Quantum scattering theory of rotational relaxation and spectral line shapes in \( \text{H}_2-\text{He} \) gas mixtures*

Richard Shafer$^1$ and Roy G. Gordon

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138
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A systematic study is presented of the rotational relaxation and spectral line shape properties of dilute gas mixtures of \( \text{H}_2 \) in \( \text{He} \), in an effort to determine the radial and angular dependence of the \( \text{H}_2-\text{He} \) intermolecular potential. The quantum mechanical theory of relaxation in gases is reviewed, and we express the results in terms of a matrix of cross sections that determines each correlation function, and thus the relaxation properties of the system. The cross section is calculated from binary collision transition amplitudes, or \( S \) matrix elements, for \( \text{H}_2-\text{He} \) scattering. A Morse-spline-fitted-van der Waals potential of the form \( V_d(R) + V_A(R) P_2(\cos\theta) \) is assumed and we treat the hydrogen molecule as a rigid rotor. The Schrödinger equation is solved in the close-coupling approximation using the method of Gordon. We apply the theory to sound absorption measurements of rotational relaxation, NMR spin–lattice relaxation times, and the \( S \) and \( Q \) branches of the pure rotational Raman spectrum of \( \text{H}_2-\text{He} \) mixtures. Elastic phase shift and reorientation effects are examined, along with the effects of energetically inelastic collisions. We find asymptotically closed channels to be unimportant, but the rigid rotor approximation breaks down in calculating the Raman line shifts due to the vibration–rotation interaction. This effect is accounted for by assuming different radial potentials \( V_d(R) \) for scattering in two spectroscopic (vibrational) states. We find a potential that can accurately fit all the experimental data as well as the theoretical calculations of the long- and short-range behavior of the intermolecular potential.

I. INTRODUCTION

The study of collisional energy transfer in gases is a very effective method for probing the interactions between atoms and molecules. From such studies, we can obtain information on the intermolecular potential for various systems and, in particular, on the angular dependence of these potentials. Experiments that measure the relaxation of internal states of molecules through collisional energy transfer are susceptible to theoretical analysis in terms of an assumed interaction potential. Comparison of experimental and theoretical results then provide the criteria necessary to evaluate the validity of the potential. Such an approach is essential because the direct, \( a \) priori calculation of the intermolecular potential can presently be carried out only at short and long distances. Predictions in the important region near the potential minimum are still inaccurate, and need to be verified by comparison with experimental results.

These experiments are conveniently analyzed in terms of a correlation function, or its spectral density, of an appropriate dynamical variable. A review of the correlation function approach has been given by Gordon$^1$ and a review of vibrational and rotational relaxation studies has been given by Gordon, Klemperer, and Steinfeld.$^2$ The quantum mechanical theory of calculating correlation functions was first developed by Baranger$^3$ and Kolb and Griem$^4$ in terms of spectral line shapes. Fano$^5$ generalized these results using the Liouville formalism and Ben Reuven$^6$ applied Fano's formulation to the study of microwave spectra of ammonia. The general approach is the following: A particular form of the potential is assumed and collisional transition amplitudes are calculated from this potential. Appropriate combinations of these amplitudes yield an effective cross section which is then averaged over all energies. This energy-averaged cross section determines the relevant correlation function which may be related to experimental results.

Our primary concern is with the \( \text{H}_2-\text{He} \) system. We have undertaken a detailed, quantum mechanical study of this system for several reasons: Molecular hydrogen is the simplest, lightest molecule with the smallest reduced mass. Thus the internal energy levels are characterized by large spacings. As a result, relaxation phenomena involving the internal states can be studied at temperatures, ranging from very low to room temperature and even higher, solely in terms of its rotational motion. Excited vibrational and electronic states are important only at temperatures above 1000$^\circ$K. Also, because of the large rotational energy-level spacings, calculations can be done with basis sets that include reasonably small numbers of rotational states. This large spacing will also result in large quantum effects, thus making hydrogen very suitable for a quantum mechanical calculation. Furthermore, \( \text{H}_2-\text{He} \) is the simplest, nonreactive atom–diatomic system and thus has been the subject of much experimental and theoretical research.$^7-^{21}$ Thus quantitative comparison between calculated and experimental results is possible.

This paper is organized in the following way. In Sec. II we briefly review the quantum mechanical theory of calculating correlation functions and in Sec. III we discuss various models for the \( \text{H}_2-\text{He} \) intermolecular potential used in our calculations. We treat the numerical solution of the scattering of an atom by a rigid rotor and the calculation of the energy-averaged cross

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sections in Sec. IV. In Sec. V we present and analyze our results for rotational relaxation, spin–lattice relaxation and the $S$ and $Q$ branches of the pure rotational Raman spectrum of $\text{H}_2$ highly diluted in $\text{He}$. Finally, in Sec. VI, we summarize our results for the best representation of the $\text{H}_2\text{–He}$ intermolecular potential.

II. QUANTUM MECHANICAL THEORY OF CORRELATION FUNCTIONS IN GASES

In this section we review the impact theory for calculating correlation functions in molecular gases. The correlation function $C(t)$ of an operator $A$ can be written as

$$C(t) = \langle AA(t) \rangle = \text{Tr} \{ \rho AA(t) \},$$

where $\rho$ is the density matrix describing the initial, usually equilibrium, ensemble: $\rho = \rho(0)$; $A(t)$ satisfies the Heisenberg equation of motion:

$$i\hbar \frac{dA(t)}{dt} = [A(t), H],$$

$$A(t) = \exp\left[(iH/\hbar)t\right]A \exp\left[-(iH/\hbar)t\right]$$

with the initial condition $A(0) = A$. $H$ is the total Hamiltonian and Tr in Eq. (1) signifies trace. Often we are interested in the spectral density $F(\omega)$ of the correlation function, which is just the Fourier transform of $C(t)$:

$$F(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} \exp(i\omega t)C(t)dt.$$

(We treat the case of positive emission frequencies.) If $H$ is time independent, $C(-t) = C^*(t)$ and

$$F(\omega) = \pi^{-1} \text{Re} \int_{0}^{\infty} \exp(i\omega t)C(t)dt.$$

The formal theory of calculating $C(t)$ is simplified by the introduction of the Liouville superoperator $L$, defined by its action on an operator $A$ as

$$LA = \hbar^{-1}[H, A].$$

Using $L$, we can rewrite Eq. (2a) as

$$\frac{dA(t)}{dt} = iLA(t)$$

with the solution $A(t) = \exp(iLt)A$. If $A$ is Hermitian, then we also have

$$A(t) = A \exp(-iLt).$$

The correlation function then becomes

$$C(t) = \text{Tr} \{ \rho AA(t) \} = \text{Tr} \{ A(t) \rho A \} = \text{Tr} \{ A \exp(-iLt) \rho A \}$$

and $F(\omega)$ can be expressed as

$$F(\omega) = -\pi^{-1} \text{Im} \text{Tr} \{ A(\omega - L)^{-1} \rho A \}.$$

We consider the case of a particular molecule of interest—the system molecule—diluted in a foreign gas that acts as a thermal bath and partition the Hamiltonian accordingly:

$$H = H_0^{(s)} + H_0^{(b)} + V,$$

where $H_0^{(s)}$ is the unperturbed system Hamiltonian, $H_0^{(b)}$ is the unperturbed bath Hamiltonian and $V$ is the system–bath interaction. Similarly, we have

$$L = L_0^{(s)} + L_0^{(b)} + \Lambda = L_0 + \Lambda,$$

where

$$L_0^{(s)} = \hbar^{-1}[H_0^{(s)}], \quad L_0^{(b)} = \hbar^{-1}[H_0^{(b)}],$$

and

$$\Lambda = \hbar^{-1}[V].$$

We now approximate $\rho$, the density operator describing the initial ensemble as the product

$$\rho = \rho^{(s)}\rho^{(b)}.$$
to the time between collisions—and thus only complete collisions need be considered.

(3) We assume the bath has a negligibly short memory (Markoff assumption).

With these assumptions, $\langle M_\omega \rangle_0$ is independent of $\omega$ and can be written as

$$\langle M_\omega \rangle_0 = n \langle m \rangle,$$

where $n$ is the bath density and

$$m = T_a(E_a) - T_\beta^*(E_\beta) + 2\pi T_a(E_a) T_\beta^*(E_\beta).$$

$T_a$ is the transition operator or $T$ matrix describing scattering in the initial spectroscopic state, $T_\beta^*$ is the adjoint of $T_\beta$ describing scattering in the final spectroscopic state. The transition operators are evaluated at total energies $E_a, E_\beta$ such that the relative kinetic energy before collision is the same for scattering in both spectroscopic states:

$$E_a = E_\beta + \hbar \omega E_b.$$

In what follows, we shall consider our system molecule to be a diatomic diluted in an isotropic monatomic host gas. Writing $m$ as $i\sigma$, where $i$ is the relative velocity before collision (which is the same for both spectroscopic states) and $\sigma$ includes the average over all bath molecule angles and the sum over all spatially degenerate levels of the system molecule, then the rotationally invariant form $\sigma^k = \sigma$ is given by

$$\sigma_s(j'_a, j'_b; j_a, j_b) = - \left( \frac{\pi}{k^2} \right) \sum_{j_a, j_b, j k} (2j_a + 1)(2j_b + 1)$$

$$\times \begin{vmatrix} j'_a & k & j'_b \\ j_a & k & j_b \\ j'_b & l' & j_a \end{vmatrix} \delta(b(j'_a, j_a) \delta(j'_b, j_b) \delta(l', l)) - S^{2j_b}(j'_b, l'; j_b, l) S^{2j_a}(j'_a, l'; j_a, l).$$

(16)

$j_a$ describes the rotational angular momentum of the system molecule in its initial spectroscopic state before collision; $j'_a$ its rotational angular momentum after collision; $j_b$ and $j'_b$ are similarly defined for the final spectroscopic state. $l$ and $l'$ are the orbital angular momentum for relative motion before and after collision, respectively, $k_j$ is the wave vector for relative motion before collision and is the same in both spectroscopic states. $J_a$ is the total angular momentum defined by

$$J_a = j_a + 1.$$

$J_b$ is similarly defined. $S^{2j_b}(j'_b, l'; j_b, l)$ is the scattering $S$ matrix connecting the channel $(j_b, l)$ before collision to the channel $(j'_b, l')$ after collision. Since the total angular momentum is conserved throughout collisions, $S^{2j_b}$ is diagonal in $J_a$. $k$ is the tensor rank of the spherical tensor operator $A$. The quantity in curly brackets is a 0-j symbol and $\delta(j'_a, j_a)$ is the Kronecker delta. Again we note that $S^{2j_a}(j'_a, l'; j_a, l)$ and $S^{2j_b}(j'_b, l'; j_b, l)$ are evaluated at total energies such that the kinetic energy of relative motion before scattering is the same in both spectroscopic states.

Since the degenerate magnetic levels of the rotational states have been summed over to obtain the rotationally invariant cross section in Eq. (16), the trace in Eq. (12) is over reduced matrix elements of $A$, as defined by Edmonds, and $\rho^{(s)}$ describes the populations of the rotational levels exclusive of the degeneracy factor:

$$\rho_{j_a, j'_a}^{(s)} = Z^{-1} \delta(j_a, j_b) \exp(-E_{j_a}/k_B T),$$

where $E_{j_a}$ is the energy of the $j_a$ rotational state, $k_B$ is Boltzmann’s constant and $Z$ is the partition function for the system molecule. The trace in Eq. (12) is given explicitly by

$$F(\omega) = -\pi^{-1} \text{Im} \sum_{j_a, j'_a} \langle j_a \ | \ A \ | | j'_a \rangle^*$$

$$\times \left\{ 1/\left[\omega - \omega_a - i\text{Im}\langle \sigma_s(j_a, j'_a; j_a, j_a) \rangle \right] \right\}$$

$$\times \rho_{j_a}^{(s)}(j_a \ | \ A \ | j_a).$$

(17)

This can be written in matrix form by associating one index to each pair of initial and final spectroscopic states, i.e., to each spectral line:

$$(j_a, j_b) \rightarrow i.$$
SPECTRAL LINE SHAPES IN H$_2$–He

This is the form of the effective cross section we shall use in the following analysis.

