A semiclassical theory for spectral line broadening in molecules

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(Received 7 April 1976)

A semiclassical $S$-matrix theory is developed and applied to spectral line broadening in linear molecules perturbed by atoms. This theory uses curved classical trajectories determined by the isotropic part of the atom-molecule interaction and the $S$-matrix is treated to all orders in the interaction. Numerical calculations can be made rather easily even for high quantum numbers. The theory is least accurate for very low quantum numbers, but even then calculations agree to within 10% with close coupling results where comparisons could be made. Comparisons were also made with other theoretical approaches using model potentials and with experiment using $ab$ initio potential surfaces.

I. INTRODUCTION

The width and shift of spectral lines are often used as a probe for measuring the pressure and temperature of gases as well as for various relaxation and energy transfer processes. In recent years, the most commonly used theory for neutral gases (where charged particle densities are negligible) is the impact theory developed by Anderson$^1$ and extended by Baranger.$^2$ In this theory, the radiation is perturbed by a random sequence of non-overlapping binary collisions. The half-width at half-maximum (HWHM) of an isolated vibration–rotation line is then given by$^3$

\[
\begin{aligned}
\Delta \nu & = \frac{2 \pi n}{\nu} \int_0^{\infty} u f(u) \, du \int_0^{\infty} b db \\
& \times \left[ 1 - \text{Re} \sum_{m_a=0}^{\infty} \sum_{m_b=0}^{\infty} (-1)^{m_a-m_b} \left( \begin{array}{c} j \\ m_a \\ -m_b \end{array} \right) \left( \begin{array}{c} j' \\ m'_a \\ q \end{array} \right) \left( \begin{array}{c} j \\ m'_a \\ q \end{array} \right) \left( \begin{array}{c} j' \\ m'_b \end{array} \right) \langle v|S(u,b)|v'\rangle \langle j|S(u,b)|j'\rangle \langle m_a|S(u,b)|m'_a\rangle \langle m'_b|S(u,b)|m_b\rangle \right],
\end{aligned}
\]  

where $n$ is the density of perturbing particles, $u$ is the relative velocity of radiator and perturber, $f(u)$ is a Maxwellian velocity distribution, and $S(u,b)$ is the classical path $S$-matrix for a binary collision with impact parameter $b$ and velocity $u$. In this expression, the translational motion of all particles is treated classically; that is, the particles are assumed to follow classical trajectories determined by some interaction potential. The internal states of the particles (e.g., vibration, rotation, etc.) are treated quantum mechanically and in Eq. (1.1) are described by the quantum numbers $(\nu, j, m)$. One could also include internal perturber states in Eq. (1.1), but in this paper we are only interested in perturbers which remain in their ground state (i.e., noble gas atoms); thus, for simplicity, we have not specified any perturber quantum numbers. The derivation of Eq. (1.1) and its conditions for validity have been discussed at length in the literature (e.g., see Ref. 3) and will not be discussed here.

In this paper we will discuss a new method of calculating the classical path $S$-matrix for rotation–vibration transitions and contrast our approach with the commonly used perturbation approach known as "Anderson theory," the "semiclassical" theory of Neilsen and Goorden,$^4$ the inelastic approximation of Murphy and Boggs,$^5$ as well as completely classical and completely quantum mechanical (i.e., close coupling) calculations. For a review of these and other theoretical approaches, see Rabitz.$^3$

In the Anderson theory, the $S$-matrix is approximated by a second order expansion in the interaction potential and the classical trajectories are taken to be straight lines. This method requires some type of impact parameter cutoff, otherwise the colliding particles would pass through one another for small impact parameters, and the approximate $S$-matrix would diverge. This physically unrealistic situation is avoided by replacing the integral over small impact parameters by a hard sphere collision cross section, $\pi b_0^2$, or something similar. In the literature, one finds a countless variety of cutoff procedures, and by trying one after another, it is eventually possible to make a calculation agree with a given experiment (e.g., see Rabitz$^2$ or Bouanich and Haeusler$^6$). Unfortunately, the calculations are very sensitive to the cutoff procedure and there is no single procedure which will describe a large number of different experiments. Thus, it is quite clear that with this method of calculation, the physically unrealistic impact...
parameter cutoff is obscuring all the information about collision dynamics and interaction potentials which one hopes to obtain from line broadening.

Our method of calculating the classical path S-matrix employs curved trajectories. These trajectories are determined by the spherically symmetric part $V_0$ of the interaction potential. The S-matrix is then calculated to all orders in the interaction potential (thus preserving its unitarity). With such realistic classical trajectories there are no unphysical divergences resulting from two particles passing through one another. Further, when the interaction potential becomes very large, the second order expansion used in the Anderson theory breaks down, whereas our calculation to all orders in the interaction remains valid. Thus it is not necessary to introduce an impact parameter cutoff in our method. Our approach is quite similar to that used by Nielsen and Gordon except that they used a numerical solution of the time dependent Schrödinger equation to obtain the S-matrix, whereas we use a numerical approximation involving the rotational quantum number $j$ to obtain an analytic solution. Our approach is therefore much simpler and permits calculations for large values of $j$.

To illustrate our approach and the accuracy attainable using it and to permit a detailed comparison with other theoretical methods, we have performed calculations for several rotation lines in HCl, CO, and CO₂ perturbed by He and Ar.

\[ \langle vjm | S'(r_p) | vjm' \rangle = \delta_{jj'} \delta_{mm'} - i \int_{-\infty}^{\infty} dt e^{i\omega v't} \langle vjm | V'(r_p(t)) | vjm' \rangle - \sum_{j''m''} \int_{-\infty}^{\infty} dt e^{i\omega v't} \langle vjm | V'(r_p(t)) | vjm'' \rangle \int_{-\infty}^{\infty} dt' e^{i\omega v't'} \langle vjm'' | V'(r_p(t')) | vjm' \rangle + \cdots. \]  

