may be still greater than the ratio $2\Gamma^2/\Delta_D^2$ as Eq. (4.19) requires. This condition does not depend on the particle density or on the form of the sub-Doppler resonance in Eq. (4.17), which is not a composite but a single line of exponential shape. Such a resonance contributes nothing into the pedestal whose appearance at short distances and at high pressure may not be consequently justified with stationary theory. Therefore we must analyze the nonstationary saturation regimes.

It is quite clear that the stationary results are valid if

$$\tau \gg \tau_E . \tag{4.20}$$

In this case the integrands in Eq. (4.10) reach their stationary values at the very beginning of the transit. Owing to condition (4.20) all these results starting from Eq. (4.16) were linear in τ. The fluorescence becomes essentially nonstationary when the inequality (4.20) is reversed.

For $\tau \ll \tau_E$ it follows from Eq. (3.11) that

$$y(v,t) \approx N g_0 n(v,t). \tag{4.21}$$

Substituting this result into Eq. (4.10) we find

$$Q = N g_0 B \left[I_+ \int_0^\tau n(\Delta/k,t)\,dt/k + I_- \int_0^\tau n(-\Delta/k,t)\,dt/k \right]. \tag{4.22}$$

Using here Eq. (4.8) and taking into account that $J(2\Delta/k,t) = J(-2\Delta/k,t)$ we obtain

$$Q = N g_0 B \varphi(\Delta) \left[(I_+ + I_-)\tau - 2B\varphi(\Delta)(I_+^2 + I_-^2) \int_0^\tau J(0,t)\,dt - 4B\varphi(\Delta) I_+ I_- \int_0^\tau J(2\Delta,t)\,dt \right]. \tag{4.23}$$

where

$$J(\omega,t) = \int_0^\tau \frac{e^{-\omega^2/2\nu\Delta_D^2 t'}}{\sqrt{2\pi\nu\Delta_D^2 t'}}\,dt' .$$

Performing the integration over t in Eq. (4.23) we finally obtain

$$Q = N g_0 B \varphi(\Delta) \left[(I_+ + I_-)\tau - 2B\varphi(\Delta)(I_+^2 + I_-^2) \frac{2\sqrt{2}\,\tau^{3/2}}{3\sqrt{\pi\nu\Delta_D^2}} - 4B\varphi(\Delta) I_+ I_- \frac{|\Delta|}{\nu\Delta_D^2\sqrt{\pi}} \int_0^\tau dt \int_{2\Delta^2/\nu\Delta_D^2 t}^\infty \frac{e^{-x}}{x^{3/2}}\,dx \right]. \tag{4.24}$$

Here the last term represents the shape of the hyperfine spectral component above the Doppler pedestal. Once again this is not a composite but a single line, which is not suitable for explanation of the pedestal origin. The width of the line increases roughly as $\Delta_D\sqrt{\nu\tau}$, being much less than the stationary one, $\Delta_0 = \Delta_D\sqrt{\nu\tau_E/2}$. Since the rotational relaxation time is longer than the transit time the latter terminates the diffusional extension of the dip burned in the velocity distribution during the transit of molecules across the laser beam. The result (4.24) does not depend on τ_E and therefore remains valid for any particular model of rotational relaxation.

A different situation is obtained with the velocity relaxation, which is still considered as diffusional. What actually happens is that the number of collisions during the molecule transit through the laser beam is limited. This number should be large to make possible the diffusional description of the velocity relaxation, stationary or nonstationary. In the latter case the necessary validity conditions of the diffusional approximation are

$$\tau_0 \ll \tau \ll \tau_E . \tag{4.25}$$

If τ is less than τ_0 there are almost no collisions during the transit time and therefore no diffusion. This limit has to be considered separately as an alternative to the diffusional approach.

V. NEAR COLLISIONLESS TRANSIT

For transit times comparable to or less than τ_0 one has to use a more general, nondiffusional approach to the velocity relaxation. The latter should be considered as a random walk in the velocity space characterized by the total frequency of the jumps $1/\tau_0$ and the velocity distribution over v, $f(v,v')$, which arises after jump if the velocity preceding the jump was v'. This distribution satisfies the detailed balance principle [25]:

$$\varphi(v) = \int f(v,v')\varphi(v')\,dv' . \tag{5.1}$$

For strong collision model $f(v,v') = \varphi(v)$ does not depend on v' while in case of weak collisions this is a narrow distribution near v' closely approximating $\delta(v-v')$. There are several ways to specify a particular shape and width of $f(v,v')$, that is, to derive it theoretically from some type of interaction potential (hard sphere, $1/r^6$, Lennard-Jones) [26,27], to deduce it from experimental data [28], or to choose the phenomenological form [29,30]. The most famous phenomenological model of such a distribution, proposed by Keilson and Storer [31], contains only one numerical parameter γ, which is a measure of the collision strength:

