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# Effect of collision-induced phase-shifts on the line widths and line shifts of $CO_2$-Ar system

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**Abstract.** The theoretical calculation of line widths and line shifts for $CO_2$-Ar system is computed by the Mehrotra-Boggs theory. It is shown for this system that the phase shift effect is very important at large values of $|m|$ where $m$ is the value of rotational quantum number $J$ in the lower vibrational state. It is also pointed out that the Salesky-Korff theory is the same as the Mehrotra-Boggs theory.

**Keywords.** Collision-induced line shape; phase shift effect; $CO_2$-Ar system; Mehrotra-Boggs theory.

## 1. Introduction

The spectral line width and shift parameters of a microwave transition from initial state $n$ to final state $m$ are related to the real and imaginary parts of interruption function $S$ given by

$$S = 1 - T_{nn} T^*_{mm} \tag{1}$$

where $T$ is the time development operator which is governed by the time-dependent interaction due to collision between two molecules. The time-development operator $T$ must be solved to get information about the line shape. Since it is not easy to solve the time-dependent Schrödinger equation for two colliding molecules, many approximations have been used. The simplest and the most popular technique for the solution of $T$ is to expand it as

$$T = T_0 + T_1 + T_2 + \ldots. \tag{2}$$

where $T_0$, $T_1$, $T_2$, ... are 0th, 1st, 2nd, .... order terms. It is practical to terminate the series at second order as was done by Anderson (1949). The third order term was also evaluated by Rabitz and Gordon (1970). The main disadvantages of this series are that it is not unitary and it is expected to be accurate only for small intervals of time and for those cases in which the perturbation $V(t)$ is much smaller than the unperturbed Hamiltonian $H_0$ of the system. So, for the treatment of intermediate interaction where the calculated transition probability is greater than one, the method is not accurate. For the treatment of strong collisions, the value of the transition probability diverges. Anderson (1949) suggested three approximations for the strong collisions (Tsao and Curnutte 1962).

Another method of expanding the time development operator is in the form (Pechukas and Light 1967)

$$T(t) = \exp\,[A_0 + A_1 + A_2 + \ldots.] \tag{3}$$

where $A_0$, $A_1$, $A_2 \ldots$ are operators. The expansion is known as the Magnus method. The method has not become popular because it is difficult to evaluate numerically an exponential of the operator.

Murphy and Boggs (1967) have expanded the diagonal element of the time development operator $T$ in exponential form neglecting some terms in the series. This formulation was suitable only for microwave spectral line broadening. Cattani (1972) has formulated a modified Murphy-Boggs theory by combining the treatments of Murphy and Boggs (1967) and Anderson (1949).

Mehrotra and Boggs (1976) treated the expansion of the time development operator in a more general way. They have shown that the $N$th term of the time-dependent perturbation theory is

$$T^{(N)}_{nm}(t) = T^{(N)}_{nm}(-\infty)\exp\Big[\int_{-\infty}^{t} \mathrm{d}t_1\; G^{(N)}(t_1)\Big]$$

$$+\int_{-\infty}^{t} \mathrm{d}t_1 \exp\Big[-\int_{t}^{t_1} \mathrm{d}t_2\, G^{(N)}(t_2)\Big]\, F^{(N)}(t_1). \tag{4}$$

The functions $G^{(N)}$ and $F^{(N)}$ can be obtained by the following recurrence formulae

$$G^{(N+1)}(t) = \sum_{\beta} G_\beta(t, t_\beta)\exp\Big[-\int_{t_\beta}^{t} \mathrm{d}t_1\, G^{(N)}(t_1)\Big] \tag{5}$$

$$F^{(N+1)}(t) = F(t) - \sum_{\beta} G_\beta(t, t_\beta)\int_{t_\beta}^{t} \mathrm{d}t_1\, F^{(N)}(t_1) \times$$

$$\exp\Big[-\int_{t_\beta}^{t_1} \mathrm{d}t_2\, G^{(N)}(t_2)\Big] \tag{6}$$

with $G^{(1)}(t) = \sum_{\beta} G_\beta(t, t_\beta)\cdot 1$ and $F^{(1)}(t) = F(t)\,(1-\delta_{nm})$.