For convenience, all factors have been absorbed in $V$ [see Eqs. (2.7)–(2.11)]. The matrix $S_0$ is comparable to the term $\exp(2\eta_0)$ obtained by Cross. In quantum mechanical expressions for the half-width (e.g., Sec. 3B of Ref. 8), one always has the matrix product $SS^*$. Thus, when Eq. (2.3) is used for $S$, the factors $S_0 \sim \exp(2\eta_0)$, which describe purely translational effects, cancel out [since the same trajectory is used for both upper and lower states; see Eq. (3.15) of Ref. 8]. The matrix $S'$ describes transitions between the rotational states induced by the collision; transitions between different vibrational levels have been ignored since they are much weaker than the rotational transitions [owing to the $\exp(\omega v_0 t)$ factors which would appear in Eq. (2.4)]. The $S'$-matrix is comparable to the factor $\exp(2\eta_0)$ obtained by Cross, except that our result is a time ordered exponential. Finally, to obtain the expression given in Eq. (1.1) it is necessary to perform an angular average over the relative directions of $p$ and $p'$. This angular average reduces the matrix product $S'(r_p)S'(r_p')^*$ to $S(u, b)S'(u, b)$ multiplied by two $3j$ symbols summed over azimuthal quantum numbers $m$ [see Eq. (1.1)]. Note that this angular average (or sum over $m$ states) leaves the final expression invariant to further rotations of the coordinate frame. The matrix elements of $S(u, b)$ are thus given by a time ordered series equivalent to that in Eq. (2.4). For simplicity, these matrix elements are written in the form

\[ \langle vjm | S(u, b) | vjm' \rangle = \langle vjm | \phi e^{-i\omega \tau} | vjm' \rangle, \]  

\[ \langle vjm | \eta' | vjm' \rangle = \int_{-\infty}^{\infty} dt e^{i\omega v't} \langle vjm | V'[\tau(t), \Theta(t), \phi] | vjm' \rangle, \]  

where $\tau$ is the time ordering operator and the coordinates $\{\tau(t), \Theta(t), \phi\}$, which are functions of the impact parameter $b$ and velocity $v$, describe the classical trajectory in the center of mass frame.

II. THE CLASSICAL PATH S-MATRIX

Our method of calculation is based on an expression for the S-matrix which employs classical trajectories for the relative motion of the colliding particles. Such expressions have been derived by Cross and by Smith et al. In these derivations, the radiatior-perturber interaction is written in the form

\[ V = V_0 + V', \]  

where $V_0$ represents the spherically symmetric part of the interaction (which is diagonal in vibration-rotation states), and $V'$ denotes the rest of the interaction. Translational scattering states $\phi_0$ are obtained by solving the Schrödinger equation for $V_0$ only. Classical path results then follow when one evaluates matrix elements of $V'$ by the method of stationary phase; for example,

\[ \int dt \phi_0(\mathbf{r}, t) V'(\mathbf{r}) \phi_0(\mathbf{r}, t) = \delta_{\mathbf{r}'} \phi_0 V'(\mathbf{r}_p(t)) \]  

where $\mathbf{r}$ and $\mathbf{r}'$ denote the relative momenta when the particles are infinitely far apart and $\mathbf{r}_p(t)$ denotes the classical trajectory for motion in $V_0$. Following the derivation given in Secs. 2 and 3 of Ref. 8, one obtains the following expression:

\[ \langle \mathbf{p} vjm | S | \mathbf{p}' vjm' \rangle = \langle \mathbf{p} | S_0 | \mathbf{p}' \rangle \langle vjm | S'(\mathbf{r}_p) | vjm' \rangle, \]  

with the $S'$ matrix elements given by the time ordered series

\[ \langle vjm | S'(\mathbf{r}_p) | vjm' \rangle = \delta_{jj'} \delta_{mm'} - i \int_{-\infty}^{\infty} dt e^{i\omega v't} \langle vjm | V'(\mathbf{r}_p(t)) | vjm' \rangle - \sum_{j''m''} \int_{-\infty}^{\infty} dt e^{i\omega v't} \langle vjm | V'(\mathbf{r}_p(t)) | vjm'' \rangle \int_{-\infty}^{\infty} dt' e^{i\omega v't'} \langle vjm'' | V'(\mathbf{r}_p(t')) | vjm' \rangle + \cdots. \]  

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frame; and \((\Theta_\text{el}, \phi)\) are the trajectory coordinates

\[
V_1(r) = \frac{4\epsilon}{R} [R_1(d/r)^{12} - A_1(d/r)^6],
\]

(2.9)

\[
V_2(r) = \frac{4\epsilon}{R} [R_2(d/r)^{12} - A_2(d/r)^6],
\]

(2.10)

\[
V_i(r) = \frac{4\epsilon}{R} [R_i(d/r)^{12} - A_i(d/r)^6], \quad i \geq 3.
\]

(2.11)

We have chosen a \((d/r)^{12}\) repulsive potential rather than an exponential form only for convenience. For thermal energy scattering, most exponential potentials can be adequately approximated by \((d/r)^{12}\) and the trajectory calculations are slightly simpler with the latter. The \(r^{-7}\) attraction in \(V_i(r)\) is chosen to conform with conventional usage for example, Eq. (4) of Nelsen and Gordon\(^8\) which is based on the known functional dependence at large \(r\). However, it should be noted that all \(V_i(r)\) can be adequately represented by the \(6-12\) form since atom–molecule line broadening calculations are relatively insensitive to the exact \(r^{-\infty}\) asymptote. In fact, the \(r^{-\infty}\) asymptotes of potentials obtained from line broadening or molecular beam and transport data often differ with calculated polarizabilities by a factor of 2 or so (for example, Pack, Ref. 9).

Equation (2.8) is adequate only for pure rotation transitions. For vibration–rotation lines, the polarizability of the initial and final states may be somewhat different owing to the change in the vibrational quantum number. The repulsive part of the interaction may also be affected owing to the fact that vibrational excitation tends to increase the size of the molecule. We therefore make the peaking approximation [i.e., the time when \(t=0\)] in order to evaluate the S-matrix elements, we first define a function \(F\) required by Eq. (3.3).

From Edmonds\(^8\) (pp. 59 and 122), we obtain an approximate expression for the \(j\) symbols so the matrix elements of \(Y^{j}_\text{el}\) may be given by

\[
\langle jm | Y^{j}_0 | j'm' \rangle = \frac{(-1)^{m}}{4\pi} \sqrt{\frac{(2j+1)(2j'+1)}{4j}} \times \left( \begin{array}{ll} j & j' \\ 0 & 0 \end{array} \right) \delta_{jj'} \delta_{m'm} P^{j}_{\text{el}}(0) P^{j'}_{\text{el}}(\cos \alpha),
\]

(4.1)

where \(\Delta j = j - j'\) and \(P^n_j\) are associated Legendre polynomials. According to Edmonds, \(\cos \alpha = m/(j+\frac{1}{2})\) since it is just as accurate and more convenient in our computer program. In the Appendix we show that the error introduced by the approximation in Eq. (4.1) is at the order of \((\Delta j/j)\).

The frequency factor \(\omega_{jj'}\) which appears in Eq. (2.4) may be approximated by

\[
\omega_{jj'} = 2\pi c B[(j+1) - j(j'+1)]
\]

\[
= 2\pi c B[j(j+1) + \Delta j]
\]

\[
= 2\pi c B(2j+1)\Delta j
\]

\[
= \omega \Delta j,
\]

(4.2)

where \(B\) is the rotational constant. It will be assumed that \(\omega\) defined by \(2\pi c B(2j+1)\) is essentially constant, that is, the \(\Delta j\) changes in \(j\) are small compared with \(j\) itself. This approximation was tested by using the next higher order approximation to \(\omega_{jj'}\) [i.e., terms of order \((\Delta j/j)^2\)] which had less than a 1% effect on our calculations (see also the discussion in the Appendix).

