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A Method of Synthesis of the Statistical and Impact Theories of Pressure Broadening

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Two types of theories of pressure broadening have been current in the literature: the "statistical" theory of Kuhn[1] and Margenau,[2] and the "impact" theory of Weisskopf,[3] Lenz,[4] and others. Spitzer[5] and Holstein[6] have indicated the limits of validity of the two types of theory: At low pressures the statistical theory is certainly valid on the wings of the line, the impact theory in the center, while at high pressures the statistical theory is valid if its fundamental assumption that the frequency perturbation for a given atom is the sum of that due to all others in the gas,

$$\nu=\sum_{j=1}^{N}\nu(R_j), \tag{1}$$

is not too seriously incorrect. Most of these discussions and this note are confined to the "adiabatic" or nondegenerate case in which the perturbations due to the atoms in the gas may be expressed simply as frequency perturbations.

Lindholm[7] carried out a complete study of the transition between the two theories for a frequency perturbation proportional to $1/R^6$. Unfortunately, he used a simplified model of the collision in which the frequency was constant during the collision and thus the perturbation started and stopped abruptly; some of his results seem to be in error because of this fact.

This note presents a more general and more workable technique for synthesizing the two theories and studying the transition between them. The spectral intensity which is desired is given by the Fourier integral

$$I(\omega)=\left|\int_{-\infty}^{\infty}\exp\left[i\left(\omega t-\int_{-\infty}^{t}\nu(t')dt'\right)\right]dt\right|^2, \tag{2}$$

where $\nu(t')$ is the frequency at the time t', given by (1) with the R_j assuming the correct values for this time. Now we transform (2) by the standard correlation-function transformation[8] and obtain

$$I(\omega)=\int_{-\infty}^{\infty}e^{i\omega\tau}\varphi(\tau); \tag{3a}$$

$$\varphi(\tau)=\int_{-\infty}^{\infty}dt\exp\left[i\int_{t}^{t+\tau}\nu(t')dt'\right]=\left\langle\exp\left[i\int_0^{\tau}\nu(t')dt'\right]\right\rangle_{\mathrm{Av}}. \tag{3b}$$

We now use (1) and obtain

$$\varphi(\tau)=\left\langle\prod_j\exp\left[i\int_0^{\tau}\nu(R_j)dt\right]\right\rangle_{\mathrm{Av}}.$$

To an approximation more than adequate for our purposes the motions of the molecules in the gas are independent, so that

$$\varphi(\tau)=\left\{\left\langle\exp\left[i\int_0^{\tau}\nu(R)dt\right]\right\rangle_{\mathrm{Av}}\right\}^N. \tag{4}$$

More general methods of averaging are possible than the following, in case the situation is more complicated, but this should suffice to show the method: Suppose that the paths of atoms are straight relative to each other; then the parameters to be averaged over are b, the impact parameter, and x_0, the position of the atom at the start of the time-interval 0 to τ along the straight line of impact parameter b. Now

$$2\pi\int bdb\int dx_0=V, \tag{5}$$

where V is the volume available to the N atoms of the gas. Then

$$\begin{aligned}\varphi(\tau)&=\Bigg(1-\frac{2\pi}{V}\int_0^{\infty}bdb\int_{-\infty}^{\infty}dx_0\\&\qquad\times\left\{1-\exp\left[i\int_0^{\tau}\nu([(x_0+vt)^2+b^2]^{\frac{1}{2}})dt\right]\right\}\Bigg)^N\\&=\exp[-nV'(\tau)].\end{aligned} \tag{6}$$

Here $n=N/V=$density of atoms per cc, and

$$V'(\tau)=2\pi\int_0^{\infty}bdb\int_{-\infty}^{\infty}dx_0\times\left\{1-\exp\left[i\int_0^{\tau}\nu([(x_0+vt)^2+b^2]^{\frac{1}{2}})dt\right]\right\}. \tag{7}$$

It is an easy matter, for which we have no space here, to show that (6) and (7), with (3a), lead to the impact and statistical theories in the proper limits. The criteria for validity of the two theories are easily derived, being the same as those given in references 5 and 6; in particular, these hold even for $\nu\sim1/R^3$, a case in which there had been some question as to the validity of the impact theory in the low-pressure limit. Analytical methods can be applied to give first corrections to the two types of theories, while V', which is a function only of one variable for a given form of $\nu(R)$, can be approximated numerically for any given $\nu(R)$ without much difficulty. The numerical calculation of the line shape for various densities, from (3a), should then be fairly easy.

Further details, and some computations using the above method, will be given in a later publication.

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Quadrupole Coupling Ratio of the Chlorine Isotopes*

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The ratio of the nuclear quadrupole coupling constants, eqQ, for the chlorine isotopes has been found to depend to about 0.02 percent on the molecular environment. Radio frequency transitions were measured for several chlorine compounds in the solid state.

A variation in the ratio $(eqQ)_{35}/(eqQ)_{37}$ with molecular species is to be expected because of nuclear polarization and certain kinds of molecular vibrations.[1] A change as large as 0.1 percent has previously been reported in microwave spectra[2], but measurements of direct quadrupole transitions[3] with an accuracy of the order of 0.01 percent had failed to show conclusively any such variation.

The lines are narrow enough to permit considerably better accuracy, and were hence measured to an accuracy of about 0.001 percent. At Columbia University this degree of precision was obtained by using a Signal Corps type BC221 frequency meter to measure differences between the line frequency and a nearby harmonic of a standard crystal oscillator. At Bell Telephone