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Calculation of Spectral Line Shapes for General Pressures[*,†]

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A method of calculating spectral line shapes at arbitrary temperatures and pressures is developed. The analysis assumes that: The two-body interaction potential is known; the potentials add as scalars; the perturbers follow classical paths determined by the equations of motion; and the collisions are adiabatic. The resulting formulas are solved numerically, using interaction potentials which are appropriate for the interaction between argon and cesium metals. The calculation is carried out for relative densities up to 160. Calculated half-widths and line shifts agree with experimental data.

I. INTRODUCTION

Theoretical study of the collision-broadened spectrum emitted (or absorbed) by a gas has been the subject of considerable research. Most of the studies in this area have considered either the limit of a rarefied high-temperature gas[1–4] (impact limit) or a dense low-temperature gas[5] (quasistatic or statistical limit). The transition between the impact and static limits has been considered in a number of publications.[6–8] The approach given by Anderson[8] enables one, in principle, to calculate the line shape from gases at an arbitrary pressure and temperature. Anderson developed an expression for the line shape from the Fourier integral formula by assuming that the molecular interactions could be added as scalars, that the collisions did not induce excitations, and that the perturbing molecules moved with a uniform velocity along classical straight-line paths. Also, the density matrix was neglected.

The method for calculating spectral line shapes developed in this paper uses a similar approach; however, the perturbing molecules move with nonuniform velocities along classical paths determined from the equations of motion (Newtonian paths), and the density matrix is included in the calculation. Finally, the results are compared with experiments in which the assumptions are justified.

The discovery[9] and measurements[10] of collision-induced absorption (CIA) in rare-gas mixtures have aroused considerable interest in recent years.[11–19] Though the mechanism which produces such absorption differs from the resonant absorption (or emission) envisaged in the present analysis, the various treatments of a similar scattering problem make reference to the calculation of CIA appropriate. There is another difference and another similarity worth emphasizing. In the interpretation of CIA data, the objective is information about the induced dipole moment and the ground-state intermolecular potential, while a systematic use of the general-pressures theory would produce data on the excited-state and ground-state potentials. The comparison of CIA calculation with experiments conducted at elevated temperatures should provide a sensitive source of data on the repulsive character of unlike atom interactions[15, 17]; the computations reported in Sec. III of this paper, in fact, proved very sensitive to the choice of potential parameters and the numerical methods used to treat close collisions.

II. THEORY

We begin the derivation of this method for calculating spectral line shapes with the Fourier integral formula.[20] The Fourier integral formula for the shape of an isolated spectral line, broadened by collisions which do not induce excitations, can be written

$$\begin{aligned} I(w) &\equiv \int C(s)\exp(iws)\,ds \\ &= \int \exp(iws)\Big(\exp\Big\{ i \int_0^s [V_{T,f}(t) \\ &\quad - V_{T,i}(t)]\,dt - \epsilon_T\Big\}\Big)_{\text{av}} ds, \end{aligned} \tag{1}$$

where $V_{T,i(f)}(t)$ is the initial (final) potential due to all the perturbing molecules (perturbers); ϵ_T is the ratio of the sum of $V_{T,i}(0)$ and the perturbers's initial kinetic energy to the gas temperature; the subscript av denotes an average over all collisions, and $C(s)$ is referred to as the correlation function. Equation (1) is written in units with both Boltzmann and Planck constants equal to unity.

For interactions which add in a scalar fashion, the correlation function can be written in terms of the two-body potentials, $V_{i(f)}$:

$$C(s) = A^{-N}\Big(\exp\Big\{i\int_0^s [V_f(t) - V_i(t)]dt - \epsilon\Big\}\Big)_{\text{av}}^{N}. \tag{2}$$