We next define a function \(F_{jj'}(t)\) by

\[
\langle jm | \eta' \rangle | j';m' \rangle = \sum_{l=0}^{\frac{2j'}{2l+1}} \langle jm | Y^{l}_0 | j';m' \rangle Y^{*\ell}_\text{el}(\Theta_\text{el}, \phi)
\]

\[
\times \int_0^\tau e^{i\omega_{jj'} t} F_{jj'}(t) dt,
\]

(3.2)

This peaking approximation has been discussed in detail by Roberts (Ref. 11).

Since Eq. (1.1) is rotationally invariant, we may rotate through the Euler angles \((- \phi, - \Theta_\text{el}, 0)\) for a given \(b\) and \(u\). That is, we rotate to a coordinate frame where the phase shift matrix becomes

\[
\langle jm | Y^{j}_0 | j';m' \rangle = \delta_{mm'} \sum_{l=0}^{\frac{2j'}{2l+1}} \langle jm | Y^{l}_0 | j';m' \rangle \times \int_0^\tau e^{i\omega_{jj'} t} F_{jj'}(t) dt,
\]

(3.3)

where we have used \(Y^{j}_0(0,0) = \delta_{jj'}(2l+1)/4\pi\) and the fact that the \(Y^{j}_\ell\) operator is diagonal in \(m\).
\[ F_{\Delta j}(t) = \frac{(l - \Delta j)!}{(l + \Delta j)!} (0 \ P^m \left( \frac{m}{j + \frac{1}{2}} \right) V_j(r(t)) \ . \quad (4.3) \]

Notice that \( F_{\Delta j} \) also depends on \( j \) through the argument of the Legendre polynomial; this will be discussed further following Eq. (4.13). Using Eq. (4.3), Eq. (3.1) becomes

\[ \langle jm | I_1 | j' m' \rangle = \int_{-\infty}^{\infty} dt F_{\Delta j}(t) \exp(i\omega(j - j')t) \ . \quad (4.4) \]

The \( S \)-matrix in Eq. (2.5) may now be written in the form

\[ \langle jm | S(u, b) | j' m' \rangle = \delta_{mm'} \sum_{\Delta j} (-1)^{\Delta j} \langle jm | I_0 | j' m' \rangle \ . \quad (4.5) \]

where \( I_0 = 1 \), and

\[ \langle jm | I_0 | j' m' \rangle = \delta_{mm'} \ . \quad (4.6) \]

We next multiply the right side of Eq. (4.6) by

\[ 1 = \sum_{\ell_1} \delta_{1, \ell_1} = \frac{1}{2\pi} \sum_{s} e^{is(j-j')} ds \]

so that we can replace \( j \) by \( j_1 \) in Eq. (4.6). Then changing summation variables from \((j_1, \ldots, j_n)\) to \((\delta_1, \ldots, \delta_n)\), where

\[ j_n = j' + \delta_n , \]
\[ j_{n+1} = j' + \delta_n + \delta_{n+1} , \]
\[ \vdots \]
\[ j_1 = j' + \delta_n + \cdots + \delta_1 \]

Eq. (4.6) finally becomes

\[ \langle jm | I_n | j' m' \rangle = \frac{1}{2\pi} \sum_{\delta_1, \ldots, \delta_n} \int_{-\infty}^{\infty} ds \exp[i\omega(j - j' - \delta_1 - \cdots - \delta_n)] ds \]

\[ \times \int_{-\infty}^{\infty} F_{s_1}(t_1) \exp[i\omega \delta_1 t_1] dt_1 \int_{-\infty}^{\infty} F_{s_2}(t_2) \exp[i\omega \delta_2 t_2] dt_2 \cdots \int_{-\infty}^{\infty} F_{s_n}(t_n) \exp[i\omega \delta_n t_n] dt_n \ . \quad (4.9) \]

Note that while \( j_1, \ldots, j_n \) were summed over the range \( 0 \) to \( \infty \), the variables \( \delta_1, \ldots, \delta_n \) are summed over the range \(-\infty \) to \( +\infty \).

Using the identity

\[ \sum_{s_1, s_2} \int_{-\infty}^{\infty} dt_1 f_{s_1}(t_1) \int_{-\infty}^{\infty} dt_2 f_{s_2}(t_2) = \frac{1}{2\pi} \sum_{s_1, s_2} \left[ \int_{-\infty}^{\infty} dt_1 f_{s_1}(t_1) \int_{-\infty}^{\infty} dt_2 f_{s_2}(t_2) + \int_{-\infty}^{\infty} dt_1 f_{s_1}(t_1) \int_{-\infty}^{\infty} dt_2 f_{s_2}(t_2) \int_{-\infty}^{\infty} dt_1 f_{s_1}(t_1) \right] \]

or, in general,

\[ \sum_{s_1, s_2, \ldots, s_n} \int_{-\infty}^{\infty} dt_1 f_{s_1}(t_1) \int_{-\infty}^{\infty} dt_2 f_{s_2}(t_2) \cdots \int_{-\infty}^{\infty} dt_n f_{s_n}(t_n) = \frac{1}{n!} \sum_{s_1, s_2, \ldots, s_n} \int_{-\infty}^{\infty} dt_1 f_{s_1}(t_1) \int_{-\infty}^{\infty} dt_2 f_{s_2}(t_2) \cdots \int_{-\infty}^{\infty} dt_n f_{s_n}(t_n) \ . \quad (4.11) \]

Equation (4.9) becomes

\[ \langle jm | I_n | j' m' \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds \ e^{is(j-j')} \frac{1}{n!} \left[ \sum_{s} e^{-is} \int_{-\infty}^{\infty} dt \ e^{i\omega t} F_s(t) \right]^n \ . \quad (4.12) \]

and Eq. (4.5) gives

\[ \langle jm | S(u, b) | j' m' \rangle = (\delta_{mm'}/2\pi) \int_{-\infty}^{\infty} ds \ e^{is(j-j')} \exp \left[-i \sum_{s} e^{-is} \int_{-\infty}^{\infty} dt \ e^{i\omega t} F_s(t) \right] . \quad (4.13) \]

In deriving this result, we have again assumed that the increments \( \delta_n = (j_n - j_{n-1}) \) in the \( j \) quantum numbers are small compared with the \( j_n \) themselves. This was done when we replaced the sum over \((j_1, \ldots, j_n)\) by \((\delta_1, \ldots, \delta_n)\) and assumed that \( F_s \) depends only on \( \delta_s \). In reality, \( F \) depends on \( j_n \) as well as \( (j_n - j_{n-1}) \) [see Eq. (4.3)]; by ignoring the former we are assuming that the incremental changes in \( j \) are small compared with \( j \).
where

\[ \text{Re}(vjm) \langle v'j'm' \mid S \rangle \mid v'j'm' \rangle^* \]

The expression for the linewidth, Eq. (1.1), is simplified by the fact that the S-matrix is diagonal in \( m \):

\[ \nu_{v'j', vj} = 2\pi n \int_0^\infty \langle vjm \mid S \mid vjm \rangle^2 \, dv \, \sum_{v'j'm'} |\langle vjm \mid S \mid v'j'm' \rangle|^2 \, dv \, \sum_{v'j'm'} |\langle vjm \mid S \mid v'j'm' \rangle|^2 \].

