RELATIONSHIP OF A SPECTRAL LINE CENTER SHIFT TO ASYMMETRY OF THE LINE WINGS

S.D. Tvorogov

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

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The shifts of a spectral line center and shapes of the line wings are shown to be interrelated.

The spectral line half–width γ and shift ε of its center ω_0 are a subject of numerous measurements and calculations (see, for example, Refs. 1–7). Normally, the quantities γ and ε are used in the well–justified symmetrical Lorentzian expression describing a central portion of a line contour (here and below we consider collisions of molecules and assume the gas to be sufficiently rarefied)

$$f \sim \frac{\gamma}{(\omega - \omega_0 - \varepsilon)^2 + \gamma^2}\,, \tag{1}$$

where ω is the frequency of the field, and f is normally associated with a contour of an isolated spectral line.

The asymmetry of the contour is at the same time less studied.[8,9] Now we are going to discuss the line contour periphery and it could seem that the asymmetry, on the one hand, and the half–width and the line center shift, on the other hand, are quite independent.

However, these quantities are closely related, this follows from the most general definition of the absorption coefficient $\kappa(\omega)$. Then normally standard relation is considered, i.e.,

$$\kappa(\omega) \sim \frac{1}{\pi}\,\mathrm{Re}\int\limits_0^\infty \mathrm{d}t(\exp i\omega t)\ \mathrm{Sp}\ \rho S^{-1}(t)\,M\,S(t)\,M\,, \tag{2}$$

where $S(t)$ and ρ are the evolution operator (t is time) and the Gibbs matrix of density for the exact Hamiltonian H (an "active" molecule interacting with the field + "buffer" molecules + centers of mass + intermolecular interaction U), M is the dipole moment of an "active" molecule, and Sp is the Spur operation over all variables of H. The problem (2) is related to the kinetic equation[10,11]

$$\rho^{(1)}M + i\omega\,Q(\omega) = (1/i\bar{h})\,\hat{L}_1 Q + \hat{\Gamma}(\omega)Q$$

with the superoperator of relaxation

$$\hat{\Gamma} = \frac{1}{\bar{h}^2}\int\limits_0^\infty \mathrm{d}t\ \mathrm{Sp}'\hat{L}(1-\hat{P})\left(\exp i\omega t + \frac{t}{i\bar{h}}(1-\hat{P})\hat{L}\right)(1-\hat{P})\hat{L}'R. \tag{3}$$

The operator Q over the variables of an "active" molecule with the Hamiltonian H_0, density matrix $\rho^{(1)}$, and quantum indices $a, b,\dots$ is defined so that $\lambda(\omega) = \sum\limits_{a,b} Q_{ab}M_{ab}$. The value $Q_{ab}M_{ab} \equiv \kappa_j$ may be interpreted as the "absorption coefficient within an isolated absorption line centered at the frequency ω_j". This term does not imply an approach (e.g., ignoring possible interference of quantum states) simply, the summing over quantum indices of H_0 is separated out from the Sp operation in Eq. (2), and j denotes the combination of these indices for the corresponding transition.

The cap sign "^" in Eq. (3) denotes the superoperators. Thus, if x and y are ordinary operators with matrix elements x_{ab} and y_{ab} the equality $y = \hat{\Gamma}x$ means $y_{ab} = \sum\limits_{a',b'} \Gamma_{ab,\,a'b'}\,x_{a'b'}$. Then $\hat{L}_1 x = [H_0, x]$, $\hat{L}x = [H, x]$, $\hat{L}'x = [U, x]$ and the meaning of "^" symbol is generalized on arbitrary operators; R is the density matrix of the subsystem "buffer" molecules + centers of mass, and Sp′ is Spur operation over these matrix variables. It is just the projecting superoperator $\hat{P}x = PSp'x$ that provides for validity of the rigourous kinetic equation.[10–13]

If one considers only the physical aspect of the problem it is much easier to explain the following idea of the approach proposed here for the case of diagonal terms $\Gamma_{ab,a'b'} = \Gamma_{ab}\delta_{aa'}\delta_{bb'}$ that means the absence of interference. By the way, this approach does not affect the final results, as will be shown below. Now, when the term "sum of frequencies" is omitted (this approach is typically used with optical waves), $\Gamma_{ab}(\omega) = \Gamma'_{ab}(\omega) + i\Gamma''_{ab}(\omega)$ and the shape of jth line is

$$f_i(\omega) = \frac{\Gamma'_j(\omega)}{(\omega - \omega_j - \Gamma''_j(\omega))^2 + \Gamma'^2_j(\omega)}\,. \tag{4}$$

The relationship between expression (1) and (4) is quite obvious. Thus at resonance ($\omega \simeq \omega_j$)

$$\Gamma'_j(\omega_j) = \gamma_j,\ \ (\omega_j) = \varepsilon_j\,. \tag{5}$$

Standard analytic continuation of function (3) over ω results in a regular function in the upper complex half–plane that together with the conditions $\Gamma'_j(-\omega) = \Gamma'_j(\omega)$ and $\Gamma''_j(-\omega) = -\Gamma''_j(\omega)$ following from Eqs. (2)–(4) gives

$$\Gamma''_j(\omega) = \frac{2\omega}{\pi}P\int\limits_0^\infty \frac{\Gamma'_j(\omega')\,\mathrm{d}\omega'}{\omega'^2 - \omega^2}\,. \tag{6}$$

