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Louis Biolsi Jr.
Missouri University of Science and Technology, biolsi@mst.edu

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Louis Biolsi

Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri 65401
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A restricted distorted-wave treatment of the total cross section when two rigid diatomic molecules with orbital and nuclear spin angular momenta collide is examined. There are certain restrictions on the intermolecular potential and on the possible combinations of the various quantum numbers. These restrictions are examined for the lowest order nonspherical elastic and the lowest order inelastic contributions to the total cross section. The effects of degeneracy averaging and of collisions between indistinguishable molecules are also briefly examined.

The purpose of this paper is to examine the restrictions on the intermolecular potential and the possible quantum states for the lowest order nonspherical elastic and the lowest order inelastic contributions to the scattering cross section for a system of colliding rigid diatomic molecules with rotational structure. A restricted distorted-wave expansion is used and the intermolecular potential is expanded in a complete set of functions. The formal results presented in this paper restrict the summations over this complete set. This work is based on the scattering formalism developed by Curtiss and his co-workers.[1]

I. APPROXIMATIONS TO THE POTENTIAL

Consider a collision between rigid diatomic molecules a and b, separated by intermolecular distance r. The rotation R makes the intermolecular axis parallel to the space fixed z axis and, in a body fixed coordinate system, S_a and S_b are the rotations that bring the internuclear axes of molecules a and b, respectively, parallel to the intermolecular axis after the rotation R has been performed. In addition, there is a body fixed nuclear spin coordinate system, denoted by Q_a and Q_b.

A complete set of functions in the space of r, R, S_a, S_b, Q_a, and Q_b is provided by the orbital angular momentum eigenfunctions (spherical harmonics), denoted by Y, and the nuclear spin eigenfunctions, denoted by $\mathcal{Y}$. The intermolecular potential is expanded in this complete set[2];

$$V(rS_aS_bQ_aQ_b) = \sum_\Lambda v(L_aL_bH_aH_b\nu_1\nu_2\nu_3 \mid r)$$
$$\times Y(L_a, -\nu_1-\nu_2-\nu_3 \mid S_a)Y(L_b\nu_1 \mid S_b)$$
$$\times \mathcal{Y}(H_a\nu_2 \mid Q_a)\mathcal{Y}(H_b\nu_3 \mid Q_b) , \qquad (1)$$

where the index Λ denotes the set of indices L_a, L_b, H_a, H_b, ν_1, ν_2, and ν_3, and $v(\Lambda \mid r)$ is the expansion coefficient of the potential.

In most applications the potential will be spin independent; i.e.,

$$H_a = H_b = \nu_2 = \nu_3 = 0$$

and the expansion of the potential in a complete set becomes

$$V(rS_aS_b) = \sum_\beta v(L_aL_b\nu_1 \mid r)Y(L_a, -\nu_1 \mid S_a)$$
$$\times Y(L_b\nu_1 \mid S_b) , \qquad (2)$$

where the index β denotes the set of indices L_a, L_b, and ν_1. Gioumousis and Curtiss[3] found certain restrictions on the expansion coefficient for a potential of the form given in Eq. (2). For instance

$$v(L_aL_b\nu_1 \mid r) = 0 \text{ if } L_a \text{ is odd}, \qquad (3)$$

when molecule a is a homonuclear diatomic molecule. An exactly similar restriction holds if molecule b is homonuclear. Also

$$v(L_aL_b\nu_1 \mid r) = (-1)^{L_a+L_b}v(L_bL_a\nu_1 \mid r) \qquad (4)$$

if molecules a and b are identical.