This equation also defines the averaged optical cross section \( \sigma(u, b) \) which will be useful in comparing theoretical results.

Another interesting expression for the linewidth can be obtained by using the identities

\[ \text{Re}(vjm \mid S \mid vjm \rangle^2 + |\langle vjm \mid S \mid vjm \rangle|^2) = \frac{1}{2} \left[ |\langle vjm \mid S \mid vjm \rangle|^2 + |\langle vjm \mid S \mid vjm \rangle|^2 \right] 
\]

and

\[ \sum_{m} |\langle vjm \mid S \mid vjm \rangle|^2/(2j + 1) = 1 - \sum_{m} |\langle vjm \mid S \mid vjm \rangle|^2/(2j + 1) = 1 - \sum_{m} \sum_{v'j'm'} |\langle vjm \mid S \mid v'j'm' \rangle|^2/(2j + 1) \]

Substituting these identities into Eq. (5.1), we obtain

\[ \nu_{v'j', vj} = \frac{1}{2} (\nu_{v'j', vj}^1 + \nu_{v'j', vj}^2) + \pi n \int_0^\infty \langle vjm \mid S \mid vjm \rangle^2 \, dv \, \sum_{m} \sum_{v'j'm'} \left| \langle vjm \mid S \mid v'j'm' \rangle \right|^2/(2j + 1) \]

where \( \nu_{v'j', vj} \) is the total inelastic rate out of the level \( vj \):

\[ \nu_{v'j', vj} = 2\pi n \int_0^\infty \langle vjm \mid S \mid vjm \rangle^2 \, dv \, \sum_{m} \left[ 1 - |\langle vjm \mid S \mid vjm \rangle|^2/(2j + 1) \right] \]

Equation (5.4) is interesting because it expresses the linewidth in terms of a purely inelastic contribution plus a coherence term which involves the difference of scattering amplitudes. The latter term, which is often neglected (for example, Murphy and Boggis),\(^1\) contains the effect of elastic collisions which interrupt the phase of the radiator without quenching it. The elastic contribution can be quite important, especially in cases such as HCl-Xe where the vibrational broadening resulting from \( K_{\nu}^{vib} \) is strong (e.g., Ref. 10). One must therefore exercise considerable care when using measured half-widths to infer inelastic cross sections.

VI. LINESWIDTH CALCULATIONS

A. General

Most of the calculations presented in this paper are based on model potentials which include anisotropy terms (see Eq. 2.8) up to order \( P_{2}(\cos \theta) \). In such cases, we need only consider

\[ K_{\nu} = \frac{1}{2} \left[ 1 - 3 \left( \frac{m}{j + \frac{1}{2}} \right)^2 \right] \int_0^\infty V_{\nu}(t) \, dt \]

The sum over Bessel functions in Eq. (6.6) converges very rapidly and it is usually necessary to include only three or four terms.

The recent theoretical potential surfaces which are based on the Gordon–Kim electron gas model\(^{18}\) include important contributions from anisotropy terms as high as \(P_3(\cos \theta)\) and \(F_6(\cos \theta)\) (see Green,\(^ {17}\) Green, and Thaddeus,\(^ {18}\) Parker et al.,\(^ {19}\)). For these potentials it is necessary to consider \(K_4(\omega)\) terms as high as \(K_4\). With such high order terms the expression for the \(S\)-matrix would be somewhat more complicated than Eq. (6.6). On the other hand, the higher order \(K_4(\omega)\) terms represent a type of multiquantum transition whose effect decreases very rapidly with increasing order. For example, \(K_4\) is proportional to a \(\cos(6\omega t)\) transform in \(V(\tau(t))\) which should be much smaller than the lower order terms such as \(K_0, K_1, \) etc. The primary effect of higher order anisotropies in \(V\) is thus found in their influence on the lower order terms such as \(K_0, K_2, \) etc. To verify this assertion we have performed calculations on \(\text{CO}_2-\text{Ar}\) and \(\text{CO}_2-\text{He}\) using the potentials of Ref. 19. For these potentials, \(V_0, V_2,\) and \(V_4\) are roughly the same order of magnitude while higher terms \(V_6, V_8\) and \(V_{10}\) are each an order of magnitude smaller than their preceding terms. We have therefore used

\[ K = 2 \sqrt{1 - \left(\frac{m}{j + \frac{1}{2}}\right)^2} \int_0^\infty V_1(r(t)) \cos(\omega t) \, dt, \quad (6.2) \]

\[ K_2(\omega) = \frac{1}{4} \left[ 1 - \left(\frac{m}{j + \frac{1}{2}}\right)^2 \right] \int_0^\infty V_2(r(t)) \cos(2\omega t) \, dt. \quad (6.3) \]

The \(S\)-matrix may then be evaluated by using the identity (Ref. 15, p. 361)

\[ \exp(-iK \cos \theta) = J_0(K) + 2 \sum_{l=1}^\infty (-i)^l J_l(K) \cos(l\theta) \]

[where \(J_l(K)\) are Bessel functions of integer order \(l\)] and

\[ \frac{1}{\pi} \int_0^\infty \cos(l\theta) \cos(l's) \, ds = \delta_{l,l'} + \delta_{l,-l'} \].