We remark that the cross section in Eq. (20) depends, in general, on the phases of the $S$ matrix elements as well as their magnitudes. The off-diagonal elements of $S$ are important for overlapping lines and they describe the transfer of amplitude from the transition $(j_n, j_s)$ to the line $(j_n', j_s')$. Also, $S^{\alpha, \beta}(j_n, j_s; j_n', j_s') = S^{\alpha, \beta}(j_n', j_s; j_n, j_s)$ if we interchange the total energies at which the $S$ matrices are evaluated as well as $\alpha$ and $\beta$. For isolated or well resolved lines, $S$ reduces to a single, complex number:

$$\sigma = \sigma_{re} + i \sigma_{im}$$

and $F(\omega)$ is Lorentzian:

$$F(\omega) = (\pi \omega^2/\pi)$$

$$\times \left[ (\omega - \omega_0 + n \langle \sigma_{re} \rangle)^2 + (n \langle \sigma_{im} \rangle)^2 \right].$$

With full width at half-height

$$\Delta \omega_{1/2} = 2n \langle \sigma_{re} \rangle$$

and line shift from the low pressure position

$$\omega - \omega_0 = -n \langle \sigma_{im} \rangle.$$  

Finally we note that our Eq. (19) is, within a normalization factor, identical to the result obtained by Gordon in his semiclassical theory of line shapes and relaxation [Eq. (10) in Ref. 23] except that our $\sigma$ is given by Eq. (20).

III. MODELS FOR THE H$_2$–He INTERMOLECULAR POTENTIAL

Figure 1 shows the coordinates used to describe the interaction potential, $V(R, \theta) = V(R, \varphi)$. We treat the diatomic as a rigid rotor. $V(R, \theta)$ can be expanded as

$$V(R, \varphi) = \sum_{\lambda=0}^{\infty} V_\lambda(R) P_\lambda(\cos \theta),$$

where $P_\lambda(x)$ is the Legendre polynomial of order $\lambda$. For a homonuclear diatomic, only even values of $\lambda$ appear in Eq. (24) and we shall keep just the first two terms:

$$V(R, \varphi) = V_0(R) + V_2(R) P_2(\cos \theta).$$

There have been three ab initio calculations of the short-range interaction for H$_2$–He,7–9 the most recent and complete being the CI calculation of Gordon and Secrest.9 The results have been fit to the form

$$V(R, \varphi) = A \exp(-\beta R)(1 + \alpha_{SR} \cos \varphi),$$

where $\alpha_{SR}$ is the short-range anisotropy. Gordon and Secrest obtain the following values in fitting their results to Eq. (26):

$$A = 11.39 \text{ a.u. (310.0 eV)},$$

$$\beta = 1.93 \text{ a.u.}^{-1},$$

$$\alpha = 0.273.$$  

Range of validity: 2.8–5.2 a.u. (1.5–2.8 Å).

Gengenbach and Hahn have refit these CI results over a smaller range of $R$ to exclude the region in which the CI values do not decrease rapidly enough.11 Their refit values are

$$A = 10.29 \text{ a.u. (279.9 eV)},$$

$$\beta = 1.9304 \text{ a.u.},$$

$$\alpha = 0.266.$$  

Range of validity: 2.8–4.5 a.u. (1.5–2.4 Å).

We note that the CI results agree well with the spherical potential obtained by Amdur and Malinauskas from diffusion experiments.10–9

The long-range $R^{-6}$ dependence has been calculated by second-order perturbation theory and error-bound techniques. A recent review of this work is given by Langhoff, Gordon, and Karplus.12 In our work we shall use the semiempirical results of Langhoff, Gordon, and Karplus,12 which can be written as

$$V(R, \varphi) = -C_\lambda R^{-6}[1 + \alpha_{LR} P_2(\cos \varphi)]$$

with $C_\lambda = 4.01 \text{ a.u. = 1.932 \times 10^4 \text{ cm}^{-1} \text{ Å}^{-6}}$ and $\alpha_{LR} = 0.105$. These values are in good agreement with the recent results of Starkschall and Gordon.13

There have been two studies of the H$_2$–He intermolecular potential based on NMR spin–lattice relaxation measurements. Riehl et al.14 fit their experimental results for relaxation times below 2000K using distorted
wave approximation calculations of reorientation cross sections ($\Delta m = 1$ changes) in the $j = 1$ manifold. They fit to an exponential $-6$ form of the potential but found their results insensitive to substitution of a Lennard-Jones potential with the same well depth and minimum. The equivalent Lennard-Jones form they obtained is

$$V(R, \theta) = \epsilon \left[ \left( \frac{R_m}{R} \right)^6 + \alpha_{SR} \left( \cos \theta \right) \right] - 2 \left( \frac{R_m}{R} \right)^6 \left[ 1 + \alpha_{LR} P_2(\cos \theta) \right]$$

with

$$\epsilon = 14.10 \text{ cm}^{-1} = 1.75 \text{ meV},$$
$$R_m = 3.338 \text{ Å},$$
$$\alpha_{SR} = 0.343,$$
$$\alpha_{LR} = 0.279.$$ 

More recently, Foster and Rugheimer\textsuperscript{16} refit the data of Riehl et al.,\textsuperscript{14} doing close-coupling calculations. They fit the data directly to a Lennard-Jones form, Eq. (26'), and obtained the following values:

$$\epsilon = 13.78 \text{ cm}^{-1},$$
$$R_m = 3.087 \text{ Å},$$
$$\alpha_{SR} = 0.380,$$
$$\alpha_{LR} = 0.190.$$ 

The major disadvantage of using a Lennard-Jones for the radial potential $V_0(R)$ is the lack of flexibility inherent in a two parameter form. Hence, in addition to Lennard-Jones potentials, we also investigated a more flexible form, the Morse-spline-fitted-van der Waals form (MSV). Writing $V(R, \theta)$ as in Eq. (25), $V_0(R)$ for the MSV potential is written as

$$V_0(R) = \epsilon \left[ \exp \left[ 2\beta \left( 1 - R/R_m \right) \right] - 2 \exp \left[ \beta (1 - R/R_m) \right] \right],$$

$$V_0(R) = \epsilon \left( b_1 + (R - R_1) \left[ b_2 + (R - R_2) \left[ b_3 + (R - R_3) b_4 \right] \right] \right),$$

$$V_0(R) = -C_b/R^6 - C_s/R^8,$$

If $R \geq R_m$, then $V(R)$ reaches its minimum at $R = R_m$ and has a well depth $\epsilon$. The parameters $b_i$ are determined by matching $V_0(R)$ and $V'_0(R)$ at $R_1$ and $R_2$. $V_2(R)$ is given by

$$V_2(R) = \alpha_{SR} \left( \exp \left[ 2\beta \left( 1 - R/R_m \right) \right] \right),$$

$$V_2(R) = \alpha_{LR} \left( -C_b/R^6 - C_s/R^8 \right),$$

and, for $R_1 \leq R \leq R_2$, $V(R)$ is determined by fitting a cubic polynomial as in $V_0(R)$.

We have obtained values for the parameters that define $V_0(R)$, Eq. (27), by fitting our MSV form to the recent results of Gengenbach and Hahn.\textsuperscript{11} They have performed low-energy $\text{H}_2-\text{He}$ beam experiments to measure the total, integrated cross section as a function of relative velocity. They fit their results to a form similar to Eq. (27). Using their results, which included setting $C_b$ to 4.01 a.u., and the CI results for the short-range behavior, we obtain the parameters for Eq. (27) given in Table I.

There have been no calculations to date for $C_s$. The value in Table I is reasonable in the sense that calculations on two other four-electron systems, $\text{He-He}$ and $\text{H}_2-\text{H}_2$, yield ratios for $C_b/C_s$ of 1.6 $\text{A}^2$ and 2.7 $\text{A}^2$, respectively:\textsuperscript{25} Our values for $\text{H}_2-\text{He}$ yield $C_b/C_s = 2.86 \text{A}^2$.

We have done calculations on three different MSV forms, all with the same $V_0(R)$ given in Table I but with different $V_2(R)$ parameters, Eq. (28). Table II summarizes these values.

For MSV(GH)1 $\alpha_{LR}$ was set at the value in Eq. (25'), $\alpha_{SR}$ was determined by fitting to rotational relaxation data (see Sec. V) and $\gamma$ was determined by requiring $V_2(R)$ to be smooth in the region of the well. By varying $\alpha_{SR}$ and $\alpha_{LR}$ in MSV(GH)2 and MSV(GH)3 we can independently study the effect of different parts of the potential on the various experimental results calculated below.

Figure 2 compares the short-range behavior of $V_0(R)$ for the MSV potentials with the CI results. Figures 3 and 4 compare $V_0(R)$ for the MSV potentials with $V_0(R)$ obtained in Ref. 14 and Fig. 5 shows $V_0(R)$ and $V_2(R)$ in the region of the well for MSV(GH)1.

### Table I. Parameters for $V_0(R)$ for MSV potentials

<table>
<thead>
<tr>
<th>Potential</th>
<th>$\alpha_{SR}$</th>
<th>$\gamma$</th>
<th>$\alpha_{LR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSV(GH)1</td>
<td>0.262</td>
<td>0.400</td>
<td>0.105</td>
</tr>
<tr>
<td>MSV(GH)2</td>
<td>0.262</td>
<td>0.400</td>
<td>0.125</td>
</tr>
<tr>
<td>MSV(GH)3</td>
<td>0.282</td>
<td>0.400</td>
<td>0.105</td>
</tr>
</tbody>
</table>
ential equations for the radial wavefunctions $F_\gamma(R)$, where $\gamma$ specifies the initial channel, characterized by the quantum numbers $j$ and $l$ ($j$ specifies the rotational angular momentum, $l$ the orbital angular momentum, and $J$ the total angular momentum):

$$\{E - E_j + \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu} (l'^2 + 1)/2\mu R^2\} F_\gamma(R) = \sum_{\gamma'} V_{\gamma'\gamma}(R) F_{\gamma''}(R), \quad (29)$$

where $E$ is the total energy, $E_j$ is the energy of the $j$th rotational level, and $\mu$ is the reduced mass of the colliding system.

$V_{\gamma'\gamma}(R)$ is given by

$$V_{\gamma'\gamma}(R) = \int \gamma_{F_{\gamma'}}(R) \gamma_{F_{\gamma'}}(R) dR d\hat{R} \quad (30)$$

We have solved these equations for $S^j(j''l';jl)$ using Gordon's method, which has been discussed in detail elsewhere. For calculations on parahydrogen we used a basis set that included the $j=0$ and $j=2$ rotational levels and for orthohydrogen we considered the $j=1$
and \( j = 3 \) levels. All experiments that were analyzed were carried out at room temperature or below. The following list gives the fractional populations of the low \( j \) states in pure para- and pure orthohydrogen at 300°K:

<table>
<thead>
<tr>
<th>( j )</th>
<th>Para-H(_2)</th>
<th>( j )</th>
<th>Ortho-H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.517</td>
<td>1</td>
<td>0.879</td>
</tr>
<tr>
<td>2</td>
<td>0.468</td>
<td>3</td>
<td>0.119</td>
</tr>
<tr>
<td>4</td>
<td>0.015</td>
<td>5</td>
<td>0.002</td>
</tr>
</tbody>
</table>

From these data it seems reasonable that our basis sets were sufficiently complete. Further discussion on the effect of closed channels is given in the next section, in which it is shown that enlarging the number of rotational states considered does not change the results significantly.