It will be useful to take ν_1 to be zero in some instances. This simplification requires the assumption that there is no component of angular momentum along the z axis. In this case Eq. (2) becomes

$$V(rS_aS_b) = (1/4\pi) \sum_{L_aL_b} [(2L_a+1)(2L_b+1)]^{1/2}$$
$$\times P_{L_a}(S_a)P_{L_b}(S_b) , \qquad (5)$$

where the P's are Legendre polynomials. This is similar to the potential considered by Takayanagi.[4]

A restricted distorted-wave expansion is obtained by considering a perturbation potential in which the unperturbed potential is taken to be the spherical approximation. Thus the expansion coefficient of the potential can be written as[5]

$$v(r) = \delta(\Lambda; 0)v^{(0)}(r) + v^{(1)}(\Lambda \mid r) , \qquad (6)$$

where $v^{(0)}(r)$ is the spherical term in the expansion and δ is the Kronecker delta; i.e.,

$$\delta(\Lambda; 0) = \delta(L_a; 0)\delta(L_b; 0)\delta(H_a; 0)\delta(H_b; 0)$$
$$\times \delta(\nu_1; 0)\delta(\nu_2; 0)\delta(\nu_3; 0) .$$

Also, if the interaction is between two electrostatic multipoles, the expansion coefficient has the form[6]

$$v^{(1)}(\Lambda \mid r) = \alpha(\Lambda)\phi(r) . \qquad (7)$$

Thus the spin independent potential in Eq. (2) can be written as

$$V(rS_a S_b) = [\delta(\beta; 0)/4\pi]\upsilon^{(0)}(r)$$

$$+ \phi(r){\sum_{\beta}}' \alpha(\beta)Y(L_a, -\nu_1|S_a)Y(L_b\nu_1|S_b) , \qquad (8)$$

where the prime on the summation sign indicates that L_a, L_b, and ν_1 cannot all be zero.

The potential in Eq. (5) is of interest since it can be compared, in a qualitative way, to the potentials used to represent atom–rotor collisions. This comparison will suggest which of the terms in the summations over L_a and L_b, and thus ν_1, will contribute most significantly to the potential. A potential that is often used to describe the interaction between an atom and a rigid rotor is[7-9]

$$V(r, \theta) = (C_1/r^{12})[1 + b_1 P_1(\cos\theta) + b_2 P_2(\cos\theta)]$$

$$- (C_2/r^6)[1 + a_2 P_2(\cos\theta)] . \qquad (9)$$

Upon orientation averaging, this gives the Lennard-Jones (12,6) potential. The form of the repulsive part of the potential is somewhat arbitrary. However, the form of the attractive part of the potential is chosen to represent the long range forces between the atom and the rotor.[10,11]

Another form used to represent interactions between atoms and rotors is[12]

$$V(r, \theta) = \sum_{\ell} \upsilon(\ell|r)P_\ell(\cos\theta) . \qquad (10)$$

If L_a or L_b is taken to be zero, Eq. (5) has this form. The good results obtained from Eq. (9)[7] and Eq. (10),[13] considering just the first few values of ℓ, suggest that the first few terms in the summations over L_a and L_b in Eq. (8) will contribute most significantly to the anisotropy in the potential during rotor–rotor collisions.

II. THE ELASTIC CROSS SECTION

One of the most fruitful methods of obtaining detailed information about intermolecular potentials is via the use of scattering theory combined with molecular beam scattering data. Both the differential and the total cross sections contain useful information about the interaction process. Since recent work[7-9] indicates that information about anisotropy in the potential can be obtained from the total cross section and, since expressions for the total cross section are less complicated than the expressions for the corresponding differential cross section, only the total cross section will be considered in this paper.

Expressions for the three lowest order contributions in a restricted distorted-wave expansion of the nondegeneracy averaged total cross section when two rigid diatomic molecules with orbital and nuclear spin angular momenta collide are available.[14-16] The contributions are labeled $Q^{(0)}$, $Q^{(1)}$, and $Q^{(2)}$, where $Q^{(0)}$ is the usual result for the scattering of spherical molecules; i.e., it accounts for the contribution of $\upsilon^{(0)}(r)$ to the scattering.

The expression for $Q^{(1)}$ contains the lowest order elastic contribution to the cross section from $\upsilon^{(1)}(\Lambda|r)$. The expression for $Q^{(2)}$ can be written as

$$Q^{(2)} = Q^{(21)} + Q^{(22)} ,$$

where $Q^{(21)}$ accounts for elastic contributions to the cross section and $Q^{(22)}$ accounts for the lowest order inelastic contribution of $\upsilon^{(1)}(\Lambda|r)$ to the scattering. Since it is reasonable to expect a close relation between inelastic scattering and anisotropy in the potential, the expression for $Q^{(22)}$ is especially interesting. Also, since $Q^{(21)}$ represents a second order nonspherical elastic effect, it will be ignored in this paper.