In (2), N is the total number of perturbers, and A is a normalization constant. The average in (2) is carried out over all initial positions and velocities of the perturbers. Expressing the initial positions and velocities in spherical coordinates (R, θ, ϕ, v_R, v_θ, v_ϕ) and taking the limit of a large number of perturbers having a finite average number density, η Eq. (2) becomes

$$\begin{aligned} C(s) = \exp\Big(&- 2\eta M \int_{-\infty}^{\infty} dV_R \int_0^{\infty} R^2\,dR \int_{-\infty}^{\infty} dV_\phi \\ &\times \exp\{-\tfrac{1}{2}[M_r V_R^{\,2} + M_r V_\phi^{\,2} + 2V_i(R)]\}\Big) \\ &\times \Big(1 - \exp\Big\{i \int_0^s [V_f(t) - V_i(t)]ds\Big\}\Big). \end{aligned} \tag{3}$$

The symbol $M(M_r)$ in (3) represents the ratio of the perturber mass (reduced mass) to the gas temperature.

Equation (3) enables one to calculate the correlation function, and therefore the line shape, when the interaction potentials are known. The line shapes predicted by the phase shift and quasistatic theories can be obtained from (3) for the appropriate physical conditions.

In order to complete the calculation of the line shape using (3), the potential must be expressed in terms of the initial coordinates (R, V_R, V_ϕ) and time t. In order to demonstrate the method used to obtain $V(R,\ V_R,\ V_\phi\ t)$, the problem will be specialized to a frequently useful empirical expression for the potential, $V(r) = B_n/r^n - B_p/r^p$.

The potential is expanded in a power series in time,

$$V(r(t)) = \sum\nolimits_h (B_h\alpha_{hn} - B_p\alpha_{hp})t^h \quad , \tag{4}$$

where the α's represent the multinomial coefficients

$$\begin{aligned} \alpha_{ho} &= A_o^{\,n}\,, \\ \alpha_{hq} &= \sum_{k-1}^{q} (kn - q + k)A_k\alpha_{h,\,m-k}\,, \quad q \geqslant 1. \end{aligned} \tag{5}$$

In (5), A_k is a function of R, v_r, and ν_ϕ, which can be obtained by equating (4) to a power series for the potential developed from the differential equation of the orbit,

$$V(r) \propto V_0^{\,2} - \dot{r}^2 - V_0^{\,2}b^2/r^2 = \sum\nolimits_h D_h t^h \quad , \tag{6}$$

where $D_0 = V_0^{\,2} - a_1^{\,2} - V_0^{\,2}b^2/R^2$,

$$\begin{aligned} D_L = &- \sum_{l=0}^{L} [(l+1)(L-l+1)a_{l+1} \\ &\times a_{L-l+1} + V_0^{\,2}b^2A_lA_{L-l}], \quad L \geqslant 1. \end{aligned}$$

In (6), b is the impact parameter, v_0 is the initial relative speed, and $a_0 = A_0^{-1} = R$. The relation between a and A is

$$A_q = -\sum_{l=1}^{q} a_l \frac{A_{q-l}}{a_o}\,. \tag{7}$$

Equations (4)–(7) uniquely determine the values of α_{hn}, and thus the potential can be written in the form required by (3).

III. APPLICATION TO CESIUM SPECTRUM BROADENED BY ARGON

The interaction potential between argon and cesium in the ground state was obtained by fitting a Lennard-Jones (12–6) potential to molecular beam data.[21] The interaction potential for an alkali atom in its excited state was assumed to have the same radial dependence as the ground-state potential, with coefficients which produced half-widths and line shifts that correspond to experimental data for the $6^2P_{1/2}-6^2S_{1/2}$ transition.