We note here that the total parity \((-1)^{\mu+j}\) is conserved during a collision and for a homonuclear diatomic, the molecular parity \((-1)^J\) is also conserved. As a consequence, for a given set of \( j \) values (even or odd) and a given total angular momentum \( J \), there are two completely uncoupled sets of corresponding \( l \) values. This significantly reduces the labor required in the scattering calculations.

All potentials considered have the form of Eq. (25). The matrix elements \( V_{\gamma \gamma'} \) in Eq. (30) then have the following form:

\[
V_{\gamma \gamma'}(R) = V_0(R) \delta_{\gamma \gamma'} + V_2(R) \langle jI \mid P_2(\cos \theta) \mid j'I' \rangle. \tag{32}
\]

The matrix element of \( P_\lambda \) in the coupled representation is given by

\[
\langle jI \mid P_\lambda(\cos \theta) \mid j'I' \rangle = (-1)^{\mu+j'+j} \times \left[ (2l+1)(2l'+1)(2j+1)(2j'+1) \right]^{1/2} \times \left( \begin{array}{ccc} l & \lambda & l' \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{c} j \\ 0 \\ j' \end{array} \right) \left( \begin{array}{c} l \\ j \\ j' \end{array} \right),
\]

where ( ) encloses a 3-\( j \) symbol and { } encloses a 6-\( j \) symbol. The phase of the 3-\( j \) symbol is determined from the relation

\[
\langle jm_1m_2 \mid J-MjI \rangle = (-1)^{j+1-M} \times (2J+1)^{1/2} \left( \begin{array}{c} j \\ m_j \end{array} \right) \left( \begin{array}{c} l \\ m_1 \end{array} \right) \left( \begin{array}{c} J \\ M \end{array} \right). \tag{33}
\]

As indicated in Eq. (19) we must calculate the quantity \( \langle \nu \sigma \rangle \), where \( \langle \rangle \) means an average over all perturber energies in the initial equilibrium ensemble. In thermal equilibrium the perturber energies are determined by a Boltzmann distribution of kinetic energy which results in a Maxwellian distribution of relative velocities. Writing

\[
E = \frac{1}{2} \mu v^2 = \frac{h^2 k^2}{2 \mu},
\]

where \( E \) is the kinetic energy of relative motion, the energy-averaged cross section has the form

\[
\langle \sigma \nu \rangle = \left( \frac{8 k_B T}{\mu \pi} \right)^{1/2} \int_0^{\infty} E \sigma \exp \left(-\frac{E}{k_B T}\right) dE, \tag{34}
\]

which can also be written as

\[
\langle \sigma \nu \rangle = \langle \nu \rangle \langle \sigma \rangle, \tag{35}
\]

The integral in Eq. (35) over the infinite energy range was converted to an integral from 0 to 1 by a change of variables and this integral was then evaluated by Gauss-Legendre quadrature. In all calculations a six-point quadrature was used for each temperature corresponding to an experimental measurement. Test calculations for rotational excitation cross sections indicated an agreement of better than 2% between four-point and six-point quadratures.

V. RESULTS

In this section we report our results from calculations on the MSV-type potentials we have considered in Sec. III. We have also done extensive calculations on Lennard-Jones-type potentials including those obtained by Refs. 14 and 15 (see Sec. III). Typically, the Lennard-Jones potentials could reproduce one experimental quantity but not another. For example, the Lennard-Jones potential of Foster and Rugheimer fit the spin-lattice relaxation data and the Raman branch linewidth very well but produced only 50% of rotational relaxation times and significantly overestimated the Raman branch linewidth. Also the rotational relaxation cross sections for all the Lennard-Jones potentials showed an incorrect temperature dependence. Thus \( \sigma_{\text{MSV}} \) could be fit to experiment at one temperature but would yield an inaccurate result at another temperature. This is due to the \( R^{-12} \) short-range behavior in the Lennard-Jones form. The CI results indicate that an exponential short-range behavior is more accurate. For details concerning the unsatisfactory results on the Lennard-Jones calculations, see Ref. 29. In the following, we shall concentrate on the results based on the more accurate MSV potential. We show that this potential can accurately fit all the experimental results, as well as theoretical calculations at both long and short distances.

A. Rotational Relaxation

Sound absorption measurements of rotational relaxation provide a means of studying energetically inelastic
collisions. Assuming the normal hydrodynamic equations to be valid, the frequency-dependent bulk viscosity \( \dot{\gamma}(\omega) \) of a dilute molecular gas can be written in terms of the spectral density of the correlation function of the internal energy fluctuations\(^{30} \):

\[
\dot{\gamma}(\omega) = \frac{4\rho}{9k_B T} \text{Re} \int_0^\infty \exp(-i\omega t) \langle \varepsilon(0)\varepsilon(t) \rangle dt,
\]  
(36)

where \( \varepsilon = E_j - \langle E_j \rangle \), \( E_j \) is the energy of the \( j \)th rotational level, \( \langle E_j \rangle \) is the average rotational energy, and \( \rho \) is the mass density. Using the results of Sec. II, we can write

\[
\langle \varepsilon(0)\varepsilon(t) \rangle = d \cdot \exp(-t/\tau) \langle \sigma_{RR}^2 \rangle \cdot d,
\]  
(37)

where the elements of \( d \) are given by the reduced matrix elements of \( d \), a tensor of rank zero:

\[
\langle j' | d || j \rangle = (E_j - \langle E_j \rangle) \delta(j', j).
\]

\( \sigma_{RR} \) is the cross section appropriate to rotational relaxation and is discussed below. Equations (36) and (37) are valid regardless of the number of levels contributing to the relaxation process. In the two-level case, we can write

\[
\langle \varepsilon(0)\varepsilon(t) \rangle = (\varepsilon(0)^2) \exp(-t/\tau)
\]

using the normalization \( d \cdot d = 1 \). The single relaxation time \( \tau \) is then given by

\[
\tau^{-1} = n(\varepsilon) \langle \sigma_{RR} \rangle + \langle \sigma_{RR} \rangle,
\]  
(38)

where \( \sigma_{RR} \) is the inelastic cross section for the transition from level 1 to level 2 normally encountered in scattering theory. This is identical to the result obtained from the kinetic equation approach.\(^{21} \)

The cross section is obtained from our general prescription, Eq. (20), by setting the tensor character \( k \) to 0, \( j_a = j_b \), \( j_a' = j_a' \), and \( J_a = J_b \). Then we have

\[
\sigma_{RR}(j', j'; j, j) = \langle \pi/k^2 \rangle \sum_{j\ell'1v} [(2j'+1)/(2j+1)] \delta(j', j)
\]

\[
\times [\delta(j', j) \delta(l', l) - S^\ell(j', l'; j, l)] \]  
(39)

For \( j' \neq j \), this reduces to

\[
\sigma_{RR}(j', j'; j, j) = -\langle \pi/k^2 (2j'+1) \rangle \sum_{j\ell'1v} (2j+1) \delta(l', l) - S^\ell(j', l'; j, l) \]  

which is just the expression Arthurs and Dalgarno\(^{38} \)

give for the inelastic cross section for the excitation of a rigid rotor by an atom. The diagonal elements \( \sigma_{RR}(j, j; j, j) \) are not the correct sections for elastic rotor-atom scattering, the latter being given by

\[
\left[ \pi/k^2 (2j+1) \right] \sum_{j\ell'1v} (2j+1) \delta(l', l) - S^\ell(j, l'; j, l) \]  

This is not the cross section appropriate for relaxation.

**Table III. Rotational relaxation times for \( \text{H}_2 \) at 1 atm pressure He.**

<table>
<thead>
<tr>
<th>Potential</th>
<th>( \tau ) at 90°K (( \times 10^{-8} ) sec)</th>
<th>( \tau ) at 170°K (( \times 10^{-8} ) sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSV(GH) 1</td>
<td>1.61</td>
<td>1.21</td>
</tr>
<tr>
<td>MSV(GH) 2</td>
<td>1.62</td>
<td>1.21</td>
</tr>
<tr>
<td>MSV(GH) 3</td>
<td>1.40</td>
<td>1.06</td>
</tr>
<tr>
<td>Experiment(^{a} )</td>
<td>1.61 ±0.08</td>
<td>1.24 ±0.02</td>
</tr>
<tr>
<td>MSV(GH) 1</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>Experiment(^{a} )</td>
<td>1.10 ±0.05</td>
<td></td>
</tr>
</tbody>
</table>

*Reference 5.*

If we add all the components of a given column of the sigma matrix in Eq. (39), we find

\[
\sigma_{RR}^{\text{tot}}(j, j; j, j) + \sum_{j' \neq j} \sigma_{RR}(j, j'; j, j) = \langle \pi/k^2 (2j+1) \rangle \times \sum_{j\ell'1v} (2j+1) \delta(j, l) \delta(l', l) - S^\ell(j', l'; j, l) \]  

Since the \( S \) matrix is unitary:

\[
S^\ell S = 1 \quad \text{or} \quad \sum_{j\ell'} S^\ell(j', l'; j, l) S(j, l'; j, l) = 1,
\]

we get the following result:

\[
\sigma_{RR}^{\text{tot}}(j, j; j, j) + \sum_{j' \neq j} \sigma_{RR}(j, j'; j, j) = 0.
\]

The diagonal element of any column, then, is the negative of the sum of all the other elements in that column. Hence, the cross section matrix for rotational relaxation is completely determined by inelastic collisions. Clearly, for a spherically symmetric potential, which results in a diagonal \( S \) matrix, the cross section vanishes completely.

We can exploit detailed balance to write the relaxation time in Eq. (38) as

\[
\tau^{-1} = n(\varepsilon) \sigma(j, j') \right\}{1 + \left[ (2j+1)/(2j'+1) \right]} \times \exp[\left( (E_j - E_{j'}) / k_B T \right)].
\]  
(40)

Thus we need only know the excitation cross section for the transition \( j \to j' \) (or equivalently just the deexcitation cross section for the transition \( j' \to j \)). In our work on parahydrogen, both \( \sigma(22; 00) \) and \( \sigma(00; 22) \) were calculated explicitly in several cases and satisfied detailed balance to within 1%-2%. Since the computer program generates an exactly symmetric \( S \) matrix, this is an indication of the accuracy of our quadrature scheme for the energy average.

We have calculated rotational relaxation times for the three MSV potentials described in Sec. III. Table III presents the results for these potentials, along with the experimental results from Ref. 16 at 90.5 and 170°K, extrapolated to infinite dilution of \( \text{H}_2 \) in He. In order to facilitate comparison and interpretation, we shall
Table IV. Energy-averaged cross sections for rotational relaxation.