Consider $Q^{(1)}$. Equation (35) in Ref. 14 is

$$Q^{(1)} = \delta(\bar{p}; p)(2\pi/k)\sum_{\lambda\Lambda}{\sum_{L_1}}^*[(2\lambda+1)(2L_1+1)]^{1/2}(-1)^{b_1}\begin{pmatrix} J_a & J_a & L_1 \\ -j_a & j_a & 0 \end{pmatrix}\begin{pmatrix} J_b & J_b & L_1 \\ -j_b & j_b & 0 \end{pmatrix}$$

$$\times \{(-i)^{\lambda+1}[\exp(-i2\eta_\lambda) - 1]\tau(g; L_1 L_1 0\Lambda; g)f(\Lambda\lambda\lambda|kk) + C.C.\} , \qquad (11)$$

where

$$b_1 = J_b - J_a + \lambda + L_1 - j_a + j_b$$

and η_λ is the phase shift. The meaning of the various symbols and indices is given in Ref. 14. Also

$$f(\Lambda\lambda\bar{\lambda}|k\bar{k}) = -(-i)^\lambda(2\mu/\hbar^2)\int \chi_\lambda(k|r)\upsilon^{(1)}(\Lambda|r)\chi_{\bar{\lambda}}(\bar{k}|r)r^2 dr , \qquad (12)$$

where the $\chi_\lambda(k|r)$ are the wavefunctions that satisfy Eq. (13) in Ref. 14 and

$$\tau(g; L_1 L_2 L\Lambda; \bar{g}) = \sum_{\ell_a I_a \ell_b \bar{\ell}_a \bar{I}_a \bar{\ell}_b \bar{I}_b} B(\bar{g}_a J_a|\ell_a I_a)^* B(\bar{g}_a \bar{J}_a|\bar{\ell}_a \bar{I}_a)B(g_b J_b|\ell_b I_b)^* B(\bar{g}_b \bar{J}_b|\bar{\ell}_b \bar{I}_b)(-1)^{b_2}$$

$$\times[(2\ell_a+1)(2\bar{\ell}_a+1)(2\ell_b+1)(2\bar{\ell}_b+1)(2I_a+1)(2I_b+1)]^{1/2}[(2J_a+1)(2\bar{J}_a+1)(2J_b+1)(2\bar{J}_b+1)(2\lambda+1)(2\bar{\lambda}+1)]^{1/2}$$

$$\times\begin{pmatrix} \ell_a & \bar{\ell}_a & L_a \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \ell_b & \bar{\ell}_b & L_b \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \lambda & \bar{\lambda} & L \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} \ell_a & I_a & J_a \\ \bar{\ell}_a & \bar{I}_a & \bar{J}_a \\ L_a & H_a & L_1 \end{Bmatrix}\begin{Bmatrix} \ell_b & I_b & J_b \\ \bar{\ell}_b & \bar{I}_b & \bar{J}_b \\ L_b & H_b & L_2 \end{Bmatrix}$$

$$\times \sum_\nu (-1)^{2\nu} \begin{pmatrix} L_1 & L_2 & L \\ -\nu & \nu & 0 \end{pmatrix} \begin{pmatrix} L_1 & L_a & H_a \\ \nu & -\nu_1-\nu_2-\nu_3 & \nu_2 \end{pmatrix} \begin{pmatrix} L_2 & L_b & H_b \\ -\nu & \nu_1 & \nu_3 \end{pmatrix},$$

(13)

where

$$b_2 = 2(J_a + \bar{J}_a) + \lambda + L + L_2 - L_1 + \bar{\ell}_a + \bar{\ell}_b - I_a - I_b - \bar{I}_a - \bar{I}_b .$$

