Velocity-changing Collisional Effects in Nonlinear Atomic Spectroscopy and Photon Echo Decay in Gases

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A general theory of atomic dipole coherence under the influence of collisional phase changes, inelastic effects and optically active atom velocity changes, including those due to anisotropic interactions is presented. Velocity change effects are obtained in closed form. Line shapes appear as convolutions of standard pressure broadening contours with velocity-change contours. Width and shift parameters for the He-broadened Na D lines at 2 m bar pressure, 380 K are calculated, as are He-induced photon echo decay rates for these lines. Overall agreement with experiment is reasonably good.

The traditional problems of collisionally induced atomic spectral line broadening and the associated phenomena of electric dipole relaxation at higher pressures are presently well understood.[1-3] With the advent of nonlinear laser spectroscopy[4] and photon echo observations in gases,[5] it is now possible to examine some different aspects of the same problem, particularly as they become relevant at low pressures ($\gtrsim$ a few millibars). In saturation spectroscopy, for example, one alters the states of atoms moving with a selected velocity component in the direction of propagation of the saturating laser beam, then probes these changes with a weaker beam, usually propagating in the opposite direction. Thus, translational velocity-changing collisional (vcc) effects become important to an extent not previously realized in the Doppler limited or higher pressure standard optical regimes. (Nothwithstanding, the motional narrowing of Doppler line contours at higher pressures[6] represents different, but related, aspects of vcc effects.)

The effects of velocity changes on dipole coherence at lower pressures has been described by several authors.[7,8] There are two distinct vcc effects. The first is that collisions can redistribute the velocities of atoms initially placed into (or deleted from) narrow velocity intervals for the final (initial) states in the absorption transition caused by the saturating beam. This produces an inhomogeneous line shape which is substantially different from the Doppler line shape associated with a thermal velocity distribution. The second vcc effect results from losses of coherence associated with phase changes in the atomic dipole-electromagnetic field interaction arising from collisionally induced velocity changes of the optically active atoms. The first of these effects can be described through kinetic theory techniques.[7] This problem has been treated quite successfully in the past, and in some problems at the lowest

pressures in nonlinear spectroscopy[7,9] is found not to be of great importance in altering the shape of the narrow velocity distribution generated by the saturating beam, acting mostly to reduce the magnitude of the sharp component.

Our efforts, in the present paper, are directed toward strengthening the existing theory for the second effect mentioned above, namely, that describing vcc effects on the coherence (or relaxation processes) associated with atoms initially propagating in any single velocity group. In our treatment we specifically avoid the use of kinetic theories, treating the problem in an impact-by-impact basis. Unlike most other treatments,[7,8] however, we find closed-form solutions for the dipole moment correlation function in a non-Markoffian form which have not yet been obtained in as general a form as appears in this paper. The present form is a generalization of a solution previously put forth in a recent article by the author and E. W. Weber (henceforth referred to as I).[9] There it was argued that this type of treatment is valid whenever successive impacts can be regarded as statistically independent. This holds whenever the typical relative velocity alterations, in those collisions which do not completely destroy the optical coherence, are quite small. For situations in which the effects of multiple collisions are important, the optically active atom initial conditions then remain essentially the same for the successive collisions--in particular with respect to the optically active atom velocity prior to the collision--following which, then, vcc effects and internal state alterations can be obtained independent of prior history. In general, these conditions hold whenever $k \gg N\sigma_{coh}$, $\vec{k}$ being the light propagation vector, N the perturber number density and σ_{coh} the total (phase shift, inelastic and vcc) coherence destruction cross section. [In the related problem of Dicke narrowing, this condition is

not satisfied at microwave frequencies. Hence, the full kinetic theory must be used[10] to find the radiative distribution associated with atoms starting out at each velocity in the thermal distribution. However, at optical and near infrared frequencies, this condition is ordinarily very well satisfied.]