<table>
<thead>
<tr>
<th>Potential</th>
<th>$\alpha_{SR}$</th>
<th>$\alpha_{LR}$</th>
<th>$\epsilon$ (cm$^{-1}$)</th>
<th>$\langle \sigma \rangle_{\text{MSV}}$ (Å$^2$)</th>
<th>$\langle \sigma \rangle_{\text{MSV}}$ (Å$^2$)</th>
<th>$\langle \sigma \rangle_{\text{MSV}}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSV(GH)1</td>
<td>0.262</td>
<td>0.105</td>
<td>10.74</td>
<td>0.908×10$^{-3}$</td>
<td>2.16×10$^{-2}$</td>
<td>2.38</td>
</tr>
<tr>
<td>MSV(GH)2</td>
<td>0.262</td>
<td>0.125</td>
<td>10.74</td>
<td>0.903×10$^{-3}$</td>
<td>2.16×10$^{-2}$</td>
<td>2.39</td>
</tr>
<tr>
<td>MSV(GH)3</td>
<td>0.282</td>
<td>0.105</td>
<td>10.74</td>
<td>1.040×10$^{-3}$</td>
<td>2.46×10$^{-2}$</td>
<td>2.37</td>
</tr>
<tr>
<td>Experiment*</td>
<td></td>
<td></td>
<td></td>
<td>0.906×10$^{-3}$</td>
<td>2.10×10$^{-2}$</td>
<td>2.32</td>
</tr>
</tbody>
</table>

* Reference 5.

examine the behavior of the energy-averaged cross section $\langle \sigma (j',j';j,j) \rangle$ that appears in Eq. (40). Table IV presents the values for these energy-averaged cross sections for the various potentials which are more directly related to the potential parameters than are the relaxation times. Included in Table IV are the three parameters most important in determining the cross sections $\epsilon$, $\alpha_{SR}$, and $\alpha_{LR}$.

Comparison of the cross sections for MSV(GH)1 and MSV(GH)3 indicates that the cross sections vary approximately as the square of the short-range anisotropy, as predicted from perturbation theory. Comparison of MSV(GH)1 with MSV(GH)2 indicates that the rotation relaxation cross sections are fairly insensitive to small changes in $\alpha_{LR}$. This is to be expected since these cross sections are determined by inelastic collisions which probe the repulsive region of the potential.

The MSV(GH)1 potential fits the experimental data best, producing results at most 3% larger than experiment.

We also include in Table III the results for the 0-2 relaxation time for H$_2$ infinitely diluted in He$^4$, the lighter helium isotope, for the potential MSV(GH)1. The good agreement between experiment and calculation complements the results on the heavier isotope case.

Figure 6 shows the rotational excitation cross section, as a function of relative kinetic energy (here the cross section is not energy averaged) for MSV(GH)1. We have also done rotational relaxation time calculations for the lowest two states in orthohydrogen. For the MSV(GH)1 potential, we obtain the following results at 1 atm:

$$\langle \sigma (33; 11) \rangle_{\text{MSV}} = 3.14 \times 10^{-4} \text{ Å}^2,$$

$$\langle \sigma (33; 11) \rangle_{\text{MSV}} = 5.54 \times 10^{-4} \text{ Å}^2,$$

and the relaxation times, at 1 atm of He, are

$$\tau_{\text{MSV}} = 4.46 \times 10^{-8} \text{ sec},$$

$$\tau_{\text{MSV}} = 3.26 \times 10^{-8} \text{ sec}$$

for orthohydrogen diluted in helium. As it is very difficult to isolate pure orthohydrogen no experiments have been done on ortho-H$_2$-He sound absorption.

Comparison of relaxation times for ortho- and pure hydrogen indicates that para-H$_2$-He collisions are more efficient than ortho-H$_2$-He collisions, as is expected since inelastic collisions in ortho-H$_2$ require a larger energy transfer than in para-H$_2$ collisions.

At all energies required for the energy-average quadrature, the $j=4$ rotational level lies too high to be asymptotically excited from the ground rotational level. The calculations described above have all been done

![Fig. 6. Rotational excitation cross sections calculated from MSV(GH)1 as a function of initial relative kinetic energy.](https://jcp.aip.org/about/rights_and_permissions)
using \( j=0 \) and \( j=2 \) states in the basis set for the computation of the \( S \) matrices. To investigate the effect of closed channels, we have calculated cross sections and relaxation times with the \( j=4 \) states also included in the basis set. This results in nine channels with the same parity as the \( j=0 \) channel. Because of the selection rules for the matrix elements of \( P_2(\cos \theta) \) the \( j=0 \) channels cannot couple directly with the \( j=4 \) channels. The \( j=4 \) channels, however, can couple to the \( j=2 \) channels which, in turn, are coupled to the \( j=0 \) channel. As this coupling is indirect, the effect should be small. The calculations we have done showed no change in the computed relaxation times or the energy-averaged inelastic cross sections, after adding the \( j=4 \) rotational levels to the basis set.

### B. Spin–Lattice Relaxation

Nuclear magnetic spin–lattice relaxation is due to the presence of time-dependent local magnetic fields that couple to the nuclear spins. The two important mechanisms responsible for relaxation in gaseous hydrogen are the spin–rotation interaction and the intramolecular spin–spin or dipolar coupling. The former arises from the coupling of the total nuclear spin with the rotational angular momentum of the molecule, the latter from the interaction of the two nuclear spins in one hydrogen molecule.

In the discussion that follows, in addition to assuming the validity of the Bloch equations, we also assume that the collision process and the coupling interactions are independent of the applied magnetic field and that the “lattice” (heat bath of gas molecules) is isotropic. Under these conditions the longitudinal relaxation time \( T_1 \) and the transverse relaxation time \( T_2 \) are equal, i.e., the relaxation process is isotropic.

First consider relaxation due to the spin–rotation interaction. The Hamiltonian, in radians/second, can be written as

\[
H_{SR} = \gamma H'I \cdot J,
\]

where \( \gamma \) is the magnetogyric ratio of the proton, \( H' \) is the spin–rotation coupling constant, \( I \) is the total nuclear spin, and \( J \) is the rotational angular momentum. \( H' \) has been accurately measured in atomic beam experiments and has the value 26.75 G; all nuclear momenta are in units of \( \hbar \).

The Hamiltonian in Eq. (41) can be written as the sum of products of spin variables with lattice variables and the resulting expression for \( T_1 \) is

\[
(T_{1SR})^{-1} = \frac{3}{2} \gamma^2 H'^2 \int_0^\infty \langle J_+(0) \cdot J_-(t) \rangle \exp(-i\omega t) dt,
\]

where \( J_+ = J_x + i J_y \) and \( \omega_L = \omega_R - \omega_J \) with \( \omega_J \) the Larmor frequency of the rotational angular momentum and \( \omega_L \) the Larmor frequency of the proton. Under isotropic conditions we have

\[
\langle J_+(0) \cdot J_-(t) \rangle = \frac{3}{8} \langle J(0) \cdot J(t) \rangle
\]

and Eq. (42) can be written as

\[
(T_{1SR})^{-1} = \frac{3}{2} \gamma^2 H'^2 \Re \int_0^\infty \langle J(0) \cdot J(t) \rangle dt,
\]

where, under extreme narrowing, \( \omega_L = 0 \). Thus, we can express \( T_1 \) in terms of the spectral density at zero frequency of the correlation function of the rotational angular momentum. Since \( J \) is a constant of the free motion, the “spectroscopic” states have unperturbed frequencies \( \omega_j = 0 \) and so we have (see Sec. II)

\[
(T_{1SR})^{-1} = \frac{3}{2} \gamma^2 H'^2 / n(\psi) \mathbf{d} \cdot (\mathbf{G}_{SR})^{-1} \cdot \mathbf{d},
\]

where \( n \) is the number density of perturbers (He atoms in our case) and \( \mathbf{G}_{SR} \) is the cross section for this relaxation mechanism, to be discussed below. The intrinsic amplitudes \( \mathbf{d} \) are given by the reduced matrix elements of \( J \), a tensor of rank 1:

\[
\langle j' || J || j \rangle = \langle j(j+1) \rangle^{3/2} (j',j).
\]

Next we shall consider the spin–spin or dipolar interaction. The Hamiltonian, in radians/second, can be written as

\[
H_{SS} = (\gamma^2 \hbar / b^2) \left[ (I_1 \cdot I_2 - 3) (I_1 \cdot n) (I_2 \cdot n) \right],
\]

where \( I_1, I_2 \) are the two nuclear spins, \( b \) is the vector distance separating them, and \( n \) is a unit vector in the direction of \( b, n = b / |b| \). We can rewrite this as

\[
H_{SS} = 2\gamma H'' \left[ (I_1 \cdot I_2 - 3) (I_1 \cdot n) (I_2 \cdot n) \right],
\]

where \( H'' \) is the spin–spin coupling constant with the value 33.86 G.

Under extreme narrowing and with the isotropic conditions, we can most easily write \( T_1 = T_2 = T \) as the isotropic average

\[
(T_{SS})^{-1} = \frac{3}{4} \left[ (T_{1SS})^{-1} + (2/T_{2SS}) \right].
\]

Defining the reduced spherical harmonics \( C_\ell(\theta, \phi) \) as

\[
C_\ell(\theta, \phi) = \left[ \frac{4\pi}{2\ell+1} \right]^{1/2} Y_\ell(\theta, \phi),
\]

we get

\[
(T_{SS})^{-1} = 8\gamma^3 H''^2 I(I+1) \Re \int_0^\infty \langle C_0(0) \cdot C_\ell(t) \rangle dt,
\]

where \( C_0 \cdot C_\ell \) is the scalar product of the reduced spherical harmonics, considered as tensor operators of rank 2, defined by

\[
C_\ell(0) \cdot C_\ell(t) = \sum_{q=2}^\infty (-1)^q C_\ell^*(q) C_\ell^{-q}(t).
\]

Here, then, we are concerned with the spectral density at zero frequency of the correlation function for the reduced spherical harmonics. In terms of the appropriate cross sections we have

\[
(T_{SS})^{-1} = \left[ 8\gamma^3 H''^2 I(I+1) / n(\psi) \right] \mathbf{d} \cdot (\mathbf{G}_{SS})^{-1} \cdot \mathbf{d}.
\]

The intrinsic amplitudes \( \mathbf{d} \) are the diagonal reduced
Experimental form of the cross section as of the corresponding operator: for spin-rotation, the MSV(GH)1
\[ 10.74 \text{ } 0.262 \text{ } 0.105 \]
MSV(GH)2
\[ 10.74 \text{ } 0.262 \text{ } 0.125 \]
MSV(GH)3
\[ 10.74 \text{ } 0.282 \text{ } 0.105 \]

\[ \text{Experimental}\]
\[ 68 \]

\[ * \text{Reference 14.} \]

Matrix elements of \( C_k \):
\[ \langle j' || C_k || j \rangle = (-1)^j [[(2j+1)!]^2 \left( \begin{array}{ccc} j' & k & j \\ 0 & 0 & 0 \end{array} \right) (48) \]

We only need the diagonal reduced matrix elements, which can be seen from the following considerations: The dipolar relaxation and rotational Raman spectrum are both determined by the correlation function of the spherical harmonics. The dipolar relaxation time is obtained in the extreme narrowing limit by evaluating the spectral density at zero frequency; this corresponds to the center of the \( Q \) branch in the Raman spectrum. Only using the diagonal reduced matrix elements \( \omega_0 = 0 \) corresponds to assuming that the \( O \) and \( S \) branches do not overlap the \( Q \) branch. In Part C of this section we demonstrate this to be a valid assumption at all gas densities, due to the small linewidth relative to the separation of the various branches.

The diagonal elements are, upon evaluating Eq. (48) with \( k=2 \),
\[ \langle j || C_2 || j \rangle = [-j(j+1)/(2j-1)(2j+3)]^{1/2} \]

The appropriate cross sections \( \sigma_{SR}, \sigma_{SR} \) appearing in Eqs. (43) and (47) differ only in the tensor character of the corresponding operator: for spin–rotation, the tensor character is \( k=1 \), for spin–spinning coupling the tensor character is \( k=2 \). We can write the detailed form of the cross section as
\[ \sigma^k(j',j;j,j) = (\pi/k^2) \sum_{J_a,J_B,I_a,l} [(2J_a+1)/(2j+1)]^{1/2} \]
\[ \times (2J_a+1)(2J_B+1) \left( \begin{array}{ccc} j' & k & j \\ J_B & l' & J_a \end{array} \right) \left[ \begin{array}{ccc} j & k & j \\ J_B & l & J_a \end{array} \right] \]
\[ \times \delta(j',j)\delta(l',l) - S^kS^k(j',j;j,j) \]

\[ (49) \]

Note that we have suppressed the Greek indices on the rotational \( j \)'s since the spectroscopic states are \( j_a=j_B, j_a'=j_B' \). (The actual spectroscopy in this case takes place among the spin levels.) Consequently the \( S \) and \( S^k \) matrices are evaluated at the same total energies. These cross sections are real, since for every term \( S^kS^k(j',j;j,j) \) there appears its complex conjugate \( S^kS^k(j',j;j,j) \). Thus, after performing the sum over the total angular momenta, the phase dependence of the cross section disappears.