The properties of the three-j coefficients lead to the result

$$\tau(g; L_1 L_1 0\Lambda; g) = \sum_{\ell_a I_a \ell_b I_b \bar{\ell}_a I_a \bar{\ell}_b I_b} B(g_a J_a | \ell_a I_a)^* B(g_a J_a | \bar{\ell}_a \bar{I}_a) B(g_b J_b | \ell_b I_b)^* B(g_b J_b | \bar{\ell}_b \bar{I}_b)(-1)^{b_3}$$

$$\times [(2\ell_a)1)(2\bar{\ell}_a+1)(2\ell_b+1)(2\bar{\ell}_b+1)(2I_a+1)(2I_b+1)(2\lambda+1)]^{1/2}$$

$$\times (2J_a+1)(2J_b+1)(2L_1+1)^{-1/2} \begin{pmatrix} \ell_a & \bar{\ell}_a & L_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_b & \bar{\ell}_b & L_b \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \ell_a & I_a & J_a \\ \bar{\ell}_a & \bar{I}_a & J_a \\ L_a & H_a & L_1 \end{Bmatrix} \begin{Bmatrix} \ell_b & I_b & J_b \\ \bar{\ell}_b & \bar{I}_b & J_b \\ L_b & H_b & L_1 \end{Bmatrix}$$

$$\times \sum_\nu (-1)^{-\nu} \begin{pmatrix} L_1 & L_a & H_a \\ \nu & -\nu_1-\nu_2-\nu_3 & \nu_2 \end{pmatrix} \begin{pmatrix} L_1 & L_b & H_b \\ -\nu & \nu_1 & \nu_3 \end{pmatrix},$$

(14)

where

$$b_3 = L_1 + \bar{\ell}_a + \bar{\ell}_b - I_a - I_b - \bar{I}_a - \bar{I}_b .$$

There are constraints on the summations in Eq. (11). Since

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 0 \text{ unless } |j_1 - j_2| \leq j_3 \leq j_1 + j_2$$

(15)

the summation over L_1 is constrained by the triangular relations $\Delta(J_a J_a L_1)$ and $\Delta(J_b J_b L_1)$. Also, since

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = 0 \text{ unless } j_1 + j_2 + j_3 \text{ is even}$$

(16)

the summations over L_a and L_b are constrained by the values of ℓ_a and $\bar{\ell}_a$ and of ℓ_b and $\bar{\ell}_b$, respectively.

For a spin independent potential, Eq. (14) becomes

$$\tau(g; L_a L_a 0\beta; g) = \delta(L_a \nu_1; L_b \nu) \sum_{\ell_a I_a \ell_b I_b \bar{\ell}_a \bar{\ell}_b} B(g_a J_a | \ell_a I_a)^* B(g_a J_a | \bar{\ell}_a I_a) B(g_b J_b | \ell_b I_b)^* B(g_b J_b | \bar{\ell}_b I_b)(-1)^{b_4}$$

$$\times [(2\ell_a+1)(2\bar{\ell}_a+1)(2\ell_b+1)(2\bar{\ell}_b+1)(2\lambda+1)]^{1/2}(2J_a+1)(2J_b+1)(2L_a+1)^{-5/2}$$

$$\times \begin{pmatrix} \ell_a & \bar{\ell}_a & L_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_b & \bar{\ell}_b & L_b \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J_a & \ell_a & I_a \\ \bar{\ell}_a & J_a & L_a \end{Bmatrix} \begin{Bmatrix} J_b & \ell_b & I_b \\ \bar{\ell}_b & J_b & L_b \end{Bmatrix},$$

(17)

where

$$b_4 = L_a + \nu_1 + J_a + J_b + \ell_a + \ell_b + \bar{\ell}_a + \bar{\ell}_b - I_a - I_b .$$

Since $\tau(g; L_a L_a 0\beta; g)$ depends on ν_1 only through $(-1)^{\nu_1}$, allowing ν_1 to be zero simply changes b_4. Only terms in which $L_a = L_b$ contribute to $Q^{(1)}$ which can be written as

$$Q^{(1)} = \delta(\bar{p}; p)\delta(L_a; L_b) \sum'_{L_a \nu_1} \sum_\lambda (2\lambda+1)^{1/2}(2L_a+1)^{3/2}(-1)^{b_5} \begin{pmatrix} J_a & J_a & L_a \\ -j_a & j_a & 0 \end{pmatrix} \begin{pmatrix} J_b & J_b & L_b \\ -j_b & j_b & 0 \end{pmatrix}$$

$$\times \{(-i)^{\lambda+1}[\exp(-i2\eta_\lambda) - 1] \tau(g; L_a L_a 0\beta; g) f(\beta\lambda\lambda | kk) + C.C. \},$$