The function $F(t)$ is given as

$$F(t) = \sum_{a=0}^{\infty} (i\hbar)^{-1-a} \sum_{m_1}{}' \dots \sum_{m_a}{}' \exp(i\,\omega_{nm_1} t)\, V_{nm_1}(t)$$

$$\times \int_{-\infty}^{t} dt_1 \exp(i\,\omega_{m_1 m_2} t_1)\, V_{m_1 m_2}(t_1) \dots \int_{-\infty}^{t_{a-1}} dt_a$$

$$\times \exp(i\,\omega_{m_a m} t_a)\, V_{m_a m}(t_a) \qquad (7)$$

and $G_\beta(t, t_\beta)$ is an integral operator which is defined as

$$G_\beta(t, t_\beta) f(t_\beta) = (i\hbar)^{-1-\beta} \sum_{m_1}{}' \dots \sum_{m_\beta}{}' \exp(i\,\omega_{nm_1} t)\, V_{nm_1}(t)$$

$$\times \int_{-\infty}^{t} dt_1 \exp(i\,\omega_{m_1 m_2} t_1)\, V_{m_1 m_2}(t_1) \int_{-\infty}^{t_1} dt_2$$

$$\times \exp(i\,\omega_{m_2 m_3} t_2)\, V_{m_2 m_3}(t_2) \dots \int_{-\infty}^{t_{\beta-1}} dt_\beta$$

$$\times \exp(i\,\omega_{m_\beta m} t_\beta)\, V_{m_\beta m}(t_\beta) f(t_\beta) \qquad (8)$$

where $f(t_\beta)$ is some function of time $t_\beta$.

The first order of the theory and neglecting the isotropic part of the potential gives the same expression as obtained by Murphy and Boggs (1967). The first order treatment has been applied to the collision induced line shape (Mehrotra and Boggs 1977) which turns out to be the same as that formulated by Cattani (1972), if the isotropic term in the potential is neglected.

## 2. Comparison with the Salesky-Korff theory

Salesky and Korff (1979) presented a graphical technique to expand the time development operator in the exponential form. The formulation (Salesky and Korff 1980) seems to be exactly the same as done by Mehrotra and Boggs (1977). Using the first approximation ($N = 1$, in (4)), one can approximate the interruption function $S(b)$ as

$$S(b) = 1 - T^{(1)}_{nn}(+\infty)\, T^{(1)*}_{mm}(+\infty)$$

$$= 1 - \exp\left[-\tfrac{1}{2}\Gamma_n - \tfrac{1}{2}\Gamma_m\right]$$

$$\times \exp\left[-\frac{1}{i\hbar}\int_{\infty}^{\infty} (V_{nn} - V_{mm})\, dt + i(\phi_n - \phi_m)\right].$$

The line width parameter $\Delta\nu$ for the transition $n \rightarrow m$ can be written as

$$\Delta\nu = N \sum_{J_2} \rho_{J_2} \int_0^\infty \mathrm{d}b \int_0^\infty \mathrm{d}v\, v f(v) \left[1 - \exp\left(-\tfrac{1}{2}\Gamma_n - \tfrac{1}{2}\Gamma_m\right)\right]$$

$$\times \cos\left(\frac{1}{\hbar}\int_{-\infty}^{\infty} (V_{nn} - V_{mm})\,\mathrm{d}t + \phi_n - \phi_m\right) \tag{9}$$

and the line shift parameter $\Delta\,\nu_s$ is given by

$$\Delta\,\nu_s = N \sum_{J_2} \rho_{J_2} \int_0^\infty \mathrm{d}b \int_0^\infty \mathrm{d}v\, v f(v) \left[\exp\left(-\tfrac{1}{2}\Gamma_n - \tfrac{1}{2}\Gamma_m\right)\right]$$

$$\times \sin\left(\frac{1}{\hbar}\int_{-\infty}^{\infty} (V_{nn} - V_{mm})\,\mathrm{d}t + \phi_n - \phi_m\right). \tag{10}$$

The same expressions for the line width and line shift have been obtained by Salesky and Korff (1980).