The most important terms are the diagonal ones \( \sigma^k(j,j;j,j) \), which describe elastic, reorientation collisions within a \( j \) manifold. Changes in the orbital angular momentum \( l \) can be related to changes in the magnetic quantum number \( m \) in the uncoupled representation. There is a nonvanishing contribution to the cross section, in general, from the diagonal \( S \) matrix elements but one can easily show that if the \( S \) matrix is calculated from a spherically symmetric potential, then the cross section vanishes, by the following argument: For a spherically symmetric potential, the \( S \) matrix is diagonal and for a given \( j, l \) is independent of \( J \). This is because the interaction potential \( V_{G,Y'} \) of (32) contains no \( J \) dependence for a spherically symmetric potential. As a result the \( S \) matrix can be written as
\[ S^k(j',j;j,l) = S(j,l)\delta(j,j)\delta(l,l). \]

Since the \( S \) matrix is unitary we get zero for the cross section in Eq. (49). \( T_1 \) has been calculated for the three MSV potentials discussed in Sec. III at room temperature (298°K). Since the \( j=3 \) rotational level in the orthohydrogen is significantly populated at this temperature (11%) we have included it explicitly in our calculations. The sigma matrix then has the following form:
\[ \sigma^k(11;11) \quad \sigma^k(11;33) \]
\[ \sigma^k(33;11) \quad \sigma^k(33;33). \]

The diagonal elements describe elastic, reorientation collisions in the \( j=1 \) and \( j=3 \) levels. The off-diagonal elements describe the coupling of the two rotational levels by inelastic collisions. As in the case of rotational relaxation, where the tensor character of the cross section is 0, the off-diagonal elements are related by detailed balance. This is true because detailed balance is a result of the symmetry of the \( S \) matrix and this symmetry is unaffected by the tensor character of the cross section for spin–lattice relaxation.

The relaxation times were calculated by direct inversion of the \( 2X2 \) sigma matrices. Table V presents the results at 298°K for the three potentials we have studied, along with the experimental results extrapolated to infinite dilution. The interpretation of these results can be facilitated by considering that \( T_1 \) is directly proportional to the cross section, neglecting the small effect of the off-diagonal elements which varied in magnitude from 5 to 100 times smaller than the diagonal elements. The explicit effect of the off-diagonal elements will be discussed later.

Table VI shows \( \sigma(11;11) \) and \( \sigma(33;33) \) at 298°K.
for the three potentials, for \( k = 1 \) and \( k = 2 \). Characteristic of all potentials is the fact that, for \( k = 1 \), the reorientation cross section is greater in the \( j = 1 \) manifold than in the \( j = 3 \) manifold. This means that relaxation due to spin–rotation occurs faster in the upper level than in the lower level. The same does not always hold for the potentials in the \( k = 2 \) case.

Comparison of the results for the three MSV(GH) potentials shows that the reorientation cross sections are more sensitive to the repulsive anisotropy than the attractive anisotropy. We expect, however, the cross sections to become more sensitive to the attractive anisotropy at lower temperatures. This behavior is discussed below.

We have investigated the temperature dependence of the relaxation time for the best-fit potential, MSV(GH)1, by calculating \( T_1 \) at four other temperatures below 298\(^\circ\)K: 200, 125, 77, and 20\(^\circ\)K. For the 20\(^\circ\)K calculation the full 2\( \times \)2 sigma matrix was calculated, but at the three lower temperatures only \( \sigma^k(11; 11) \) was calculated. This can be justified because the population of the \( j = 3 \) level is less than 0.3% at 125\(^\circ\)K. In the computation of the \( S \) matrices, the basis set included the \( j = 1 \) and \( j = 3 \) levels for all temperatures except 20\(^\circ\)K, where only the \( j = 1 \) state was included. At all of the energies needed for the energy average quadrature at 77 and 125\(^\circ\)K the \( j = 3 \) channels were asymptotically closed. To determine the effect of these closed channels, the calculation at 125\(^\circ\)K was repeated using only \( j = 1 \) in the basis set. The resulting cross sections were approximately 1% higher than in the calculation using the larger basis.

In Table VII we represent the results for \( T_1/n \) at the various temperatures along with the experimental results extrapolated to infinite dilution. These results are plotted in Fig. 7. Note that at 20\(^\circ\)K we report the value for \( T_1/n \) determined by Riehl.\(^\text{35}\) This is significantly different from that determined by Bloom\(^\text{27}\) at the same temperature: \( \approx 50 \mu \text{sec/amagat} \). The larger value suggests a minimum in the \( T_1 \) versus temperature curve, whereas the lower value gives no such indication. Our calculations on MSV(GH)1 agree with the lower value. The potential derived by Riehl \( et \ al.\)\(^\text{14}\) fits their experimental results and also predicts a minimum in the \( T_1 \) versus temperature curve, as does the Foster–Rugheimer\(^\text{26}\) potential obtained by refitting the Riehl \( et \ al.\) data by more accurate calculations. One thing in common with both of these potentials is that they both have large long-range anisotropies, 0.279 and 0.190, respectively. The theoretical value is 0.105 (see Sec. III). At high temperatures the short-range anisotropy will dominate the scattering, while at low temperatures it is the long-range anisotropy that becomes more important. At intermediate temperatures the cross sections and \( T_1 \) may have a minimum due to the cancellation of the two anisotropies. The large values for \( \alpha_{LR} \) in these potentials overestimate the low-temperature, slow collisions and thus predict a minimum at a relatively high temperature: Lalita and Bloom\(^\text{18}\) predict a minimum in \( T_1 \) versus temperature at about 70\(^\circ\)K for the Riehl \( et \ al.\) potential. Assuming the more recent, lower value for \( T_1 \) at 20\(^\circ\)K to be correct, the \( T_1 \) versus temperature curve does not show a minimum in agreement with our calculations, although it may be that it occurs at very low temperatures, below 20\(^\circ\)K.

In Fig. 8 we show the variation of \( \sigma^k(11; 11) \) for MSV(GH)1 with initial relative kinetic energy for both \( k = 1 \) and \( k = 2 \). Figure 9 shows the same for \( \sigma^k(33; 33) \). None of these plots shows a minimum. If there is a minimum it must occur below a relative energy of 4 cm\(^{-1}\) for \( \sigma^k(11; 11) \).

It is interesting to note that in the \( j = 1 \) manifold, the spin–rotation \( (k = 1) \) reorientation cross section is always greater than the spin–spin cross section \( (k = 2) \), while in the \( j = 3 \) manifold just the opposite occurs, for the MSV(GH)1 potential. Since the total relaxation time \( T_1 \) is written as

\[
T_1^{-1} = (T_{SR})^{-1} + (T_{SS})^{-1},
\]

the smaller the appropriate cross section, the larger the effect on \( T_1 \). Thus, for the MSV(GH)1 potential we

### Table VI. Reorientation cross section at \( T = 298^\circ \)K in square angstroms.

<table>
<thead>
<tr>
<th>Potential</th>
<th>( \epsilon ) (cm(^{-1}))</th>
<th>( \alpha_{SR} )</th>
<th>( \alpha_{LR} )</th>
<th>( k = 1 ) ( (\sigma(11; 11)) )</th>
<th>( k = 1 ) ( (\sigma(33; 33)) )</th>
<th>( k = 2 ) ( (\sigma(11; 11)) )</th>
<th>( k = 2 ) ( (\sigma(33; 33)) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSV(GH)1</td>
<td>10.74</td>
<td>0.262</td>
<td>0.105</td>
<td>0.710</td>
<td>0.175</td>
<td>0.430</td>
<td>0.334</td>
</tr>
<tr>
<td>MSV(GH)2</td>
<td>10.74</td>
<td>0.262</td>
<td>0.125</td>
<td>0.706</td>
<td>0.175</td>
<td>0.427</td>
<td>0.333</td>
</tr>
<tr>
<td>MSV(GH)3</td>
<td>10.74</td>
<td>0.282</td>
<td>0.105</td>
<td>0.819</td>
<td>0.202</td>
<td>0.495</td>
<td>0.387</td>
</tr>
</tbody>
</table>

### Table VII. \( T_1/n \) for potential MSV(GH)1.

<table>
<thead>
<tr>
<th>Temperature ((^\circ)K)</th>
<th>( T_1/n ) calc (( \mu \text{sec/amagat} ))</th>
<th>( T_1/n ) expvl (( \mu \text{sec/amagat} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>71.1</td>
<td>68.0a</td>
</tr>
<tr>
<td>200</td>
<td>55.6</td>
<td>49.7a</td>
</tr>
<tr>
<td>125</td>
<td>36.0</td>
<td>27.7a</td>
</tr>
<tr>
<td>77</td>
<td>19.9</td>
<td>19.0a</td>
</tr>
<tr>
<td>20</td>
<td>4.0</td>
<td>2.5b</td>
</tr>
</tbody>
</table>

\(^a\) From Ref. 14.

\(^b\) From Ref. 35.
can conclude that at low temperatures, where the $j=1$ manifold is the only one significantly populated, the relaxation will be dominated by the spin–spin coupling. Then as the temperature increases, making the $j=3$ level more important, we expect the spin–rotation interaction to become more and more important. Another factor that increases the relative importance of the spin–rotation interaction at higher temperatures is the weighting of the cross sections determined by the intrinsic amplitudes $d$. Considering only the diagonal elements, Eq. (44) shows that the $j$th rotational state is weighted by the factor

$$d_j^2 = j(j+1)$$

for the spin–rotation while from Eq. (48') we get the factor

$$d_j^2 = j(j+1)/(2j-1)(2j+3).$$

Clearly for a given $j$, $d_j^2(SR)$ is greater than $d_j^2(SS)$ and also, as $j$ increases, $d_j^2(SR)$ increases while $d_j^2(SS)$ decreases. Thus at higher temperatures, the spin–rotation interaction is more and more heavily weighted than the dipolar coupling interaction.

In order to examine closely the relative effects of the long- and short-range anisotropies we have calculated $T_1$ at $20^\circ$K for four different MSV(GH) potentials, the three discussed throughout our calculations and a fourth described below in Table VIII. As men-
SPECTRAL LINE SHAPES IN H₂–He

TABLE VIII. Relaxation times and reorientation cross sections at 20°K.

<table>
<thead>
<tr>
<th>Potential</th>
<th>( \alpha_{SR} )</th>
<th>( \alpha_{LR} )</th>
<th>( T_{1/n} ) ( \mu \text{sec/amagat} )</th>
<th>( k=1 ) ( \langle \sigma(11;11) \rangle ) ( \text{Å}^2 )</th>
<th>( k=2 ) ( \langle \sigma(11;11) \rangle ) ( \text{Å}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSV(GH)1</td>
<td>0.262</td>
<td>0.105</td>
<td>4.01</td>
<td>0.0823</td>
<td>0.0669</td>
</tr>
<tr>
<td>MSV(GH)2</td>
<td>0.262</td>
<td>0.125</td>
<td>3.75</td>
<td>0.0769</td>
<td>0.0625</td>
</tr>
<tr>
<td>MSV(GH)3</td>
<td>0.282</td>
<td>0.105</td>
<td>4.75</td>
<td>0.0948</td>
<td>0.0793</td>
</tr>
<tr>
<td>MSV(GH)4</td>
<td>0.262</td>
<td>0.085</td>
<td>4.34</td>
<td>0.0889</td>
<td>0.0724</td>
</tr>
</tbody>
</table>

As mentioned earlier, the necessary \( S \) matrices were computed from a basis set that included \( j=1 \) only at this temperature. The results are given in Table VIII.