$$f(v,v') = f(v - \gamma v').$$

At $\gamma \approx 1$ collisions are weak and the velocity (spectral) exchange may be considered as a diffusional process. It follows from Eq. (5.1) that for the Maxwellian $\varphi(v)$ defined in Eq. (3.3) the distribution has a Gaussian form [10]:

$$f(v,v') = \frac{e^{-(v-\gamma v')^2/(1-\gamma^2)\overline{v^2}}}{\sqrt{\pi(1-\gamma^2)\overline{v^2}}} . \tag{5.2}$$

The important simplification of our problem comes from the fact that we are interested only in the narrow dip arising near $v \approx 0$, where

$$\varphi(v) \approx \varphi(0) \quad \text{and} \quad f(v,v') \approx f(v - v'). \tag{5.3}$$

This is exactly the same simplification that allowed us to use the operator Eq. (4.1) instead of the general one defined by Eq. (3.7). Due to this simplification the random walk in the velocity space is described by the integral operator $\hat{L}$ [25]

$$\hat{L} n = -\frac{1}{\tau_1} \left[n - \int dv' f(v - v') n(v',t) \right]. \tag{5.4}$$

In a weak collision limit when $\gamma\to 1$, $\nu=(1-\gamma)/\tau_0$, the velocity migration is actually diffusional and the kernel of the operator (5.4) takes the form

$$f(v-v')=\frac{e^{-(v-v')^2/2\delta^2}}{\sqrt{2\pi\delta^2}}, \tag{5.5}$$

where

$$\delta^2=\int (v-v')^2 f(v-v')dv=(1-\gamma)\overline{v^2}/2 \tag{5.6}$$

is the mean square velocity jump per collision that determines the diffusion coefficient in the velocity space used in Eq. (4.1):

$$D=\frac{\nu\overline{v^2}}{2}=\frac{\delta^2}{\tau_0}.$$

However, the differential operator (4.1) may be employed in Eq. (3.12) for either stationary saturation or nonstationary saturation, but for times greater than τ_0 as was mentioned in Eq. (4.4). To extend the theory for shorter times we should use the general operator of the frequency migration (5.4) that leads to a more complex, integral equation similar to that considered in Ref. [32]:

$$\dot{n}=-2W_n-\frac{1}{\tau_0}\left[n-\int dv' f(v-v')n(v',t)\right]. \tag{5.7}$$

Generally speaking, not the simplified expression (4.5) but the original form of $W(v)$, Eq. (2.6) should be used in this equation as well as in Eq. (3.9).

One may use an iteration procedure to solve Eq. (5.7) for short times. In the zero-order approximation $n^{(0)}=\varphi(0)$ while the next iteration corresponds to an absolutely free transit when the collisional term in Eq. (5.7) should be omitted:

$$\dot{n}^{(1)}=-2W\varphi(0), \quad n^{(1)}=\varphi(0)[1-2Wt]. \tag{5.8}$$

Using this result in Eq. (5.7) for the next iteration, we first obtain the correction sensitive to collisions:

$$n^{(2)}=\varphi(0)\left[1-2Wt+2W^2t^2-\frac{t^2}{\tau_0}\int f(v-v')W(v')dv'\right]. \tag{5.9}$$

Inserting Eq. (5.9) into Eq. (4.21) we obtain

$$y=Ng_0\varphi(0)\left[1-2Wt-\frac{t^2}{\tau_0}\int f(v-v')W(v')dv'\right], \tag{5.10}$$

where only the first-order terms with respect to W were left. Substituting Eq. (5.10) into Eq. (3.9) we obtain after integration over t:

$$Q=\frac{Ng_0\tau}{\sqrt{\pi}\Delta_D}\int W(\omega)\left[1-W(\omega)\tau-\frac{\tau^2}{3\tau_0}\int \times f(\omega-\omega')W(\omega')d\omega'\right]d\omega, \tag{5.11}$$

where $f(\omega-\omega')$ is normalized to 1 in the frequency space. The first terms in the brackets correspond to the free transit through the light beam, whereas the last term accounts for the single collision that may occur during the transit time. Inserting Eq. (2.6) in Eq. (5.11) and assuming contrary to Eq. (3.8)

$$\delta \gg \Gamma/k, \tag{5.12}$$

one can simply find

$$Q=\frac{Ng_0B\tau}{\sqrt{\pi}\Delta_D}\Big\{I_++I_--(I_+^2+I_-^2)B\tau\int g^2(\Delta-\omega)d\omega-2BI_+I_-\tau\int g(\Delta-\omega)g(\Delta+\omega)d\omega -\frac{B\tau^2}{3\tau_0}[I_+^2f(0)+I_-^2f(0)+2I_+I_-f(2\Delta)]\Big\}. \tag{5.13}$$