As in the dispersion relations of electrodynamics,[14] it is just relation (6) which is pragmatic, since physically relations (5) mean that $'_j$ is always positive while Γ''_j can change its sign. By substracting $\Gamma'_j(\omega)$ from $'_j(\omega')$ integral (6) is reduced to the Riemannian that yields, according to relations (5), the following relation for the line center shift:

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$$\varepsilon_j = \frac{2\omega_j}{\pi}\int\limits_0^\infty \frac{\Gamma\,'_j(\omega) - \gamma_j}{\omega^2 - \omega_j^2}\,d\omega\,. \tag{7}$$

As the analysis has shown, one can replace $\Gamma\,''_j(\omega)$ by ε_j in relation (4) at any shifted frequency $(\omega - \omega_j)$. Therefore, the use of $\Gamma\,''_j(\omega)$ becomes meaningful only at resonance $(\omega \simeq \omega_j)$. This fact underlines the leading role of $'_j(\omega)$ in constructing the line contour.

Now one can formulate the principal result of interpreting expression (7) as follows. The spectral properties of a line profile (with the asymmetry being necessary among them) govern the shift of its center.

This statement can be made very clear if one uses the approach[10] to the kinetic equation. In this case $\Gamma\,'_j = I_j(\xi) + \xi^2\Gamma^{(\pm)}_j(|\xi|)$, where $\xi = \omega - \omega_j$ and the signs (±) emphasize the fact that G'_j, to say generally, is different in the regions to the left and to the right from the point $\xi = 0$. For a relatively small ξ ($|\xi| < \gamma_j$) the even function $I_j(\xi)$ is equal to $\gamma_j + O(\xi^2)$ and $\Gamma^{(\pm)}_j = O(1/\gamma_j)$. For this reason there are no any mathematical problems with the point $\xi = 0$ as well as with the representation $\int\limits_{-\infty}^{+\infty} d\xi = \int\limits_0^{\infty} d\xi + \int\limits_{-\infty}^{0} d\xi$ being followed by the change of variable ξ to $-\omega$ in the second integral (it is obvious that integration over ξ gives $\int\limits_{-\xi}^{\infty} d\xi \simeq \int\limits_{-\infty}^{+\infty} d\xi$).

Physical meanings of terms in the expression for $'_j$ differ quite distinctly.[10] Thus the first term dominates at small $|\xi|$, while the second at large $|\xi|$ values.

Just this circumstance makes it possible to construct a spline that combines the asymptotics of small and large frequency shifts,[10] as shown in the figure.

After such simple transformations (an additional approach $2\omega_j/(2\omega_j + \xi) \simeq 1$ is quite obvious) one obtains from Eq. (7) that

$$\varepsilon_j = \frac{\gamma_j}{\pi}\ln\frac{\xi^{(+)}_j}{\xi^{(-)}_j} + \frac{1}{\pi}\int\limits_{\xi^{(+)}_j}^{\infty}\frac{\psi^{(+)}_j(\xi)\,d\xi}{\xi} - \frac{1}{\pi}\int\limits_{\xi^{(-)}_j}^{\infty}\frac{\psi^{(-)}_j(\xi)\,d\xi}{\xi}. \tag{8}$$

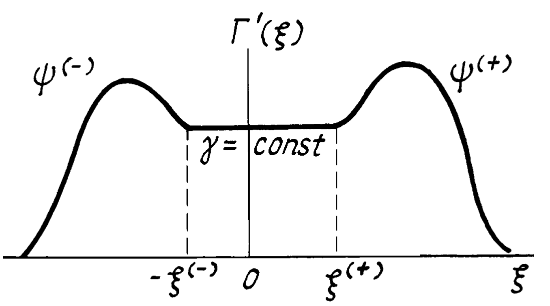

FIG. 1.

Thus, one can see that formula (8) explicitly describes the relation of the line center shift to the line shape symmetry. For example at $\xi^{(+)}_j = \xi^{(-)}_j$ and $\psi^{(+)}_j = \psi^{(-)}_j$ the value $\varepsilon_j = 0$ and vice versa if $\varepsilon_j \neq 0$ the line wings to the left and to the right from $\xi = 0$ have different shapes. The asymmetry of the line contour is associated with the line wings since, as has already been shown, the function I_j is symmetric relative to $\xi = 0$.

An empirical approximation of the form $\varepsilon_j = \alpha\gamma_j - \beta$ from Ref. 15, where the data of half–widths and shifts of water vapor absorption lines in the mixtures with N_2, O_2, and Ar were statistically analyzed, is a good experimental proof of relation (8). Constant values α and β may be reasonably interpreted in terms of relation (8).

This general conclusion on the relationship of a line under and asymmetry of its wings in no ways can be affected by interfering of the quantum states, i.e., when one cannot neglect nondiagonal matrix elements (3). Really, the main procedure of the above analysis is the use of dispersion relations whose derivation requires only integral (3) to be of the Fourier type with the integration over a semi–infinite interval. As well known (see Refs. 14 and 16) this fact is backed by the principle of causality that is essential when deriving the kinetic equation. Mathematical proofs of this statement can be found in Refs. 10–13. As the analysis of Eq. (3) shows the interference of quantum states does not affect the inherent symmetry of I_j as well. This means that the integral (7) is, as formerly, determined by the line contour periphery.

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