Here we see that, as the long-range anisotropy increases, the reorientation cross sections and \( T_1 \) decrease. As the short-range anisotropy increases, the cross sections and \( T_1 \) increase. Here we clearly see the cancelling effect of the two anisotropies. For the long-range anisotropy to dominate, it would appear necessary to go to extremely low temperatures.

As mentioned earlier, the off-diagonal elements of the sigma matrix are quite small and we give below, as an example, the complete sigma matrix for the MSV(GH)1 potential at 298°K. With all cross sections in square angstroms, we have for spin–rotation

\[
\langle \sigma^{km}(11;11) \rangle \quad \langle \sigma^{ml}(33;11) \rangle \\
0.710 \quad -0.0617 \\
\langle \sigma^{km}(33;11) \rangle \quad \langle \sigma^{ml}(33;33) \rangle \\
-0.0076 \quad 0.175
\]

For spin–spin coupling, we get

\[
\langle \sigma^{km}(11;11) \rangle \quad \langle \sigma^{ml}(33;33) \rangle \\
0.430 \quad -0.0388 \\
\langle \sigma^{km}(33;11) \rangle \quad \langle \sigma^{ml}(33;33) \rangle \\
-0.0048 \quad 0.334
\]

We have calculated \( T_1 \) for this potential at 298°K, setting the off-diagonal elements of the sigma matrix to zero and found that \( T_1 \) as a result increased by 4%.

C. Raman Line Shapes

1. Introduction

When a molecule is exposed to electromagnetic radiation at a frequency far from any absorption band the radiation, or photons, can be elastically or inelastically scattered. Elastic scattering gives rise to the Rayleigh spectrum and inelastic scattering produces the Raman spectrum. The difference in energy of the incident and scattered photon results from changes in the internal energy of the irradiated molecule. The intensity of the scattered radiation depends on the polarizability of the molecule, not on the dipole moment as in absorption spectroscopy.

The shape of the spectral line is determined by the interactions of the radiating molecule with its surroundings. Thus a study of the Raman line shapes arising from H₂ diluted in He will yield information concerning the intermolecular potential for this system. In what follows, we will examine the pure rotational Raman spectrum, in which case the Rayleigh scattering is referred to as the \( Q \) branch, and the \( S \) and \( O \) branches arise when the molecule undergoes a transition \( j\rightarrow j+2 \) and \( j\rightarrow j-2 \), respectively.

2. Correlation Function Formulation of Line Shapes

Let \( \alpha \) be the molecular polarizability, considered constant in a coordinate system rotating with the molecule. The polarizability is, in general, a tensor and can be decomposed into two terms, a spherical one and a traceless, anisotropic one, as

\[
\alpha = \begin{pmatrix} \frac{1}{3} \text{Tr} \alpha \end{pmatrix} \mathbb{I} + \beta, \\
\text{Tr} \beta = 0.
\]

Here \( \mathbb{I} \) is the unit matrix. The depolarized spectrum \( I(\omega) \), the intensity distribution of scattered radiation at right angles to the incident radiation, can be written in terms of the spectral density of the correlation function of the anisotropic part \( \beta \) of the polarizability:

\[
I(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} \langle \text{Tr} \beta(0) \cdot \beta(t) \rangle e^{i\omega t} dt,
\]

where \( \omega = \omega_0 - \omega_s \), the difference between incident and scattered frequencies, which is positive for the \( S \) branch. Usually we are interested in the normalized spectrum \( \tilde{I}(\omega) \) which we can write as

\[
\tilde{I}(\omega) = \pi^{-1} \text{Re} \int_{0}^{\infty} \tilde{C}(t) e^{i\omega t} dt,
\]

where \( \tilde{C}(t) \) is the normalized correlation function defined as

\[
\tilde{C}(t) = \langle \text{Tr} \beta(0) \cdot \beta(t) \rangle / \langle \text{Tr} \beta(0) \cdot \beta(0) \rangle.
\]

Gordon has shown that, for a diatomic molecule, \( \tilde{C}(t) \) is the same correlation function that determines the nuclear spin–spin coupling relaxation time in NMR, i.e., the correlation function of the spherical harmonics:

\[
\tilde{C}(t) = \langle C_4(0) \cdot C_4(t) \rangle / \langle C_4(0) \cdot C_4(0) \rangle,
\]

(50)
where \( C^g \) is the normalized spherical harmonic defined in Eq. (45).

We can write \( I(\omega) \) in terms of the expression for the spectral density developed in Sec. II, namely,

\[
I(\omega) = \frac{1}{\Delta} \text{Im} \cdot (\omega - \omega_0 - i\gamma) (\sigma^{RB})^{-1} \cdot \mathbf{P} \cdot \mathbf{d}
\]

with the normalization

\[
\mathbf{d} \cdot \mathbf{P} \cdot \mathbf{d} = 1.
\]

Here \( \omega_0 \) is a diagonal matrix of Raman frequencies of the free molecule and \( \sigma^{RB} \) is the cross section appropriate to Raman scattering and will be discussed in detail below. The (unnormalized) line amplitudes are the reduced matrix elements of the spherical harmonics and are given in Eq. (48).

These are the same as those used for the spin–spin coupling relaxation times with the difference that here we need the off-diagonal elements (S branch) as well as the diagonal elements (Q branch). Direct calculation of the matrix elements gives

\[
\langle j || C_2 || j+2 \rangle = \frac{\text{[ch}(j+1)/(2j+3)]^{1/2}}{k_{j_2} \cdot \Delta_{J_2}} \sum_{J_2, l_2} \left[ \frac{2j_a'+1}{2j_a+1} \right]^{1/2} \times (2J_a+1) (2J_{l_2}+1) \left[ \begin{array}{cc} j_a' & 2 \\ J_{l_2} & J_a \end{array} \right] \left[ \begin{array}{cc} j_a & 2 \\ J_2 & J_{l_2} \end{array} \right] \left[ \begin{array}{cc} j_b' & j_b \\ J_{l_2} & J_b \end{array} \right] \delta(j', l_2) \delta(l, l_2) - S^{RB}(E_0)(j_b', j_b; j_a, j_a) \times S^{Sa}(E_0)(j_a, l; j_a, l). \]

We have explicitly indicated that \( S^* \) and \( S \) are evaluated at different total energies so that the relative kinetic energy before collision is the same for scattering in the two spectroscopic states. Although this is the appropriate form for \( k=2 \), the following discussion of general properties of the line shape cross section will also hold for dipole spectra characterized by a tensor character \( k=1 \).

For well-resolved or isolated lines, all that is needed are the diagonal elements \( \sigma^{RB}(j_a, j_b; j_a, j_b) \). We shall first consider what happens when the intermolecular potential is spherically symmetric. In this case, no inelastic or reorientation collisions occur, and \( S \) is diagonal in the coupled representation and independent of the total angular momentum \( J \). With these restraints and unitarity, we can write

\[
S^{Sa}(E_0)(j_a, l; j_a, l) = \exp(2i\delta_a),
\]

where \( \delta_a \) is the elastic phase shift and the cross section amplitude for the \( j=3 \) manifold as a function of initial relative kinetic energy.
takes on the form

\[ \sigma^{RS}(j_a, j_b; j_a, j_b) = \left( \frac{\pi}{k^2} \right) \sum_{J_a J_b J} (2J_a + 1)(2J_b + 1) \]

\[ \times \left[ \begin{array}{c} j_a \ k \ j_b \\ J_b \ l \ J_a \end{array} \right]^2 \left[ 1 - \exp i(\delta_a - \delta_b) \right]. \] (55)

We note immediately that if the phase shifts are the same in both spectroscopic states, then the cross section is zero and the line has no width or shift. If the potentials are different for scattering in the two spectroscopic states, thereby giving rise to different phase shifts, then the width is determined by the real part of Eq. (55):

\[ \text{Re} \sigma^{RS}(j_a, j_b; j_a, j_b) = \left( \frac{\pi}{k^2} \right) \sum_{J_a J_b J} (2J_a + 1)(2J_b + 1) \]

\[ \times \left[ \begin{array}{c} j_a \ k \ j_b \\ J_b \ l \ J_a \end{array} \right]^2 \left[ 1 - \cos(2\delta_a) \right] \] (55a)

and the shift by the imaginary part:

\[ \text{Im} \sigma^{RS}(j_a, j_b; j_a, j_b) = -\left( \frac{\pi}{k^2} \right) \sum_{J_a J_b J} (2J_a + 1) \]

\[ \times (2J_b + 1) \left[ \begin{array}{c} j_a \ k \ j_b \\ J_b \ l \ J_a \end{array} \right]^2 \sin(2\delta_a), \] (55b)

where \( \delta_a \) is the relative phase shift for the two spectroscopic states, defined by

\[ \delta_a = \delta_c - \delta_a. \]

Equations (55a) and (55b) are the quantum mechanical version of the semiclassical, adiabatic theories of Lindholm and of Foley for dipole spectra.

In the presence of a nonspherical potential, we have the effects of inelastic and reorientation collisions as well as the effects of elastic phase shifts. The width is then determined by

\[ \text{Re} \sigma^{RS}(j_a, j_b; j_a, j_b) = \left( \frac{\pi}{k^2} \right) \sum_{J_a J_b J} (2J_a + 1)(2J_b + 1) \]

\[ \times \left[ \begin{array}{c} j_a \ k \ j_b \\ J_b \ l \ J_a \end{array} \right]^2 \left[ 1 - \exp i(\delta_a - \delta_b) \right]. \] (55a)

\[ \text{Im} \sigma^{RS}(j_a, j_b; j_a, j_b) = -\left( \frac{\pi}{k^2} \right) \sum_{J_a J_b J} (2J_a + 1) \]

\[ \times (2J_b + 1) \left[ \begin{array}{c} j_a \ k \ j_b \\ J_b \ l \ J_a \end{array} \right]^2 \sin(2\delta_a), \] (55b)

These equations are the quantum mechanical generalization of the semiclassical theory of Anderson and the classical theory of Gordon, both of which include the effects of inelastic collisions.

As the lines are all well resolved at pressures of interest to us (see below), we will not need the off-diagonal elements of the cross section for the S branch. In the Q branch, however, the spectroscopic states are the same for a given line and all rotational states give rise to lines at zero frequency. Hence the Q branch consists of several lines that overlap completely and so we will need the off-diagonal elements of the cross section, which have the form

\[ \sigma^{RS}(j', j'; j, j) = \left( \frac{\pi}{k^2} \right) \sum_{J_a J_b J} (2J_a + 1)(2J_b + 1) \]

\[ \times \left[ (2J' + 1)(2J + 1) \right]^{1/2} \left[ \begin{array}{c} j' \ 2 \ j' \\ J_b \ l' \ J_a \end{array} \right] \left[ \begin{array}{c} j \ 2 \ j \\ J_b \ l \ J_a \end{array} \right] \]

\[ \times [\delta(j', j)S(j', j; j, j) - S^{*}(j', j; j, j)S^{*}(j', j; j, j)]. \] (58)
Note that this is identical to the spin–spin coupling cross section [Eq. (49)] for NMR relaxation times. The S matrices above are evaluated now at the same total energies since \( j_a = j_b = j \). Consequently, the imaginary part vanishes and there is no shift. Since all rotational states of the molecule radiate at the same frequency, inelastic collisions do not interrupt the radiation and thus do not affect the linewidth for individual lines. Thus, the Q branch linewidth is mainly determined by reorientation collisions.