## 3. Discussion of results for $CO_2$-Ar system

The theory of Mehrotra and Boggs (1977) is applied to $CO_2$-Ar system. The potential is taken as (Boulet *et al* 1974)

$$V = V_{LJ} + 4\,\epsilon\,(\sigma/R)^{12}\, a_2\, p_2\,(\cos\theta) - 4\,\epsilon\,(\sigma/R)^6\, b_2\, p_2\,(\cos\theta)$$

where $V_{LJ}$ is the Lennard-Jones potential. The coefficient of $p_1$ $(\cos\theta)$ for the system will not be important because the center of mass of the molecule coincides with its center of charge.

The calculated results are shown in figure 1 along with the experimental results of Boulet *et al* (1974). As pointed out by Boulet *et al* (1974) that a short range anisotropic potential must be introduced in the calculation of the interruption function, the same conclusion is also obtained here. The significant aspect of the results is that the effect of collision induced phase shift (*i.e.* cosine term in (9)) is also very important to explain $|m|$ dependence. Curve (b) of figure 1 is obtained when the cosine term in (19) of Mehrotra and Boggs (1977) is approximated to one as done in the Murphy-Boggs theory. It can also be seen from the curve that the effect of the cosine term is more important for large values of $|m|$ for vibrational-rotational spectral lines. The collision induced line shift is also computed and shown in figure 1 (curve c). The experimental data for shift is not known, but it can be seen that shifts are not negligible and can be measured by the present experimental techniques.

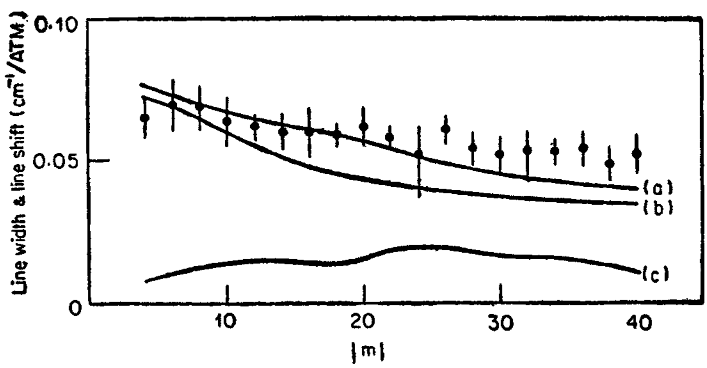


**Figure 1.** Collision induced line width and line shift in $cm^{-1}$/Atm for 001—(10°0, 02°0) of $CO_2$-Ar system *vs* | *m* |. Experimental results (Boulet *et al* 1974); **a.** theoretical results with phase shift; **b.** theoretical results without phase shift; **c.** the calculated values of collision induced line shift. The parameters chosen are $\epsilon = 150{\cdot}00$ °K, $\sigma = 3{\cdot}95$ Å, $a_2 = b_2 = 0{\cdot}27$, $B_0 = 11{\cdot}6139$ GHz, and $B_1 = 11{\cdot}7060$ GHz. $B_0$ is the rotational constant in the lower vibrational state and $B_1$ is that in the upper vibrational state.

## 4. Conclusions

The conclusions of the paper are as follows:

(i) The theoretical formulation of Salesky and Korff (1979, 1980) is not new as claimed by Salesky and Korff (1979) but is the same as obtained earlier by Mehrotra and Boggs (1977). (ii) The Mehrotra and Boggs theory (1977) as the Anderson theory (Boulet *et al* 1974) predicts that the microwave-infrared spectral line shapes are sensitive to the short range interaction. Unlike for microwave spectral lines, one must take the short range interaction to explain $|m|$ dependence. (iii) It is shown here foı the first time that the $|m|$ dependence of the microwave-infrared spectral line shapes is also dependent on the phase shifts which appear as cosine term in the Mehrotra and Boggs theory (1977). In the previous calculations (Boulet *et al* 1974), the $|m|$ dependence was explained only by taking the repulsive part of the isotropic potential but one must consider the phase shift effect as well as the repulsive part of the potential to explain the $|m|$ dependence of microwave-infrared spectral line shape. This is not so in the case of microwave spectral line shape. (iv) The collision induced line shifts are found to be significant and can be measured experimentally.

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