The diagonal matrix elements of Eq. (4.16) are thus given by

\[ \langle jm | S(a, b) | jm \rangle = \frac{1}{2 \pi} \int_0^\infty ds \exp[-iK_0 - iK_1 \cos(2\omega s) - iK_2 \cos(2\omega s)] \]

\[ = e^{-iK_0} \left[ J_0(K) J_0(K) + 2 \sum_{l=1}^\infty (-i)^l J_2(K) J_1(K) \right]. \quad (6.6) \]

\[ K_0 = \frac{1}{4} \int_0^\infty dt \left[ (1 - 3\mu^2) V_2 + \frac{1}{4} \left( 35\mu^4 - 30\mu^2 + 3 \right) V_4 - \frac{1}{24} \left( 231\mu^6 - 315\mu^4 + 105\mu^2 - 5 \right) V_6 \right] \]

\[ + \frac{1}{48} \left( 6435\mu^8 - 12012\mu^6 + 6930\mu^4 - 1260\mu^2 + 35 \right) V_8, \quad (6.7) \]

\[ K_2 = \frac{1}{2} (1 - \mu^2) \int_0^\infty dt \left[ V_2 + \frac{1}{16} \left( 33\mu^4 - 18\mu^2 + 1 \right) V_4 - \frac{1}{64} \left( 143\mu^6 - 143\mu^4 + 33\mu^2 - 1 \right) V_6 \right] \cos(2\omega t) \],

\[ (6.8) \]

\[ K_4 = \frac{1}{48} (1 - \mu^3) \int_0^\infty dt \left[ V_4 + \frac{1}{64} \left( 11\mu^2 - 2 \right) V_6 + \frac{1}{576} \left( 65\mu^4 - 26\mu^2 - 1 \right) V_8 \right] \cos(4\omega t), \]

\[ (6.9) \]

where \(\mu = m/(j + \frac{1}{2})\). Since \(K_4\) made about 0.5% change in the calculated half-widths, we did not bother to include a \(K_4\) term. This result confirms our assertion that the higher order \(K_4\) terms are relatively unimportant and the main effect of higher order anisotropies comes in via the \(K_0, K_1,\) and \(K_2\) terms.

### B. HCl-Ar

The pressure broadening of HCl by argon is an extremely valuable test case for a theory because (1) Neilsen and Gordon\(^4\) have performed a numerical solution of Schrödinger’s equation (using classical trajectories for the translational motion), which should be very accurate and may be used to test other classical path approaches, (2) there are some very good theoretical potential surfaces for this system, and (3) there are experimental data ranging from low \(j\) (the 1–0 transition) where quantum effects are important to high \(j\) (the 11–10 transition) which is well into the classical region.

Neilsen and Gordon\(^4\) have calculated the broadening, by argon, of the HCl pure rotation lines from the 1–0 transition of the 6–5 transition. They used classical paths determined by the isotropic part of the potential and solved the Schrödinger equation by a numerical technique. While this calculation is not as accurate as a fully quantum mechanical close coupling approach, it is certainly more accurate than our theory for low values of \(j\). For high values of \(j\), our results should agree with Neilsen and Gordon’s,\(^4\) as they do. This comparison thus gives an idea of the accuracy of our theory for low \(j\), as well as providing a test of our numerical calculations.

In our calculation, we used the potential labeled \(NC = 52\) by Neilsen and Gordon.\(^4\) Our anisotropy parameters (see Eq. (2.9) and (2.10)) are \(A_2 = 0.37, A_4 = 0.65, A_1 = 0.33, A_6 = 0.14,\) which differ slightly from those given by Neilsen–Gordon\(^4\) (on p. 4153) because they used an exponential repulsion rather than \(1/j^{12}\). Our parameters were obtained by numerically fitting their potential.

Figure 1 compares the unaveraged cross section \(\sigma(u, b)\) defined by Eq. (5.1) with that obtained by Neilsen–Gordon\(^4\) for the 5–4 line at 400 K. In Table I, we have also listed various cross sections averaged over \(b\) and \(u\) which are defined by (again suppressing the vibrational quantum number)

\[ \sigma_{1p}(u) = 2\pi \int_0^\infty b \sigma_{1p}(u, b) \, db, \quad (6.10) \]
TABLE I. HCl–Ar cross sections for pure rotation transitions (i.e., $v = v' = 0$) in $\text{Å}^2$. The unaveraged cross sections $\sigma_{j,j'}(u)$ [Eq. (6.10)] are evaluated for two kinetic energies $E = mu^2/2k$ wherein $k$ is Boltzmann’s constant. The averaged cross sections [Eq. (6.11)] are evaluated for a temperature of $T = 300$ K.

<table>
<thead>
<tr>
<th>$j$</th>
<th>$T = 398$ K</th>
<th>$T = 300$ K</th>
<th>$T = 404$ K</th>
<th>$T = 808$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>57.4</td>
<td>56.26</td>
<td>59.16</td>
<td>63.7</td>
</tr>
<tr>
<td>3</td>
<td>45.16</td>
<td>46.08</td>
<td>47.40</td>
<td>48.3</td>
</tr>
<tr>
<td>4</td>
<td>37.38</td>
<td>33.73</td>
<td>38.0</td>
<td>36.5</td>
</tr>
<tr>
<td>5</td>
<td>39.32</td>
<td>29.31</td>
<td>31.48</td>
<td>31.0</td>
</tr>
<tr>
<td>6</td>
<td>25.75</td>
<td>25.55</td>
<td>26.42</td>
<td>25.6</td>
</tr>
</tbody>
</table>
TABLE II. Unaveraged HCl–Ar j → j–1 cross sections [see Eq. (6.14)] for a kinetic energy E = mu^2/2k = 404 K.

<table>
<thead>
<tr>
<th>j</th>
<th>(\sigma_{J_{L=1}}(u))</th>
<th>(\sigma_{J_{L=0}}(u))</th>
<th>(\sigma_{J_{L=-1}}(u))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>51.3</td>
<td>12.4</td>
<td>63.7</td>
</tr>
<tr>
<td>4</td>
<td>30.5</td>
<td>7.5</td>
<td>38.0</td>
</tr>
<tr>
<td>6</td>
<td>19.9</td>
<td>5.7</td>
<td>25.6</td>
</tr>
<tr>
<td>8</td>
<td>10.3</td>
<td>4.5</td>
<td>14.8</td>
</tr>
<tr>
<td>10</td>
<td>4.1</td>
<td>3.4</td>
<td>7.5</td>
</tr>
</tbody>
</table>

TABLE III. CO–He j → j–1 cross sections in \(\text{Å}^2\). Unaveraged cross sections [Eqs. (6.10) and (6.14)] are evaluated for kinetic energy \(E = mu^2/2k = 272\) K (\(k\) is Boltzmann’s constant). The velocity averaged cross sections [Eq. (6.11)] are evaluated for a temperature of \(T = 300\) K, and comparison is made with (a) Green and Thaddeus, 16 (b) Fitz and Marcus, 25 (c) Gordon, 23 (d) Gordon and McGinnis, 24