It is easy to show that the pure rotational Raman spectrum of \( \text{H}_2 \) consists of well-separated lines in the \( S \) branch. Consider the \( S_0(0) \) line, where the subscript describes the final vibrational state and the number in parentheses refers to the \( j \) value of the initial rotational state in the spectroscopic transition. Thus \( S_0(0) \) refers to the pure rotational transition \( j = 0 \rightarrow j = 2 \) in the ground vibrational state. A molecule in the \( j = 0 \) level can suffer a rotationally inelastic collision to the \( j = 2 \) level and then give rise to the \( S_0(2) \) line. Denoting the energy of the rotational level specified by \( j \) as

\[
E_j = j(j+1)B,
\]

where \( B \) is the rotational constant (we have used \( B = 60.99 \text{ cm}^{-1} \)), then the \( S_0(0) \) line occurs at a frequency of \( 6B \), assuming the Q branch to occur at zero frequency. The \( S_0(2) \) line appears at a frequency of \( 14B \), \( 8B \) higher than the \( S_0(0) \) line. At room temperature, the experimental width of the \( S_0(0) \) line is \( 1.75 \times 10^{-3} \text{ cm}^{-1} \text{/amagat} \). Thus, the two lines are well separated at all but the highest pressures. Similarly, the \( S_0(1) \) line occurs at a frequency of \( 4B \) above the \( S_0(0) \) line and has a similar width. The Q branch has an experimental width, resulting from the superposition of all the lines in the Q branch, of \( 2.6 \times 10^{-3} \text{ cm}^{-1} \text{/amagat} \), and consequently is well separated from the lines of the S branch. Since collisions that change \( j \) by 1 are not allowed in homonuclear diatomics, amplitude cannot be transferred from the \( S_0(0) \) line to the \( S_0(1) \) line by collisions.

We have calculated the line shape for the \( S_0(0) \) and \( S_0(1) \) lines for \( \text{H}_2 \) diluted in \( \text{He} \). As they are well separated, each one can be treated independently and the cross section reduces to a single, complex number in each case. First we will discuss the linewidths (full width at half-height). They have been calculated for the three potentials we have studied earlier. The relevant formula giving the linewidth in terms of the cross section [see Eq. (22)] for the transition \( j_a \rightarrow j_b \) is

\[
\Delta\omega_{12}/\pi = 2\langle e \rangle \left| \sigma_{\text{ee}}(j_a, j_b; j_a, j_b) \right|,
\]

where \( n \) is the gas density. Table IX presents the results for the three potentials along with the experimental results for both lines. Both lines were originally measured in Ref. 19 but the \( S_0(1) \) line has been re-measured recently in a more precise experiment. The earlier experiments were done on a mixture of \( \text{He} \) and \( \text{H}_2 \) in a ratio of 4:1 while the more recent measurement was done on a mixture of \( \text{He} \) and \( \text{H}_2 \) in a ratio of 10:1. The two measurements disagree considerably for the widths of the \( S_0(1) \) line: \( 2.5 \times 10^{-3} \text{ cm}^{-1} \text{/amagat} \) and \( 1.75 \times 10^{-3} \text{ cm}^{-1} \text{/amagat} \). Thus, with only the older measurement for the \( S_0(0) \) line, it is difficult to make quantitative comparisons. The magnitude of the cross section produced by MSV(GH) is in good agreement with the recent measurement for the \( S_0(1) \) line:

\[
\frac{\sigma_{\text{ex}} - \sigma_{\text{cal}}}{\sigma_{\text{ex}}} = +6\%
\]

but agreement with the older measurement for the \( S_0(0) \) line is considerably poorer:

\[
\frac{\sigma_{\text{ex}} - \sigma_{\text{cal}}}{\sigma_{\text{ex}}} = -17\%.
\]

Until a more precise experiment is done for this line it will be difficult to analyze the source of this discrepancy. Again we see that the cross sections are most sensitive to the short-range anisotropy. Since energetically inelastic collisions are infrequent, the principal effect of \( \sigma_{\text{ab}} \) is to produce reorientation collisions (\( \Delta m \) changes in the uncoupled representation).

The imaginary part of the cross section, which determines the Raman line shift, converges much more slowly in the sum over total angular momentum. It was found typically that for an imaginary cross section on the order of \( 10^{-1} \text{ A}^2 \), convergence to one part in \( 10^4 \) required summing up to total angular momentum values as high as 100 for the energies needed in the energy-average quadrature at room temperature. For large \( J \) values, the S matrix is diagonal and the phase shifts are small, making a Born approximation calculation appropriate. Thus, for low \( J \) we used the close-coupling results and for high \( J \) we used the Born approximation. For details of this calculation, see Ref. 29. At the highest relative kinetic energy before collision (1100 \text{ cm}^{-1} \), the matching region occurred at values of \( J \) around 38–40 and at the lowest relative kinetic energy (60 \text{ cm}^{-1} \) the matching region was around 14–16. Typical values of the imaginary part of the diagonal S matrix elements varied from 0.05 to 0.2 in the matching regions. Agreement between the close-coupling and Born calculations varied from 1%–3% over a range of 4 or 5 \( J \) values at the lowest energies to 0.5%–1% over a range of 10–12 \( J \) values at the higher energies. The resulting cross sections which are given by the difference of two numbers, each of similar magnitude, agreed to within 3%–10%. The magnitude of the cross sections at and beyond the matching points was usually small but the sign would change frequently with \( J \).

In our study of the line shift results, we will concentrate on the \( S_0(1) \) line which has been recently re-measured. The discrepancy between the older and more recent measurements of the shift for this line is about 40%. If one assumes that a measurement of the \( S_0(0) \) line would produce a similar discrepancy compared to the only one we have now, it is difficult to...
discuss quantitative comparison between theory and experiment for the line shift of $S_0(0)$. The line shifts are very sensitive to the difference in the elastic scattering in the two spectroscopic states. Preliminary calculations of the line shifts were done using the same $V_0(R)$ and $V_3(R)$ to determine the scattering in the two states. These calculations yielded the linewidth cross sections presented in Table IX. The line shifts were in poor agreement with experiment: MSV(GH)1 produced a line shift of correct sign but less than 65% in magnitude. In treating the radial dependence as the same for the scattering in the two spectroscopic states, the only difference comes from the matrix elements of $P_2(\cos\theta)$ in the anisotropic terms of the potential.

The most probable source of the discrepancy is the neglect of vibration and vibration–rotation interaction inherent in the rigid rotor approximation. Centrifugal distortion due to the rotation of the molecule results in a larger effective bond length the higher the rotational state of the molecule. This will create a $j$ dependence in the radial potential. It is not yet possible to determine directly the vibration–rotation effect on the $\text{H}_2$--He intermolecular potential but we can estimate it indirectly. From measurements on normal and para-hydrogen, Hermans et al. have found orthohydrogen to have a static polarizability 0.2% larger than that of parahydrogen. They also found the second virial coefficient to be $1\pm0.2\%$ larger in normal hydrogen than in para, in good agreement with work done by Beenakker et al. Since we have found the cross sections to be much more sensitive to short-range effects than to long-range effects, we concentrate on the second virial coefficient. Following Hirschfelder, Curtiss, and Bird, we can write the second virial coefficient $B$ for a Lennard-Jones 12–6 potential at high temperatures $T$ as

$$B\sim\sigma^2(\epsilon/T)^{1/4}+O(T^{-3/4}),$$

where $V(\sigma)=0$ and $\epsilon$ is the well depth. From this we can see that a 1% difference in $B$ can be explained by a 0.33% difference in $\sigma$. By the usual combining rules, $\sigma_2=\frac{1}{2}(\sigma_{12}+\sigma_{22})$, this would result in a difference of 0.16% in $\sigma$ for $\text{H}_2$–He. We can expect the stretching to get larger as the molecule is excited to higher rotational states and the difference in effective bond lengths to be greater between the $j=1$ and $j=3$ levels than between the $j=0$ and $j=2$ levels.

There are several possible ways to take such effects into account in calculating the $S$ matrices. One could include several vibrational levels in the basis set but this would make the calculation more complicated and longer. Also, we do not really have enough information on how the potential depends on the vibrational states. In this work we have included the vibration–rotation effect by increasing the $R_m$ value in the MSV potential for the upper spectroscopic state as suggested by the virial coefficient discussion above, giving rise to different radial potentials for the two states. The $S$ matrices are calculated independently for the two states, thus neglecting the effect of the larger $R_m$ in the upper state potential on the lower state. As we only need the elastic $S$ matrix elements for each state to compute the line shifts, this coupling effect can be expected to be small. Now the difference in scattering is not solely due to the matrix elements of $P_2(\cos\theta)$ but also due to differences in $V_0(R)$ and $V_3(R)$, which depend exponentially on $R_m$ for the MSV potentials.

Our results, summarized in Table X, show the Raman $S_0(1)$ line shift cross sections $\langle\sigma_{im}(13;13)\rangle$ to be very sensitive to changes in $R_m$ in the upper state. Trial 1 shows the effect of different $R_m$'s when the potentials are spherically symmetric. Since no inelastic or reorientation collisions occur in this case, we obtain a small linewidth $\langle\sigma_{im}(13;13)\rangle$. A significant shift is produced, however, since this is sensitive to differences in elastic scattering in the two spectroscopic states. Trials 2 and 3 show the combined effect of different $R_m$'s and anisotropic potentials and Trial 4 the effect of anisotropy alone. Changing $R_m$ by the same amount in both states produces little change, as Trial 5 indicates. Finally, best agreement with experiment is obtained in Trial 6, where the difference in $R_m$'s is only 0.0013 Å. One could continue decreasing this difference until exact agreement with experiment is obtained. The

<table>
<thead>
<tr>
<th>Trial</th>
<th>$R_m$ Lower state (Å)</th>
<th>$R_m$ Upper state (Å)</th>
<th>Anisotropy</th>
<th>$\langle\sigma_{im}(13;13)\rangle$ (Å²)</th>
<th>$\langle\sigma_{im}(13;13)\rangle$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.3815</td>
<td>3.3836</td>
<td>None</td>
<td>1.14 × 10^{-3}</td>
<td>-0.254</td>
</tr>
<tr>
<td>2</td>
<td>3.3815</td>
<td>3.3836</td>
<td>MSV(GH)1</td>
<td>0.271</td>
<td>-0.477</td>
</tr>
<tr>
<td>3</td>
<td>3.3815</td>
<td>3.3857</td>
<td>MSV(GH)1</td>
<td>0.279</td>
<td>-0.736</td>
</tr>
<tr>
<td>4</td>
<td>3.3815</td>
<td>3.3815</td>
<td>MSV(GH)1</td>
<td>0.263</td>
<td>-0.207</td>
</tr>
<tr>
<td>5</td>
<td>3.4150</td>
<td>3.4150</td>
<td>MSV(GH)1</td>
<td>0.273</td>
<td>-0.209</td>
</tr>
<tr>
<td>6</td>
<td>3.3815</td>
<td>3.3828</td>
<td>MSV(GH)1</td>
<td>0.269</td>
<td>-0.381</td>
</tr>
</tbody>
</table>

*Reference 20.*
nature of the model, however, does not warrant such efforts. We certainly cannot claim to have determined \( R_m \) to four figures; what is significant is that a difference of only \( \approx 0.001 \text{ \AA} \) in \( R_m \) is sufficient to almost double the shift cross section and produce satisfactory agreement with experiment.