In I, the dipole-dipole correlation function for any group of atoms moving, at time t = 0, with velocity $\underset{\sim}{v}$ was found simply to be

$$C_{fi;\vec{v}}(\tau) = |\mu_{fi}|^2 \, e^{i(\omega^o_{fi} + \vec{k}\cdot\vec{v})\tau} \quad \exp\left\{- N\bar{v}\,\tau\, 2\pi \int_0^\infty bdb\, S_{fi;\vec{v}}(b,\bar{v},\tau)\right\} \tag{1}$$

b and $\bar{v}$ being the impact parameter and mean relative speed for the absorptive transition i→f having unperturbed natural frequency ω^o_{fi} , μ_{fi} being the (Schrödinger) dipole moment matrix element, and $S_{fi;\underset{\sim}{v}}(b,\bar{v},\tau)$ the "collision efficiency" function. The latter is given by

$$S_{fi;\vec{v}}(b,\bar{v},\tau) = 1 - (i/\Omega\tau)\, e^{i\eta_{fi}(b,\bar{v})} \int_\Omega d\vec{\Omega} \int_0^\tau dt \;\; e^{i\vec{k}\cdot\Delta\vec{v}_{fi}(b,\bar{v},\vec{\Omega})\,t} \tag{2}$$

for isotropic interaction potentials. Here, $\eta_{fi}(b,\bar{v})$ specifies the collisionally induced phase shift (within the classical path picture) difference between the upper (f) and lower (i) states, while $\Delta\vec{v}_{fi}(b,\bar{v},\vec{\Omega})$ is the effective collisional velocity change, which depends upon the collisional angles $\vec{\Omega}$ within the appropriate domain Ω. Within the wave packet picture the appropriate classical path, for purposes of calculating η_{fi} and $\Delta\vec{v}_{fi}$, is that which would be followed by the domain of maximum overlap for identical initial and final state translational wave packets in the distant past as they scatter from the different isotropic potentials for the f and i states. Consistent with this, $\Delta\vec{v}_{fi}$ is the <u>average</u> velocity change for the two states, while the classical path appropriate

to the calculation of η_{fi} and $\Delta\vec{v}_{fi}$ is the average path.[11] The average $1/\tau\int_0^\tau dt$ . . . , appearing in eq. (2) represents the average vcc effect, for collisions occurring at random within the interval $0\to\tau$, on the phase of the dipole interaction with the radiation field. Because the vcc phase factors continue to change following the collisions, the statistics indeed are non-Markoffian, ultimately causing deviations from exponential behavior for $C_{fi;\vec{v}}(\tau)$, and from Lorentz-shaped spectral lines.[12]

The generalization of eq. (2) to account for anisotropic interactions and possible inelastic effects is, in part, well known.[1-3] For standard pressure broadening, regarding η_{fi} as the phase shift between the f,i states caused by isotropic interactions alone, $e^{i\eta_{fi}(b,\bar{v})}$ is now replaced by a factor involving collision-angle-averaged elastic scattering amplitude overlaps, within the classical path representation, $1/\Omega\int_\Omega d\vec{\Omega}T^p(b,\bar{v},\vec{\Omega})$, with

$$T^p(b,\bar{v},\vec{\Omega}) = e^{i\eta_{fi}(b\bar{v})}\left\{1 - \frac{1}{\hbar^2}\sum_{f'}\left[\int_{-\infty}^{\infty} dt\, V'_{ff'}(t) \int_{-\infty}^{t} dt' V'_{f'f}(t')\right]^*_{\text{collision}(b,\bar{v},\vec{\Omega})}\right.$$

$$\left.\frac{1}{\hbar^2}\sum_{f'i'}{}' \frac{\mu_{f'i'}}{\mu_{fi}}\int_{-\infty}^{\infty} dt\, V'^{*}_{f'f}(t)\int_{-\infty}^{\infty} dt\, V'_{i'i}(t) - \frac{1}{\hbar^2}\sum_{i'}\int_{-\infty}^{\infty} dt\, V'_{ii'}(t)\int_{-\infty}^{t} dt' V'_{i'i}(t')\right\} \qquad (3)$$

to second order in $V'(t)$, the anisotropic part of the interaction potential in the interaction representation. The symbol $\sum'$ restricts the summation to states f',i' degenerate with f,i for isolated spectral lines. For now, first order terms in $V'(t)$ have been omitted, because they disappear under spherical average. Equations (2) and (3) may now be employed in standard fashion[9] to obtain line shape parameters which include vcc effects arising from isotropic interactions.