<table>
<thead>
<tr>
<th>j</th>
<th>This work, unaveraged (E = 272) K</th>
<th>Averaged, (T = 300) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>25.3</td>
<td>26.0</td>
</tr>
<tr>
<td>4</td>
<td>22.6</td>
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<td>21.9</td>
</tr>
<tr>
<td>12</td>
<td>21.0</td>
<td>21.2</td>
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<td>20.8</td>
<td>26.0</td>
</tr>
<tr>
<td>20.6</td>
<td>20.8</td>
<td>26.0</td>
</tr>
</tbody>
</table>

TABLE IV. HCl–He j → j–1 cross sections in \(\text{Å}^2\). Unaveraged cross sections [Eqs. (6.10) and (6.14)] are evaluated for kinetic energies \(E = mu^2/2k = 450\) K (\(k\) is Boltzmann’s constant) of 480 K and 450 K. Averaged cross sections, Eq. (6.11), are evaluated for a temperature of \(T = 300\) K. Data are obtained from this work and (a) Green and Monchick, 26 (b) Fitz and Marcus, 25 (c) Gordon, 23

<table>
<thead>
<tr>
<th>j</th>
<th>This work, unaveraged (E = 480) K</th>
<th>Unaveraged (E = 450) K</th>
<th>Averaged, (T = 300) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.72</td>
<td>6.36</td>
<td>8.2(a)</td>
</tr>
<tr>
<td>3</td>
<td>5.72</td>
<td>5.87</td>
<td>6.0(a)</td>
</tr>
<tr>
<td>5</td>
<td>6.01</td>
<td>6.04</td>
<td>5.94</td>
</tr>
<tr>
<td>7</td>
<td>6.49</td>
<td>6.27</td>
<td>6.30</td>
</tr>
<tr>
<td>9</td>
<td>6.40</td>
<td>6.04</td>
<td>6.30</td>
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<tr>
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<td>5.58</td>
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<td>3.88</td>
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</tr>
<tr>
<td>19</td>
<td>3.49</td>
<td>3.40</td>
<td>3.95</td>
</tr>
</tbody>
</table>

This situation is rather surprising, since it is generally thought that the classical theory should be good for large \(j\); furthermore, the classical HCl–Ar calculations agree very well (within 10%) with the close-coupling results of Green and Monchick, whereas the close-coupling results of Green and Monchick were performed for a single velocity corresponding to a kinetic energy of 450 K. The comparison is nonetheless valid since the velocity averaged cross section at 300 K is essentially the same as the unaveraged cross section at 450 K due to the increase of \(\sigma_{J_{L=1}}(u)\) as a function of \(u\) (for example, note the corresponding data in Table III of Green and Monchick). 26 Again, our results differ by about 10% from the close coupling calculations and lie a factor of 2 or 3 below the classical theories. The classical results are clearly in error since they lie well above the close coupling calculation and the half-width decreases with increasing \(j\) (due to a decreased inelastic contribution).
D. \( \text{CO}_2\)-Ar and \( \text{CO}_2\)-He

The HCl–Ar, CO–He, and HCl–He calculations were used to provide a test of our theory by comparing it with other theoretical methods. The potentials used in those calculations were model potentials which were, in most cases, designed to provide agreement with experimental data. Comparisons with experiment would thus be somewhat misleading, especially since recent theoretical work has shown that higher order anisotropies must be included in the interaction potentials.

The purpose of the \( \text{CO}_2\)-Ar and \( \text{CO}_2\)-He calculations is to use some of the new theoretical potential surfaces based on the Gordon–Kim electron-gas model\(^{16}\) and thus obtain a more realistic comparison with experimental data over a wide range of \( j \) values. We also wanted to see if the higher order \( K_4 \) terms would be negligible (as discussed in Sec. VI.A) and \( \text{CO}_2 \) provides a very stringent test of this approximation owing to its small rotational constant.

In our calculations we used the potentials obtained by Parker et al. (Ref. 19) fitting their \( V_j(r) \) functions to 6–12 functions of the form shown in Eq. (2.11). For \( \text{CO}_2\)-Ar, our parameters were \( \epsilon = 97.95 \text{ K}, d = 3.86 \text{ Å}, R_4 = 2.24, A_4 = 0.549, R_4 = 1.09, A_4 = 0.167, R_6 = 0.52, A_6 = 0.034, R_8 = 0.059, A_8 = 0.111. \) Figure 5 shows the comparison of our calculations with the experimental results of Boulet et al. (Ref. 28) for \( j \) values ranging from 3 to 40. The dashed and dotted curves represent the effect of \( V_0 \) only and \( V_2 + V_4 \) terms. The solid curve represents the combined effect of \( V_2, V_4, V_6, \) and \( V_8. \) The addition of \( V_6 \) raised the curve less than 2\% so the \( V_2, V_4, V_6 \) curve was not plotted. Ignoring the \( K_4 \) term [i.e., the \( \cos(4\omega t) \) transform in Eqs. (4.10) and (6.9)] had less than 1\% effect. Thus, the effect of higher order anisotropies in the potential is important up to the \( V_6 \) term, but the effect of these anisotropies enters only through the \( K_4 \) and \( K_6 \) terms in Eqs. (4.6), (6.7), and (6.6).

The agreement between theory and experiment is quite good, considering that there are no adjustable parameters in either the line shape theory or the \( \text{ab initio} \) potential. Nonetheless, it is clear that the theoretical results lie about 12\% too low. This is probably due to vibrational effects which will enter via the \( K_4^{(16)} \) term discussed in Sec. II. Since these radiative transitions in \( \text{CO}_2 \) take place between two different vibrational modes, one would expect the vibrational effects to be relatively important, and they should be evaluated before drawing any final conclusions regarding the theoretical–experimental comparison.

As a further check on the vibrational broadening effect, we performed \( \text{CO}_2\)-He calculations. The contribution of vibrational broadening is much smaller for He perturbers than for Ar perturbers (see Refs. 10 and 29) because the smaller He polarizability makes long range forces less important; consequently, the \( \text{CO}_2\)-He broadening is dominated by short range forces which seem to be less affected by molecular vibration (for example, Tipping and Herman,\(^{20}\) p. 693, et seq.). It was more difficult to fit the \( \text{CO}_2\)-He potentials of Parker et al.\(^{19}\) to the 6–12 functions which we used in our computer program, and this difficulty introduced a ±2\% uncertainty into our calculations. The parameters used were \( \epsilon = 20.25 \text{ K}, d = 3.72 \text{ Å}, R_2 = 2.85, A_2 = 0.71, R_4 = 1.44, A_4 = 0.07, R_6 = 0.52, A_6 = 0.10, R_8 = 0.13, \) and \( A_8 = 0.048. \)

Our results, given in Fig. 6, agree quite well with the experimental data of Meyer et al.,\(^{30}\) Judd,\(^{31}\) and Abrams\(^{32}\) for the 10 \( \mu \text{m} \) band and lie about 15\% below the \( P(20) \) measurement of Meyer et al.\(^{30}\) for the 9 \( \mu \text{m} \) band.
Theoretical calculations (solid curve) compare favorably with experimental data analyzed by Judd. Since Meyer et al. point out (on p. 2002) that their 9 µm data seem a bit high, this agreement could be interpreted as closer than that for CO₂-Ar, thereby supporting our assertion that the disparity in the CO₂-Ar case is due to vibrational broadening. As in the CO₂-Ar case, the addition of the V₄ anisotropy raised the calculations by about 2% and the addition of the K₄ term had less than 1% effect.