(18)

where

$$b_5 = J_b - J_a + \lambda + L_a - j_a + j_b .$$

Notice that anisotropy in the potential contributes to $Q^{(1)}$ not only through the "anisotropy parameter" α, contained in f, but also through the coupling coefficients. The summation over L_a is constrained by the triangular relations $\Delta(J_a J_a L_a)$ and $\Delta(J_b J_b L_a)$.

Equation (18) results from a spin independent potential and a spin dependent wavefunction. If all spin dependence is removed, the result

$$Q^{(1)} = \delta(\bar{p}; p)\delta(L_a; L_b)\delta(J_a; \ell_a; \bar{\ell}_a)\delta(J_b; \ell_b; \bar{\ell}_b)(2\pi/k)(2\ell_a + 1)(2\ell_b + 1)\sum_{L_a \nu_1}' \sum_{\lambda}{}^* (-1)^{b_6}(2L_a + 1)^{-1}$$

$$\times \begin{pmatrix} \ell_a & \ell_a & L_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_b & \ell_b & L_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_a & \ell_a & L_a \\ -m_a & m_a & 0 \end{pmatrix} \begin{pmatrix} \ell_b & \ell_b & L_a \\ -m_b & m_b & 0 \end{pmatrix} \{(-i)^{\lambda+1}[\exp(-i2\eta_\lambda)-1]f(\beta\lambda\lambda|kk)+\text{C.C.}\} \tag{19}$$

is obtained where

$$b_6 = \lambda + \nu_1 + m_a + m_b .$$

The restriction in relation (16) means that there is no contribution to Eq. (19) unless L_a is even. This restriction does not apply if the wavefunction is spin dependent.

Using Eqs. (7) and (12), the expression for f in Eq. (19) is

$$f(\beta\lambda\lambda|kk) = -(-i)^\lambda(2\mu/\hbar^2)\alpha(L_a L_a \nu_1)\int \chi_\lambda(k|r)\phi(r)\chi_\lambda(k|r)r^2 dr \tag{20}$$

with L_a even. It is important to realize that α is not necessarily an arbitrary parameter. For instance, the interaction of two nonoverlapping charge distributions is given by[17]

$$V(rS_aS_b) = \sum_{L_a L_b \nu_a \nu_b \nu_1} i^{b_7}(-1)^{L_b+\nu_1}[(L_a - |\lambda_a|)!(L_b - |\lambda_b|)!]^{1/2}(L_a+L_b)![[(L_a + |\nu_1|)!(L_a - |\nu_1|)!(L_a + |\lambda_a|)!(L_b + |\nu_1|)!]^{-1/2}$$

$$\times [(L_b - |\nu_1|)!(L_b + |\lambda_b|)!]^{-1/2}\bar{Q}_{L_a}^{\lambda_a}{}^* \bar{Q}_{L_b}^{\lambda_b} D(L_a\lambda_a\nu_1|S_a)^* D(L_b\lambda_b\nu_1|S_b)r^{-(L_a+L_b+1)} ,$$

where

$$b_7 = \lambda_a - |\lambda_a| - \lambda_b + |\lambda_b|$$

and the D's are the irreducible representations of the rotation group. Also, the $\bar{Q}$'s are defined in Ref. 17. The coordinate system used requires that λ_a and λ_b be zero. The relation between the spherical harmonics and the irreducible representations[11] leads to the result

$$\mathfrak{v}^{(1)}(\beta|r) = 4\pi(-1)^{L_b}(L_a+L_b)!\,\bar{Q}_{L_a}^{0*}\bar{Q}_{L_b}^0[(2L_a+1)(2L_b+1)(L_a+|\nu_1|)!(L_a-|\nu_1|)!(L_b+|\nu_1|)!(L_b-|\nu_1|)!]^{-1/2}r^{-(L_a+L_b+1)} , \tag{21}$$

where L_a, L_b, and ν_1 are not all zero. Clearly, depending on the definition of $\phi(r)$, then $\alpha(\beta)$ is determined by Eq. (21).