The question remaining is how to make a suitable generalization of $\Delta\vec{v}$ to account for anisotropic interactions. While detailed justification is too lengthy for the present article, consideration of the first Born approximation, using wave packets, leads to the result that the outgoing waves f' are generated according to the interaction $V'_{f',f}$ from the state f, with maximum overlap of translational wave functions, throughout the interaction region. For very small energy differences between states f,f', the translational states for f,f' are virtually identical (particularly if one considers wave packets for which $k_f a >> 1$, a being the typical wave packet dimension, only for $\vec{k}_{f'}$ parallel to $\vec{k}_f$ at each moment of interaction. The potentials $V_{ff}(t)$ and $V_{f',f'}(t)$ guide the wave packets prior to and just following the interaction. Accordingly, to good approximation, one finds that the velocity appropriate to each term of $S_{fi}(b,\bar{v},\vec{\Omega})$ depends upon the overall initial and final states involved in the interaction matrix elements. In general, let

$$\Delta\vec{v}_{f'f,i'i} = \frac{1}{2}(\Delta\vec{v}_{f',f} + \Delta\vec{v}_{i',i}) \quad , \tag{4}$$

the group velocity change for the initial and final state wave packet overlap centroid, with

$$\Delta\vec{v}_{f',f} = \frac{1}{M}\frac{\left[\int_{-\infty}^{\infty} dt\, V'_{f',f}(t)\nabla_{\vec{R}}\left[\int_{-\infty}^{t} dt' V_{ff}(\vec{R}(t)) + \int_{t}^{\infty} dt' V_{f',f'}(\vec{R}(t))\right]\right]_{\text{coll.}(b,\bar{v},\vec{\Omega})}}{\int_{-\infty}^{\infty} dt\, V'_{f',f}(t)} \quad , \tag{5}$$

etc. for $\Delta\vec{v}_{i',i}$, in accordance with the above description, M being the mass of optically active atom. Accordingly, the appropriate generalization for eq. (3) is

$$T_{fi;v}(b,\bar{v},\vec{\Omega}) = e^{i\eta_{fi}(b,\bar{v})}\left[\left[1 + \frac{i}{\hbar}\int_{-\infty}^{\infty} dt\left(V^{*}_{ff}(t) - V_{ii}(t)\right)\right.\right.$$

$$\left.\left. - \frac{1}{\hbar^2}\left(\sum_{f'}\int_{-\infty}^{\infty} dtV'_{ff'}(t)\int_{-\infty}^{t} dt'V_{f'f}(t') + \sum_{i'}\int_{-\infty}^{\infty} dtV'_{ii'}(t)\int_{-\infty}^{t} dt'V'_{i'i}(t')\right)\right)\right.$$

$$\left.\times \frac{1}{\tau}\int_{0}^{\tau} e^{i\vec{k}\cdot\Delta\vec{v}_{ff,ii}t}dt + \frac{1}{\hbar^2}\sum_{f'i'}\frac{\mu_{f'i'}}{\mu_{fi}}\int_{-\infty}^{\infty} dtV'_{f'f}(t)\int_{-\infty}^{\infty} dtV'_{i'i}(t)\,\frac{1}{\tau}\int_{0}^{\tau} e^{i\vec{k}\cdot\Delta\vec{v}_{f'f,i'i}t}dt\right] , \qquad (6)$$

again to second order. The most important differences between eq. (6), which has here been established for the first time, and eq. (3) are twofold: first, that the first order anisotropic terms will, when combined with the velocity changes arising from anisotropic interactions (and in point of fact, from isotropic interactions as well) no longer vanish, in general leading to additional line shift contributions; and second, that the velocity changes in the $\vec{k}$ direction will in general not be the same for all magnetic substates, thereby providing that the different magnetic substates, quantized along the axis of laser propagation, will not be identically broadened.