The procedure given by (4)–(7) was truncated at t^3 terms. The time integration in (3) becomes trivial when (4)–(7) are used to obtain $V(R, v_R, v_\phi, t)$, and the integration over V_ϕ can be completed analytically. The expression for the correlation function becomes

$$C(s) = \exp\Bigg[-2\eta M \int_0^\infty R^2\, dR \int_{-\infty}^{\infty} dV_R \exp\{-\tfrac{1}{2}[m_\gamma V_R{}^2 + 2V_i(R)]\}(\pi/\beta)^{1/2}$$

$$- e^{i\sigma}\left(\frac{(\beta^2+d^2)^{1/2}+\beta}{\beta^2+d^2}\right)^{1/2} - i\,e^{i\sigma}\left(\frac{(\beta^2+d^2)^{1/2}}{\beta^2+d^2}+\beta\right)^{1/2}\Bigg] , \qquad (8)$$

where $d = \{[\tfrac{1}{2}(C-A)n]/R^{n+2} + [\tfrac{1}{2}(B-D)p]/R^{p+2}\}\tfrac{1}{3}S^3$,

$$\sigma = [(A-C)/R^n - (B-D)/R^p]S + [n(C-A)V_R/R^{n+1} - p(D-B)V_R/R^{p+1}]\tfrac{1}{2}S^2 + \{p(p-1)(D-B)(\tfrac{1}{2}V_R{}^2)/R^{p+2}$$

$$-n(n-1)(C-A)(\tfrac{1}{2}V_R{}^2)/R^{n+2} + [\tfrac{1}{2}n^2(C^2-A^2)]/(M_\gamma{}^{2n+2}) + [\tfrac{1}{2}p^2(D^2-B^2)]/(M_\gamma R^{2p+2})$$

$$-np(CD-AB)/(M_\gamma R^{p+n+2})\}\tfrac{1}{3}S^3, \quad \beta = \tfrac{1}{2}M$$

and where A, B and C, D represent the potential coefficients B_n, B_p for the ground state and excited state, respectively. The integrations over v_R and R, as well as the Fourier transform in (1) were carried out numerically.

For the results displayed in Figs. 1–3 the potential coefficients were, in cgs units: $A = 3.43 \times 10^{-102}$, $B = 3.3 \times 10^{-58}$, $C = 8.02 \times 10^{-102}$, $D = 5.55 \times 10^{-58}$, $n = 12$, and $p = 6$. Figure 1 demonstrates the broadening, shifting, and distortion of the spectral line which results when the relative density is changed from 3 to 95. Figures 2 and 3 compare the line shifts and half-widths obtained from the theory with the previously unexplained experimental data of Chen and Garrett.[22]

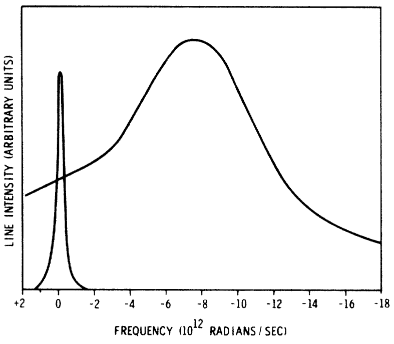

FIG. 1. Comparison of the theoretical line shape at relative densities of 3 and 95.

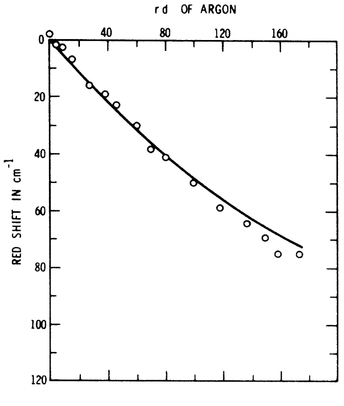

FIG. 2. Comparison of the computed line shifts and experimental data for $6^2P_{1/2}-6^2S_{1/2}$ transition in Cs broadened by argon (Ref. 22).

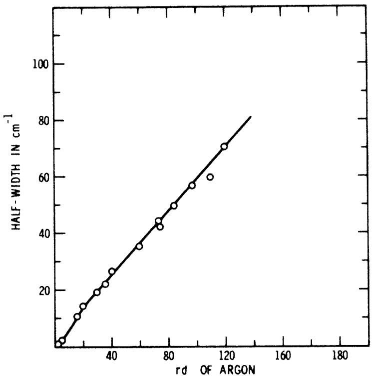

FIG. 3. Comparison of the theoretical half-width and experimental data for 6^2P-6^2S transition in Cs broadened by argon (Ref. 22).

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