Equation (21) represents the long range forces. It only contributes to $Q^{(1)}$ in the spin independent case if $L_a = L_b$ and L_a is even. Thus the lowest order contribution to $Q^{(1)}$ in this case has the dependence r^{-5}. If the states are spin dependent but the potential is spin independent, the restriction $L_a = L_b$ requires the lowest order contribution to $Q^{(1)}$ to have the dependence r^{-3} which represents the interaction between two rigid spheres with embedded dipoles.

III. THE INELASTIC CROSS SECTION

The expression for the lowest order inelastic contribution to the cross section, Eq. (B1) in Ref. 16, is considerably more complicated than the expression for $Q^{(1)}$. Thus, to simplify the analysis, all spin dependence will be removed. The result is

$$Q^{(22)} = \Delta(\ell_a\bar{\ell}_aL_a)\Delta(\ell_b\bar{\ell}_bL_b)\Delta(\lambda\bar{\lambda}L)\Delta(L_aL_bL)\delta(\ell_a\ell_b\bar{\ell}_a\bar{\ell}_b; J_aJ_b\bar{J}_a\bar{J}_b)\sum_{\lambda\bar{\lambda}L}{}^*(2\ell_a+1)(2\bar{\ell}_a+1)(2\ell_b+1)(2\bar{\ell}_b+1)\begin{pmatrix} \lambda & \lambda & L \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times \left| \sum_\beta (-1)^{L_a+L_b}\begin{pmatrix} \ell_a & \bar{\ell}_a & L_a \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \ell_b & \bar{\ell}_b & L_b \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L_a & L_b & L \\ -\nu_1 & \nu_1 & 0 \end{pmatrix}\begin{pmatrix} \ell_a & \bar{\ell}_a & L_a \\ m_a - \bar{m}_a & \bar{m}_a - m_a \end{pmatrix}\begin{pmatrix} \ell_b & \bar{\ell}_b & L_b \\ m_b - \bar{m}_b & \bar{m}_b - m_b \end{pmatrix} \right.$$

$$\times \left. \begin{pmatrix} L_a & L_b & L \\ m_a - \bar{m}_a & m_b - \bar{m}_b & \bar{m} - m \end{pmatrix}f(\beta\lambda\bar{\lambda}|k\bar{k}) \right|^2 , \tag{22}$$

where the triangular relations constrain the summations.

Notice that if ν_1 is zero; i.e., the potential is of the form given in Eq. (5), other constraints on the summations occur. In this case $L_a + L_b + L$ must be even. If $L_a + L_b$ is even (i.e., L_a and L_b are both odd or both even), then $\lambda + \bar{\lambda}$ must be even; i.e.,

$$\lambda = \bar{\lambda} \pm n , \tag{23}$$

where n is an even integer. This restricts the summation over λ. If one of the molecules is homonuclear then,

using relation (3), both L_a and L_b must be even.

Now consider the consequences if $L_a + L_b$ is odd (i.e., L_a even and L_b odd or vice versa). Then $\lambda + \bar{\lambda}$ must be odd; i.e.

$$\lambda = \bar{\lambda} \pm n' , \tag{24}$$

where n' is an odd integer. In this case if molecule a is homonuclear, then L_b must be odd and vice versa. These arguments are unchanged if the potential is spin independent and the wavefunction is spin dependent.

Assume that the most important long range contribution to $Q^{(22)}$ comes from dipole forces. In this case, using Eq. (21), $L_a + L_b = 2$. Thus if ν_1 is zero, expression (23) restricts the summations in Eq. (22). If both molecules are heteronuclear then the possible values of L_a and L_b are $L_a = 2$, $L_b = 0$ and vice versa and $L_a = L_b = 1$. The last case corresponds to the interaction between two point dipoles. If molecule a is homonuclear then, using relation (3), L_a is restricted to 0 and 2 with L_b restricted to 2 and 0, respectively. An exactly similar result is obtained if molecule b is homonuclear.