The consequences of eq. (6) cannot be fully explored within the present article. However, one can obtain several useful results for the reasonably well understood Na D-lines perturbed by He, for which we employ the potentials of Baylis.[13] For this system all perturbational effects on the ground state are negligable.

i. The photon echo signal decays as observed by Kachru et al.[5] and analyzed according to the theory of Berman et al.[14] and Mossberg et al.[15] can now be more rigorously explained using the theoretical expressions (1) and (6). For the delay times considered, our expressions reveal that the salient velocity changes are far too large to permit a one or two term expansion of the velocity change integrals as would be implied by the past treatments. Through the present analysis we obtain β/τ (their relaxation parameter) values, for T = 410 K, as shown in Table 1, in fair agreement with the measurements for the D_2 line, but not so good for D_1 . From the values listed in Table 1, one concludes that the previously used theoretical form is not valid over this large a range of τ-values (being adequate only for $\tau \lesssim 10$ ns) and that the simple extrapolation procedure[5] used to obtain β/τ for $\tau = 0$ has questionable validity. Accordingly, the high pressure relaxation rates so obtained have doubtful accuracy.

ii. One now factors $C_{fi;\vec{v}}(\tau)$ into a product

$$C_{fi;\vec{v}}(\tau) = C^{p}_{fi;\vec{v}}(\tau)\; C^{vcc}_{vi;\vec{v}}(\tau) \quad , \tag{7}$$

where the standard pressure broadening correlation function is

$$C^{p}_{fi;\vec{v}}(\tau) = |\mu_{fi}|^2\; e^{i(\omega^{0}_{fi}+\vec{k}\cdot\vec{v})\tau} \exp\left\{-Nv\tau\,\frac{2\pi}{\Omega}\int_0^{\infty} bdb \int_{\Omega} d\vec{\Omega}\,\left(1-T^{p}(b,\vec{v},\vec{\Omega})\right)\right. . \tag{8}$$

The other correlation function is given by the exponential of the difference between eqs. (6) and (3), and depends upon vcc effects as modified by internal state dynamical changes,

$$C^{vcc}_{fi;\vec{v}}(\tau) \cong \exp\left[-\frac{2\pi N\bar{v}\tau}{\Omega} \int_0^\infty bdb \int_\Omega d\vec{\Omega}\, T^p_f(b,\bar{v},\Omega) \right.$$

$$\left. \times \left[1 - \frac{1}{\tau}\int_0^\tau e^{1/2\ i\vec{k}\cdot\Delta\vec{v}_{ff}(b,\bar{v},\vec{\Omega})\,t}\, dt \right] \right] \qquad (9)$$

with

$$T^p_f(b,\bar{v},\vec{\Omega}) = e^{i\eta_f(b,\bar{v})} \left[1 + \frac{i}{\hbar}\int_{-\infty}^{\infty} V_{ff}(t)\,dt - \frac{1}{\hbar^2}\sum_{f'} \int_{-\infty}^{\infty} dt V'_{ff'}(t) \int_{-\infty}^{t} dt' V_{f'f}(t') \right]_{b,\bar{v},} \qquad (10)$$

to second order in $V'(t)$. For He-Na D lines, only f-state perturbations have been retained.

One now finds the resultant line profile as a <u>convolution</u>,

$$I_{fi;\vec{v}}(\omega) = I^p_{fi;\vec{v}}(\omega) \otimes I^{vcc}_{fi;\vec{v}}(\omega) \quad . \qquad (11)$$

Here $I^p_{fi;\vec{v}}(\omega)$ is the standard (Doppler-shifted) Lorentz contour, being pressure broadened and shifted in the usual manner while $I^{vcc}_{fi;\vec{v}}(\omega)$, which has unit area, is decidedly non-Lorentzian. The latter contour is somewhat difficult to obtain in general. We proceed by expanding $C^{vcc}_{fi;\vec{v}}(\tau)$ to order τ^3,

$$C^{vcc}_{fi;\vec{v}}(\tau) \cong 1 - N\bar{v}\,\delta^{vcc}_f \tau^3 \qquad (12)$$

which represents an excellent approximation for line-broadening at $\gtrsim$1 m bar pressures, with δ^{vcc}_f given in the closed form

$$\delta_f^{vcc} = \frac{\pi k^2}{12\Omega} \int_0^\infty bdb \int_\Omega d\vec{\Omega}\, T_f^P(b\bar{v}\vec{\Omega})\ \Delta v_{ff}^2(b,\bar{v},\vec{\Omega})\ \text{cm}^2\ \text{s}^{-2} \quad . \tag{13}$$