VII. CONCLUSIONS

We have formulated a new type of exponential approximation for the S-matrix which is designed to be valid for large j values. Our main approximation, introduced in Eqs. (4.1) and (4.2), was the assumption that the change in j in a single V matrix element is small compared with j itself. In the Appendix, it is shown that the error introduced by this approximation is at most the order of (Δj/j)². In our calculations, we have found that the error is usually considerably less than this. For example, in the case of CO₂-He, the interaction contained terms up to P₃(cosθ), so that our error could be as large as (2j/j)². However, for the 1–0 and 2–1 transitions our results lie within 10% of the close-coupling results.

Another approximation whose validity is difficult to assess is the use of classical trajectories determined only by the isotropic part, V₄₀, of the potential. If we were looking directly at the angular distribution of the scattered particles, as in a beam experiment, this approximation would not be adequate. However, for the processes in a gas where one is looking at spherically averaged phenomena, it should be much better. The agreement of our results with close-coupling calculations would tend to support such a conclusion, but this certainly does not constitute a proof. The validity of this approximation should be investigated further.

The main virtue of our approach is that it enables one to use curved classical trajectories which are far more realistic than the straight path trajectories of the Anderson type theories. It also treats the classical path S-matrix to all orders, thereby avoiding the problems attendant with impact parameter cutoffs, etc., which tend to obscure the physical analysis in perturbative approaches such as the Anderson theory.

Apart from close-coupling methods, which are expensive and, for practical purpose, limited to very low quantum numbers, the only other theories which use realistic trajectories and treat the S-matrix to all orders are those classical and semiclassical theories in which the radiating molecule is treated as a classical radiator, usually by means of action angle variables. Since one expects this approach to be valid in the limit of high quantum numbers, we were quite surprised to find that our results for CO₂-He and HCl-He differ by as much as 100% from these classical and semiclassical calculations. We obtained good agreement with semiclassical theories for HCl-Ar but in that case the line-widths are strongly affected by elastic broadening. The use of continuous rather than discrete variables in the classical theories makes it rather difficult to obtain expressions for inelastic transition probabilities and, as discussed in Sec. IV, we suspect that this might be the source of the disagreement for CO₂-He and HCl-He. In defense of the classical theories, it should be noted that they use classical trajectories which are determined by the full interaction potential and are thus more accurate than ours. We had therefore suspected that our results were in error rather than those of the classical theories; however, the fact that the classical calculations at high j lie above the close-coupling calculations at low j clearly indicates that it is in fact the classical calculations which are in error (linewidths decrease as a function of j owing to a decrease in the inelastic collision cross section).

In the theory of Murphy and Boggs, it is suggested that the linewidths may be regarded as a sum of inelastic cross sections. That is, the elastic term in our equation (5.4) would be ignored. This would be a very useful approximation, if correct, because one could obtain a set of inelastic rates simply by measuring a set of linewidths. This procedure is sometimes used in laser modeling where linewidth measurements are often much easier than direct measurements of inelastic processes. We tested this idea by calculating the elastic and inelastic linewidth contributions separately. For pure rotation lines, we found very little elastic broadening except in the case of HCl-Ar, where the elastic contribution began to approach 50% for the large j values. For all other pure rotation lines, the Murphy-Boggs approximation would have been quite accurate. For vibration–rotation lines, one has to be very careful in applying their approximation because there can be a large elastic contribution from vibrational broadening as there seems to be in the case of CO₂-Ar, for example.

We calculated several linewidths for CO₂-Ar and...
CO₂-He using the ab initio potentials of Parker et al. ¹⁻¹⁹ Ab initio potential surfaces such as these typically contain strong contributions from rather high order anisotropies such as $P_2(\cos \theta)$ and $P_4(\cos \theta)$, whereas most semiempirical potentials contain only $P_1(\cos \theta)$ and $P_2(\cos \theta)$ terms. In these calculations we found that the higher order anisotropies influenced the linewidth only through their $\Delta j=0$ and $\Delta j=2$ matrix elements. Thus, as far as linewidths are concerned, one could have approximated the effect of the higher order anisotropies by simply changing the $P_2(\cos \theta)$ coefficients. This probably explains why the simple semiempirical potentials are able to give such good agreement with experimental results even though they strongly disagree with ab initio calculations.

ACKNOWLEDGMENTS

The authors would like to thank Russel Pack of the Los Alamos Scientific Laboratory for sending us the CO₂-He, Ar potential calculations of Parker et al. (1976) in advance of publication. We also wish to thank O’Dean Judd of LASL and D. Truhlar of the University of Minnesota for several useful comments and suggestions. One of the authors (M.G.) wishes to express his gratitude to the Gaseous Electronics Section of the National Bureau of Standards for the hospitality shown him during his stay.

APPENDIX A

In order to discuss the approximations to $\omega_{jj'}$ and $\langle jm | Y_1^{\text{nf}} | j'm \rangle$ introduced in Sec. IV, we will consider the second order term in the correct classical path $S$ matrix [given by Eqs. (2.5) and (3.3)] where these approximations have not been made. The peak approximation is already built into Eq. (3.3), but that approximation has been shown to be very good by Roberts¹¹ in cases similar to those encountered here. In line broadening, we are interested only in diagonal $S$ matrix elements, thus the second order term is

$$S_2 = \sum_{j,m} \langle jm | Y_1^{\text{nf}} | j'm \rangle \langle j'm | Y_1^{\text{nf}} | jm \rangle$$

where $\omega = 2\pi c B(2j + 1)(2j'+1)$ as in Eq. (4.2). The classical expression for the $3j$ symbol used in Eq. (4.1) (see Edmonds¹⁸ or Brussard and Tolhoeck¹⁹) is correct to within terms of order $(\Delta j/j)^2$; thus, using Eqs. (4.1) and (A3), we have

$$S_{\text{approx}} = - 2 \sum_{\omega_{\Delta j}} K_{\Delta j}^3(\omega)$$

where $\omega = 2\pi c B(2j + 1)$ as in Eq. (4.2). (A5)

To second order, we can ignore the effect of time ordering because the correction term is imaginary and thus contributes to the line width only when squared (i.e., in fourth order). Furthermore, since our approximations are exact for $j' = j$ (see Sec. IV), we will only consider those terms for which $j' \neq j$.