Equation (22) only gives the lowest order inelastic contribution to the cross section. However, using the S-matrix formalism, an expression for the total inelastic cross section has been obtained. The result is given in Appendix B in Ref. 16. For a spin independent potential this result reduces to

$$Q^{IN} = \delta(H_a H_b \nu_2 \nu_3 \bar{L}_1 \bar{L}_2; 0000 L_a L_b)(16\pi\mu^2 k/\hbar^4 \bar{k})(2\bar{J}_a + 1)(2\bar{J}_b + 1)\sum_{\bar{\lambda}\bar{\lambda}L} (2\bar{\lambda} + 1)(-1)^{b_8}$$

$$\times \left| \sum_{L_1 L_2} (-1)^{2L_1}[(2L_1+1)(2L_2+1)]^{1/2}\begin{pmatrix} J_a & \bar{J}_a & L_1 \\ j_a & -\bar{J}_a & \bar{J}_a - j_a \end{pmatrix}\begin{pmatrix} J_b & \bar{J}_b & L_2 \\ j_b & -\bar{J}_b & \bar{J}_b - j_b \end{pmatrix}\begin{pmatrix} L_1 & L_2 & L \\ j_a - \bar{J}_a & j_b - \bar{J}_b & \bar{m} - m \end{pmatrix}\right.$$

$$\left.\times \sum_{r'\beta}\sum_{L_1' L_2' L'}^* \mathcal{W}(\bar{q}\beta; ZZ')\int \chi_\lambda(k|r)\upsilon^{(1)}(\beta|r)\chi(\bar{g}Z'|r)r dr \right|^2 , \tag{25}$$

where

$$b_8 = 2(\bar{J}_a + \bar{J}_b + m)$$

and $\mathcal{W}$ is given by Eq. (15) in Ref. 15. Since $\mathcal{W}$ contains the product of three-j coefficients

$$\begin{pmatrix} \lambda & \lambda' & \bar{L} \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \bar{L} & L_a & L_b \\ 0 & -\nu_1 & \nu_1 \end{pmatrix}$$

then the choice of L_a and L_b, i.e., $L_a + L_b$ either even or odd, restricts the summation over λ in the same way that it was restricted for $Q^{(22)}$.

In the Born approximation, it is assumed that the nonspherical terms make no contribution to the expression for χ. This leads to considerable simplification of the expression for Q^{IN}. The result is given by Eq. (B2) in Ref. 16; i.e.,

$$Q_B^{IN} = (16\mu^2 k/\hbar^4 \bar{k})\sum_{\bar{\lambda}\bar{\lambda}L} (2L+1)(-1)^{b_9}\left| \sum_{L_1 L_2}^* (-1)^{L_1 + L_2}\begin{pmatrix} J_a & \bar{J}_a & L_1 \\ j_a & -\bar{J}_a & \bar{J}_a - j_a \end{pmatrix}\begin{pmatrix} J_b & \bar{J}_b & L_2 \\ j_b & -\bar{J}_b & \bar{J}_b - j_b \end{pmatrix}\right.$$

$$\left.\times \begin{pmatrix} L_1 & L_2 & L \\ j_a - \bar{J}_a & j_b - \bar{J}_b & \bar{m} - m \end{pmatrix}\sum_\Lambda \tau(g; L_1 L_2 L\Lambda; \bar{g})\int \chi_\lambda(k|r)\upsilon^{(1)}(\Lambda|r)\chi_{\bar{\lambda}}(\bar{k}|r)r^2 dr \right|^2 , \tag{26}$$

where

$$b_\ell = 2(J_a + J_b + m) .$$

Using Eq. (13), the summations over $\ell_a + \bar{\ell}_a + L_a$; $\ell_b + \bar{\ell}_b + L_b$; and $\lambda + \bar{\lambda} + L$ must be even. Also, if ν_1 is restricted to zero, the summation $L_1 + L_2 + L$ must be even.