We have done some calculations on the line shift for the \( S_0(0) \) line and they are presented in Table XI. Assuming the stretching effect to depend on \( j \) as \( j(j+1) \), the differences in \( R_m \) values for the upper and lower states of the \( S_0(1) \) and \( S_0(0) \) lines should stand in a ratio of 10:6. Evidence for this behavior is contained in LeRoy's results for \( \langle r \rangle \), the expectation value of the internuclear separation, in \( H_2 \) calculated from the relativistic, adiabatic potential of Ko\l os and Wolniewicz. Then we would predict a value of 3.3823 \( \text{\AA} \) for \( R_m \) in the \( j=2 \) state assuming \( R_m=3.3815 \) in the \( j=0 \) state. Linearly interpolating the cross sections, which should be reasonable from examining Table X, predicts the following cross sections for the \( S_0(0) \) line:

\[
\begin{align*}
\langle \sigma_{2m}(02;02) \rangle &= 0.349 \text{ \AA}^2, \\
\langle \sigma_{1m}(02;02) \rangle &= -0.382 \text{ \AA}^2.
\end{align*}
\]

The only experimental results for the width and shift cross sections are 0.290 and \(-0.148 \text{ \AA}^2\), respectively. Because of the uncertainty in these measurements mentioned earlier, meaningful comparison with experiment will have to await more precise measurements.

We have already shown that the \( Q \) branch of the pure rotational spectrum is well separated from the other branches and thus we need only consider spectroscopic transitions giving rise to the \( Q \) branch, i.e., zero-frequency transitions in which the initial and final spectroscopic states are the same. The diagonal matrix \( \omega_0 \) then contains zeroes everywhere. As mentioned earlier, each rotational level gives rise to a line at zero frequency and so the \( Q \) branch consists of several lines, arising from states with a significant population at any given temperature, superimposed on each other and centered on the same (zero) frequency since there are no line shifts. Rotationally inelastic collisions will transfer molecules from one rotational level to another, but, since all levels radiate at the same frequency, this will not interrupt the radiation process. The scattering due to the spherical part of the intermolecular potential is the same for the two spectroscopic states and so the only collisional effect on the individual line shapes will be one of reorientation due to the anisotropic part of the potential. Since reorientation effects are \( j \) dependent, there will be a coupling of lines within the \( Q \) branch by rotationally inelastic collisions, giving rise to off-diagonal cross section matrix elements of the form \( \sigma_{Rm}^\text{RQL} (jj';ij) \).

The similarity between the \( Q \) branch and the spin-spin coupling relaxation in NMR should be apparent: Both effects are related to the spectral density of the correlation function of second rank spherical harmonics and both produce real cross sections that measure reorientation within a \( j \) manifold as well as collisional coupling between the manifolds. One difference between the two effects is that the NMR relaxation time is determined by the spectral density at a particular frequency (zero in the extreme narrowing limit) while the \( Q \) branch requires the complete spectrum centered at zero. Another important difference is that the NMR relaxation is determined by the odd rotational states of the molecule only \((j=1, 3 \text{ at room temperature})\), while the \( Q \) branch depends on all rotational levels except the \( j=0 \) level \((j=1, 2, 3 \text{ at room temperature})\).

Experimentally, the \( Q \) branch consists of one single line resulting from the superposition of all the rotational lines. Thus the experimental width is not due to any single line but an effective width due to all the zero-frequency lines. We have calculated this effective width in the following manner: The line shape is given by

\[
\hat{I}(\omega) = \sigma^{-1} \text{Im} \cdot (\omega - in(\omega))^{-1} \cdot p \cdot d.
\]  

The line amplitudes are the diagonal matrix elements of the spherical harmonics [see Eq. (48')] and we now suppose the matrix \( M \) diagonalizes the matrix \( \langle \sigma \rangle \):

\[
M^{-1}(\sigma)M = Q,
\]

where \( Q \) is a diagonal matrix

\[
(Q)_{ij} = q \delta (ij).
\]

Then we can write \( \hat{I}(\omega) \) as

\[
\hat{I}(\omega) = \text{Im} \cdot M \cdot (\omega - in(\omega)Q)^{-1} \cdot M^{-1} \cdot p \cdot d.
\]
The effective cross section can be obtained from Eq. (22). We have computed the effective Q branch widths for all three potentials and the results are given in Table XII.

The normalized correlation function for the Q branch has the form

\[ \hat{C}(t) = d \cdot M^{-1} \cdot P \cdot d \]

with the normalization

\[ d \cdot P \cdot d = 1. \]

The normalized correlation function of the Q branch is given by

\[ \hat{C}(t) = d \cdot \exp(-n \langle \sigma \rangle t) \cdot M \cdot M^{-1} \cdot P \cdot d, \]

where \( X = d \cdot M, Y = M^{-1} \cdot P \cdot d \)

we have

\[ I(\omega) = \pi^{-1} \text{Im} \sum_j \left[ X_j Y_j / (\omega - i n_j) \right] \]

This is now just a weighted sum of Lorentzians centered at zero frequency. The effective width is then obtained by determining the width at half-height of the complete expression in Eq. (62). This then gives a full width at half-height as

\[ \Delta \omega_{1/2} = 2 \omega_{1/2} \]

where \( \omega_{1/2} \) is given by

\[ I(\omega_{1/2}) = I(0) / 2 \]

and an effective cross section can be obtained from Eq. (22).

We have explicitly calculated the correlation function for the potential MSV(GH) 1. Table XIII presents the diagonal sigma matrix elements, the eigenvalues \( \lambda_i \), the \( \lambda_j \) evaluated at room temperature and 1 amagat pressure, the corresponding relaxation times \( \tau_j \) and the weights \( w_j \). The sigma matrix elements for the rotational levels 1 and 3 are the same as those for the spin-spin coupling relaxation in NMR.

We can see that the off-diagonal elements have very little effect. The difference in the reorientation cross sections for different levels results in different relaxation times for each level. The weighting singles out the \( j = 1 \) rotational level as the predominant one. From Table XII the total, effective cross section for potential MSV(GH) 1 is 0.423 Å², very close to the value for just the \( j = 1 \) level (0.430 Å²). Thus we can conclude that at room temperature, the Q branch is essentially determined by the \( j = 1 \) level.

Figure 10 shows the correlation function \( \hat{C}(t) \) plotted against time, along with the three individual terms \( c_j(t) \) defined in Eq. (65), at 1 amagat pressure. Here again we see that the \( j = 1 \) level very much determines the relaxation for the whole set of levels. This implies that the total correlation function \( \hat{C}(t) \) behaves almost

<table>
<thead>
<tr>
<th>Potential</th>
<th>( \epsilon ) (cm(^{-1}))</th>
<th>( \alpha_{SR} )</th>
<th>( \alpha_{LR} )</th>
<th>Half-width at half-height (cm(^{-1})/amagat)</th>
<th>Effective cross section (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSV(GH) 1</td>
<td>10.74</td>
<td>0.262</td>
<td>0.105</td>
<td>1.31</td>
<td>0.423</td>
</tr>
<tr>
<td>MSV(GH) 2</td>
<td>10.74</td>
<td>0.262</td>
<td>0.125</td>
<td>1.30</td>
<td>0.420</td>
</tr>
<tr>
<td>MSV(GH) 3</td>
<td>10.74</td>
<td>0.282</td>
<td>0.105</td>
<td>1.51</td>
<td>0.488</td>
</tr>
<tr>
<td>Experiment*</td>
<td></td>
<td></td>
<td></td>
<td>1.30±0.07</td>
<td>0.42±0.02</td>
</tr>
</tbody>
</table>

* Reference 19 (experimental mixture of He and H₂ in ratio of 8.7:1).
Table XIV. Parameters for the MSV(GH) 1 potential for H₂+He, which best fit both theory and experiment.

<table>
<thead>
<tr>
<th>$\varepsilon$ (well depth)</th>
<th>$R_m$ (Å)</th>
<th>$C_s$ (cm⁻¹ Å⁸)</th>
<th>$C_6$ (cm⁻¹ Å¹⁸)</th>
<th>$\alpha_{SR}$</th>
<th>$\gamma$</th>
<th>$\alpha_{LR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cm⁻¹)</td>
<td>(meV)</td>
<td>(°K)</td>
<td>(Å)</td>
<td>(a.u.)</td>
<td>(cm⁻¹ Å⁸)</td>
<td>(a.u.)</td>
</tr>
<tr>
<td>10.74</td>
<td>1.332</td>
<td>15.45</td>
<td>3.3815</td>
<td>6.3902</td>
<td>5.532×10⁴</td>
<td>41</td>
</tr>
</tbody>
</table>

exponentially, with one relaxation time. Figure 11 is a plot of the logarithm of $\tilde{C}(t)$ versus time, and indeed the deviation from a straight line is small.

In a system with more closely spaced rotational energy levels than H₂, we expect the contributions of the various relaxation times to be more nearly equal, and therefore expect $\tilde{C}(t)$ to be less accurately represented by a single exponential.

VI. SUMMARY

The results from Sec. V clearly indicate that of the potentials studied, best agreement with experiment is obtained with the MSV(GH)1 potential. The short-range behavior of this potential is in good agreement with the CI results (see Fig. 2) and has a short-range anisotropy of 0.262, which is very close to the value of 0.266 obtained in the CI study (see Sec. III). Both the spherical and angular parts of the long-range $R^{-4}$ dependence were determined by the semiempirical calculations. We present values for the potential parameters for MSV(GH)1 in Table XIV [see Eqs. (27) and (28) for definitions].

Further tests of the potential will be possible when more experimental properties are measured. Obtaining the differential scattering cross sections from molecular beams should provide a good test of the radial potential. Sound absorption measurements in highly diluted mixtures of H₂ in He near room temperature, where three levels of parahydrogen ($j=0, 2, 4$) contribute to the relaxation, would offer further tests of the short-range potential. Experiments on other lines in the Raman spectrum would also add more data for comparison. Until further measurements are made, we can conclude that MSV(GH)1 gives the best representation of the angle-dependent H₂–He intermolecular potential to date.

Our calculations also indicate that a significant portion of the Raman line shifts arises from the dependence of the H₂–He potential on the vibrational coordinate of H₂. (The angle dependence of the potential also contributes significantly to the Raman line shifts.) It would be interesting to pursue this further, perhaps by investigating the effect of including one or more excited vibrational levels in the calculations.

Our reasonable success in quantum mechanically calculating the relaxation properties for the H₂–He system offers encouragement for similar studies on other systems. Because of the rapid increase in the size of the calculations with the decrease in rotational and vibrational energy-level spacings, suitable molecules would have to be characterized by small moments of inertia. Certainly one can study mixtures of H₂ with other noble gases, and also HD (and possibly HF)–noble-gas mixtures. H₂–He is characterized by rather weak inter-
actions and a small well depth. Other systems with larger interactions such as H₂–Ar, interact strongly enough to produce collision-induced spectra which further help specify the intermolecular potential. Work on H₂–Ar is in progress at present. The increased strength of interaction may, however, produce resonances in the various cross sections that would require special attention in the energy-averaging procedure.

For systems with larger masses and hence higher quantum numbers, the fully quantum methods described here become impractical to apply to all quantum numbers. Classical or semiclassical methods must then be used to approximate the cross sections for the higher quantum numbers. However, even for these heavy systems, the quantum method may still be valuable for calculating those cross sections which have low quantum numbers, for which classical or semiclassical methods should be least accurate. Thus we expect both quantum and classical methods to be used in studying inelastic molecular collisions.

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†Present address: Department of Chemistry, University of California at San Diego, La Jolla, CA.


17M. Bloom, Physica (Utr.) 23, 237 (1957).