We first determine the effect of our approximation on $\omega_{jj'}$. If $V(r(t))$ vanishes in a time $\tau$ much less than $1/\omega_{jj'}$, any errors due to our approximate $\omega_{jj'}$ may be ignored. The worst possible case (i.e., the most sensitive to $\omega_{jj'}$) is thus when $\omega_{jj'} > 1$. To estimate that case let $V(r(t)) = V$ for $-\tau < t < \tau$ and zero for $|t| > \tau$. We then obtain for the unordered second order integral

$$S_2 = - \frac{1}{2} \sum_{j,m} \langle jm | Y_1^{\text{nf}} | j'm \rangle \langle j'm | Y_1^{\text{nf}} | jm \rangle$$

In the last two lines of Eq. (A2), the exact $\omega_{jj'}$ has been used and the result has been expanded to order $(\Delta j/j)^3$.

The $j'$ sum in Eq. (A1) runs from $j - l$ to $j + l$; thus, $\Delta j$ will run from $-l$ to $l$. Consequently, when Eq. (A2) is substituted into Eq. (A1) by unity. This is equivalent to approximating $\omega_{jj'}$ by $2\pi c B(2j + 1)\Delta j$ [compare the first and third lines of Eq. (A2)]; thus, our $\omega_{jj'}$ approximation is correct to order $(\Delta j/j)^2$. Using this approximation, Eq. (A1) becomes

$$S_{\text{approx}} = - 2 \sum_{\omega_{\Delta j}} K_{\Delta j}^3(\omega)$$

where $\omega = 2\pi c B(2j + 1)$ as in Eq. (4.2). (A5)
where we have used the fact that the term being summed is invariant under \( \delta \rightarrow -\delta \) to replace \( Z_2 \) by \( Z_2 \), a sum over both positive and negative \( \delta \) (the limits on this summation are discussed below). We have also omitted the \( \delta = 0 \) terms since they are identical to the \( j = j' \) terms excluded above, and we again used Eq. (A2) to approximate the interaction integrals to order \((\delta/j)^2\).

Since our approximate result, Eq. (A5), is identical to the result obtained from an expansion of an exact S-matrix, Eq. (A4), our approximation would seem to be accurate to within terms of order \((\delta/j)^2\). There is, however, one slight complication which must be considered before one can draw this conclusion. The “exact” result, Eq. (A4), contains a sum over intermediate states \( j' \) which are restricted by the correct 3j symbols, whereas in our exponential approximation, the sum over \( \delta \) simply runs from \(-l \) to \( +l \) (or from \(-l' \) to \( +l' \) if \( l' < l \)). For example, consider fixed values of \( m, l, \) and \( l' \) such that \( l < l' \). The sum over \( j' \) normally ranges from \(-j \) to \( +j \); however, we must also have \( j' \geq m \) [see Eq. (A3)], and for large values of \( m \) it may happen that \( m > j - l \). In that case, \( j' \) ranges from \( m \) to \( j + l \) and \( \delta \) in Eq. (A5) should run from \(-l \) to \(-j \). Unfortunately, there is no such restriction on \( \delta \) in our approximate S-matrix (this is a general problem with all exponential approximations to S matrices); thus, we are adding in some terms which should not be counted.

Fortunately, the terms which are counted incorrectly add only an amount of order \((\delta/j)^2\) compared with unity. To show this we note first that the problem occurs only when \( m \) is large (i.e., \( \delta \) of \( m = j \)); thus, in the sum over \( m \) [Eq. (5.1)] we are making an error in at most \( \delta \) of the \((j + 1)\) terms. If all terms in the sum over \( m \) were weighted equally, this error would be at most \((\delta/j)^2\) compared with unity. However, these terms are not weighted equally. For dipole transitions they are weighted by \([cf. \ Eq. (5.1)], noting that \( j' = j + 1 \) for dipole transitions) the factor

\[
\begin{align*}
\begin{pmatrix} j' & j' + 1 \cr m & m \end{pmatrix} =
\begin{pmatrix} j & j \cr m & m \end{pmatrix} (j + 1)^2
\end{align*}
\]

which vanishes for large \( m \). When \( m \) is within \( \delta \) of \( j \), Eq. (A6) is \((\delta/j)^2\) smaller than its value at \( m = 0 \); our error is thus reduced to the order of \((\delta/j)^2\) compared with unity. Furthermore, the Legendre polynomials in Eq. (A4) vanish as \( 1 - m^2/(j + 1)^2 \) or faster as \( m \rightarrow j \). Thus, the terms which are incorrectly included in the summation produce an error the order of \((\delta/j)^2\).

We may thus conclude that the error introduced by using the 3j symbol approximation of Eq. (4.1), and the approximate frequency \( \omega_{jj'} \approx \omega_j \) of Eq. (4.2) is at most the order of \((\delta/j)^2\) in the second order term. Since higher order terms are if anything smaller, their error should be relatively less important.

**\footnote{Supported by the exchange program between the Centre National de la Recherche Scientifique and the National Science Foundation.}
**\footnote{This research was supported in part by ARPA Contract 981 Amendent #9, ERDA Contract F(49-1)-3800, and by National Science Foundation Grant MPS 72-05619.}
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**\footnote{J. P. Bouanich, and C. Haeusler, J. Quant. Spectrosc. Rad. Transfer 12, 695 (1972).}

It should be noted that the broadening due to “m-changing collisions” (for example, effect #3 discussed by Gordon, Ref. 23) is also included in the present theory even though the S-matrix given in Eq. (4.13) is diagonal in \( m \). This is due to the fact that our coordinate frame is not a space fixed frame such as those usually employed in collision theory. As discussed in Sec. III, for each collision (i.e., for each value of impact parameter and velocity) we rotate to a coordinate frame in which \( m \) is conserved for that specific collision. Our coordinate frame is usually referred to as a "collision frame" in the line broadening literature. Our S-matrix in a space fixed frame would be given by \( S_{\text{time}} D \) for \( \theta, \phi, m \). When the angle of closest approach, \( \theta_m \), is a function of impact parameter, \( S_{\text{time}} \) is a rather complicated nondiagonal function of \( m \). Of course the half-width, Eq. (1.1), may be evaluated using either \( S_{\text{time}} \) or \( S_{\text{time}} \) since Eq. (1.1) is rotationally invariant. To verify this one may substitute the expression \( D^{-1} S_{\text{time}} D \) for each \( S \) in Eq. (1.1); then, using Eqs. (4.3.2) and (4.2.7) from Edmonds (Ref. 12), one obtains an expression identical to Eq. (1.1) with \( S_{\text{time}} \) in place of \( S \).

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