For a spin independent potential, Eq. (26) becomes

$$Q_B^{IN} = (16\mu^2 k/\hbar^4 \bar{k})\sum_{\bar{\lambda}\bar{\lambda}L} (2L_1+1)(-1)^{b_9}\left| \sum_B (2L_a+1)(2L_b+1)(-1)^{L_a+L_b}\begin{pmatrix} J_a & \bar{J}_a & L_a \\ j_a & -\bar{J}_a & \bar{J}_a - j_a \end{pmatrix}\begin{pmatrix} J_b & \bar{J}_b & L_b \\ j_b & -\bar{J}_b & \bar{J}_b - j_b \end{pmatrix}\right.$$

$$\left.\times \begin{pmatrix} L_a & L_b & L \\ j_a - \bar{J}_a & j_b - \bar{J}_b & \bar{m} - m \end{pmatrix}\tau(g; L_a L_b L\beta; \bar{g})\int \chi_\lambda(k|r)\upsilon^{(1)}(\beta|r)\chi_{\bar{\lambda}}(\bar{k}|r)r^2 dr \right|^2 . \tag{27}$$

The choice of L_a and L_b; i.e., $L_a + L_b$ either even or odd, restricts the summation over λ in the same way that it was restricted for $Q^{(22)}$.

IV. THE DEGENERACY AVERAGED CROSS SECTION

In most molecular beam experiments the z-component states are not selected. Then the cross section should be degeneracy averaged. In this case[8,14]

$$Q_{DA}^{(1)} = 0. \tag{28}$$

Thus, for the degeneracy averaged cross section, the lowest order non-spherical elastic contribution is from $Q_{DA}^{(1)}$, given by Eq. (42) in Ref. 14. For a spin independent potential this becomes

$$Q_{DA}^{(21)} = \delta(\bar{g};g)\Delta(L_a L_b L)[2\pi/(2J_a+1)(2J_b+1)k]\sum_{\beta\lambda\epsilon'L}(2L_a+1)(2L_b+1)(2L+1)(-1)^{b_{10}}$$

$$\times\{i^{\lambda+1}\tau(g;L_aL_bL\beta;g')\tau(g';L_aL_bL\beta;g)[\exp(-i2\eta_\lambda)-1]f(\beta\beta\lambda\lambda'\lambda\,|\,kk'k)+\text{C.C.}\}, \tag{29}$$

where

$$b_{10} = J_a + J_b + \lambda + J'_a + J'_b + \lambda' + L_a + L_b + L$$

and

$$f(\beta\beta'\lambda\lambda'\bar{\lambda}\,|\,kk'\bar{k})$$

$$= -(-i)^\lambda(2\mu/\hbar^2)\int\chi_\lambda(k\,|\,r)\upsilon^{(1)}(\beta\,|\,r)G_{\lambda'}(k')$$

$$\times\{\upsilon^{(1)}(\beta'\,|\,r)\chi_{\bar{\lambda}}(\bar{k}\,|\,r)\}r^2dr. \tag{30}$$

Interestingly, there are no more restrictions on the summations over L_a, L_b, and L for $Q_{DA}^{(21)}$ than were obtained for $Q^{(22)}$. The removal of all spin dependence does not further restrict the summations over L_a, L_b and L.

An expression for $Q_{DA}^{(22)}$ is given by Eq. (43) in Ref. 14. However the restrictions on the summations are the same as those obtained without degeneracy averaging.

V. COLLISIONS BETWEEN INDISTINGUISHABLE MOLECULES

When indistinguishable molecules collide, the wavefunction must be properly symmetrized. In this case the lowest order nonspherical elastic contribution to the degeneracy averaged total cross section is not zero but is given by Eq. (13) in Ref. 16. The restrictions on the summations over L_a, L_b, and L are the same as those obtained for $Q^{(1)}$. Similarly the restrictions on the summations over L_a, L_b, and L for the lowest order inelastic contribution to the total degeneracy averaged cross section when indistinguishable molecules collide, given by Eqs. (16) and (17) in Ref. 16, are the same as those obtained for $Q^{(22)}$.

The results given in this paper are still quite formal. However, in actual numerical calculations, attention is almost always restricted to a very limited set of transitions upon molecular collision, thus severely restricting the possible values of the various quantum numbers. In such calculations, the more general restrictions on the quantum numbers and the intermolecular potential presented here should be useful.

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