For the linewidth of 2 MHz, a rather small value of 230 cm/s was obtained for Γ/k [3]. With an average velocity of 10^5 cm/s the inequality (5.12) is easy to satisfy in this case if γ used in Eq. (5.6) is in the range $1\gg 1-\gamma\gg 0.003$. This is a reasonable and very soft requirement for weak collisions.

Inserting g from Eq. (2.4) we obtain after integration

$$Q=\frac{Ng_0B\tau}{\sqrt{\pi}\Delta_D}\left\{I_++I_--(I_+^2+I_-^2)B\tau\left[\frac{1}{2\pi\Gamma}+\frac{\tau}{3\tau_0}f(0)\right]-B\tau I_+I_-\left[\frac{1}{\pi}\frac{\Gamma}{\Gamma^2+\Delta^2}+\frac{2\tau}{3\tau_0}f(2\Delta)\right]\right\}. \tag{5.14}$$

The last term in this expression represents the sub-Doppler resonance in the fluorescence spectrum, which has the maximum intensity at $I_+ = I_-$. The resonant component consists of two lines centered at $\Delta = 0$. One of them is the narrow Lorentzian line, which accounts for the molecules passed through the laser beam without collisions. The other term corresponds to a molecule that experienced a single collision during the transit. This term is much broader and its shape reproduces the velocity distribution after collision, $f(\omega)$, which may have either Gaussian shape (5.5) or slightly different and more realistic form derived in Ref. [33]. The integral intensity of this term relates to the Lorentzian one as $\tau/3\tau_0 \ll 1$.

This is what we actually searched for: the composite resonance is actually a sum of two lines of different widths. This structure of hyperfine components allows one to explain the emergence of a pedestal in the multicomponent sub-Doppler spectra.

VI. THE AVERAGING OVER TRANSIT TIME

Let us consider further the case of almost collisionless transit when

$$\tau \lesssim \tau_0 \tag{6.1}$$

for the majority of the molecules. Crossing the laser beam without collisions but with different velocities w, the molecules spend different times for transit, $\tau = d/w$, where d is the width of the beam. The averaging over transit times, $\langle\,\rangle$, is actually an averaging over the velocity distribution along the beam, $\Phi_x(w)$. The latter depends strongly on the distance x from the nozzle to the intersection of the molecular and laser beams.

Thus, the problem is reduced to the calculation of

$$\langle Q \rangle = \int_0^\infty Q(w)\Phi_x(w)\,dw. \tag{6.2}$$

Only the last term in Eq. (5.14) represents the frequency-dependent resonant part of the signal that is of interest. By substituting only this term in Eq. (6.2) one can find the shape of a single sub-Doppler component:

$$\langle \Delta Q \rangle = \frac{N g_0 B^2 I_+ I_- \langle \tau^2 \rangle}{\sqrt{\pi}\Delta_D}\left[\frac{1}{\pi}\frac{\Gamma}{\Gamma^2+\Delta^2} + \mathcal{J}2\, f(2\Delta)\right], \tag{6.3}$$

where the intensity of the broad pedestal relative to the intensity of the narrow Lorentzian line is

$$\mathcal{J}(x) = \frac{\alpha d}{3\tau_0 \overline{w}} = \frac{\alpha d \sigma_0}{3}\frac{\rho \overline{v}}{\overline{w}}. \tag{6.4}$$

Here $\overline{w} = \langle w \rangle$, ρ is the density of atoms in the beam, σ_0 is the total cross section of their collisions with molecules, and

$$\alpha(x) = \frac{\langle w^{-3}\rangle\langle w\rangle}{\langle w^{-2}\rangle} \tag{6.5}$$

is a numerical factor.

Although not much is known about the transformation of $\Phi_x(w)$ along x, it may not essentially affect α. For instance, $\alpha(0) = 3\pi/4$ near the nozzle where $\Phi_x(w)$ is expected to be a well-known equilibrium distribution in a flux [34]

$$\Phi_0(w) = 2\beta^2 e^{-\beta w^2} w^3, \quad \text{where} \quad \beta = m/2kT. \tag{6.6}$$

On the other hand, far away from the nozzle $\alpha \approx 1$, because after significant translational cooling of the gas due to expansion one may expect that

$$\Phi_\infty(w) \approx \delta(w - \overline{V}).$$

Therefore α may be excluded from further consideration.