(Our $\bar{v}\delta_f^{vcc}$ corresponds to $(ku_0)^2\ \gamma_{vcc}$ of previous treatments.[5] Forms similar to eqs. (12), (13) have been obtained previously, but with substantially different expressions for δ_f^{vcc}.) Using Baylis' potentials, one obtains δ_f^{vcc} values $(40.8 + i\ 4.15)\text{cm}^2\ \text{s}^{-2}$ for the D_1 line and an <u>average</u> value $(40.5 + i\ 17.62)$ for D_2 at 380 K. Under the assumption that the linehsape observations were made following the physical convolution of the saturation contour with the probe contour, the resulting effective (not quite Lorentzian) contours for either process by itself are found to have shifts and FWHM width parameters (as defined in I) as shown in Table 2. Also shown are other relevant values for comparison. The shifts are somewhat sensitive to the convolution procedure outlined here in an almost equal and opposite manner to their sensitivity to the inclusion of the anisotropic potential contributions to velocity changes, while the widths are much less sensitive to both. Of course, the actual profile for the D_2 line is now a sum of two independent profiles, one for transitions to the $|m_j| = 3/2$ states and the other to the $|m_j| = 1/2$ states, as quantized along the $\vec{k}$ direction, ignoring hyperfine mixings. We report only on the composite profile here. For reference, the line shift parameters corresponding to those reported in Table 2 would, for the D_1 and D_2 lines respectively, be $(-0.047, -0.047) \times 10^{-9}$ rad $\text{s}^{-1}\ \text{cm}^3$ for isotropic interactions together with the influence of the real second order terms in $V'(t)$ (no vcc effects); $(-0.118, -0.011)$ for the standard optical result (no vcc effects but imaginary $V'(t)$ second order effects included)[16]; $(-0.189, -0.123)$ with only isotropic potential vcc effects included, together with all of the above influences for standard pressure broadening; and $(-0.189, -0.201)$ with the further inclusion of vcc effects arising from anisotropic potentials.

The present discrepancies between theory and the two types of nonlinear optical experimental results appear not to be systematic, in view of the better agreement with D_1 observed parameters in nonlinear spectroscopy and with D_2 observations in the photon echo studies. At this stage, further experimental effort may be required in order to clarify the situation.

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11. This picture is in full agreement with similar conclusions reached through the use of WKB methods (P. S. Herman and K. M. Sando J. Chem. Phys. 68, 1153 (1978)) It also agrees with the "diffractive" scattering picture as described by Berman et al., ref. 8, with the understanding that whenever collisions are strong enough to substantially separate the wave packets corresponding to the different internal states in question, the phase shifts in the longitudinal direction have long since been large enough to already effectively cause the destruction of atomic coherence. It is these latter which are associated with the phase shifts of importance in classical path theories.

12. While the relationships are not yet fully understood, it seems that in the present treatment, one is able implicitly to sum the collisional kernal sequences, which have been extensively studied in other articles (see refs. 7, 8 and articles cited therein), for the very large numbers of successive collisions involved in coherence destructio.. All strength collisions are included in the sum, as are the simultaneous nonseparable competing effects of phase shifting and inelastic coherence termination. The present treatment is general with respect to classical mechanics and statistical physics, with the optically active atom initial velocity $\vec{v}$ playing its proper role in determining $\Delta\vec{v}$, and detailed balance considerations being satisfied.

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Table 1. Relaxation parameters β/τ of Kachru et al.[5] for Na-He Photon echos, T = 410 K ($torr^{-1}$ ns^{-1})

Pulse delay time τ	β/τ					
	D_1			D_2		
	Observed	Theory	(this work)	Observed	Theory	(this work)
0.0 ns			0.181			0.182
27.2 ns	0.168(1)		0.226	0.187(2)		0.228
40.5 ns	0.188(1)		0.246	0.206(1)		0.248
53.9 ns	0.200(1)		0.260	0.224(1)		0.262

Table 2. Lineshape parameters at 2 m bar, T = 380 K for Na-He (rad s^{-1} cm^{1}).

Parameter	Line	Observed[a]	Theory[b]	This work
Shift d/N	D_1	$-0.12(4)\times10^{-9}$	-0.23×10^{-9}	-0.189×10^{-9}
	D_2	-0.35(9)	-0.20	-0.201
Width parameter $\frac{d\Delta\omega(FWHM)}{dN}$	D_1	3.2(9)	3.5	3.42
	D_2	2.2(6)	3.5	3.39

[a] Weber and Jungmann[17]

[b] Herman and Weber (I)[9]