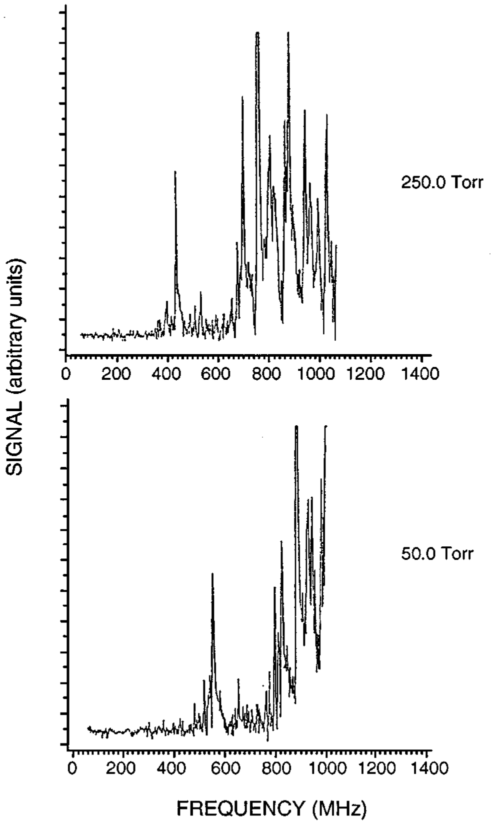

FIG. 3. A few hyperfine transitions of $^{127}I_2$, $P10$ rotation, expanded in various pressures of Ar, showing the behavior of the background pedestal with pressure. The spectra have been measured at $X/D = 12$ and are represented at the same scale.

The slipping effect is more important [35]. Since iodine molecules are rather heavy their average velocity $\overline{w}(x)$ is initially much less than that of light He atoms, V. However, the difference should disappear with time due to the velocity changing collisions:

$$\dot{\tilde{w}}=\tilde{w}\,\frac{d\tilde{w}}{dx}=\sigma\rho\overline{v}(\overline{V}-\overline{w}), \tag{6.7}$$

where σ is their effective cross section. Both ρ and $\overline{v}\sim T^{1/2}$ decrease with x, but the average velocity of atoms $V(x)$ increases during expansion according to the thermodynamics of free jets [36]. Since $V>\overline{w}$ the molecules in the supersonic jet are accelerated. Correspondingly the average transit time decreases with the distance to the intersection region and with the carrier pressure.

The influence of the heavier carriers (the active-to-perturber mass ratio) was actually tested experimentally in a few runs, by using Ar gas instead of He (mass ratio of about ten) [3]. A few hyperfine lines of the iodine, P10 transition, expanded in different backing pressures of Ar and measure at $X/D=12$, are depicted in Fig. 3. They show the qualitative behavior of the background development with the carrier pressure, which is consistent with the expectations following from Eq. (6.4) after $\overline{w}$ approaches V. Since the latter is smaller for argon than for helium [35] the related value of $\mathcal{J}$ is higher and the pedestal is more pronounced at the same backing pressure and distance (see Fig. 2 for comparison).

VII. DISCUSSION

We have come to important conclusions giving us insight into understanding the phenomenon under study:

(i) Since the product $\rho\overline{v}$ decreases while $\overline{w}$ increases with distance the pedestal intensity given by Eq. (6.4) is diminished and the spectral resolution improves with the distance downstream of the nozzle.

(ii) Close to the nozzle where $\overline{w}=\sqrt{9\pi/16\beta}=\sqrt{9\pi k_BT/8m}$ depends only on the equilibrium temperature, the pedestal intensity increases proportionally to the gas density ρ, so that the increase in the backing pressure deteriorates the spectral resolution.

(iii) At larger distances not only ρ but also $\overline{w}$ increases with the pressure and their competition may result in the nonmonotonic rise of $\mathcal{J}$, that is the pedestal decreases at intermediate pressure to a certain extent.

The conclusions we have made explain qualitatively some features of the phenomenon mentioned in the Introduction. For the quantitative description of sub-Doppler spectra obtained from supersonic jet one needs to know more about the space and pressure dependence of $\overline{w}(x,\rho)$.

Fortunately, there is a simpler way to check whether it is precisely the transit time that restricts the spectral resolution at low $\overline{w}$ and high densities. This may be done by reducing the laser beam width d. It is quite clear from Eq. (6.4) that by focusing the light at the intersection region one can reduce d and suppress the pedestal.

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