

Theory of angular distributions of electrons resonantly scattered by molecules. I. Vibrational and rotational excitation of diatomic molecules

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Resonant angular distributions for low-energy electrons scattered by diatomic molecules are derived. For homonuclear molecules, our expression for vibrational excitation is equivalent to those of others. However, we are able to clarify the role of parity favoredness. For heteronuclear molecules, our expressions are new. In particular, they contain only one parameter and are necessarily symmetric about 90° . Furthermore, the individual rotational cross sections within the vibrational band can be determined in terms of the same parameter. Asymmetry about 90° is predicted for these. Finally, a theorem relating these integrated rotational cross sections is derived. Results for the angular distributions are given in tabular form for easy usage.

I. INTRODUCTION

The general theory of angular distributions can be found in standard textbooks which deal with angular momentum.¹ Specific application to resonant scattering of electrons by molecules is found in the recent works of O'Malley and Taylor² and Read.³ These are similar in that the molecular axis is assumed to be fixed during the lifetime of the resonance. A classical method has been proposed⁴ to correct for the rotation of the axis, but the need for the correction appears to be in doubt.⁵ Other questions raised in their approach are whether the total angular momentum is conserved, and whether parity is conserved.

The present work examines the resonant angular distributions from the viewpoint of the frame-transformation theory.⁶ In this approach, the wave functions of the system (electron and target) are explicitly eigenfunctions of both total angular momentum and parity. Thereby, we can ensure that angular momentum and parity are always preserved. Further, the question of correction for the rotation of axis never arises, as the axis is not assumed to be fixed in our approach.

We will show that the angular distributions are given by a sum of terms characterized by the angular momentum transfer j_t . Each term is the product of certain Clebsch-Gordan (CG) coefficients containing information on the resonance and a standard angular function Θ which depends only on j_t and the participating partial waves. The same angular functions appear in the theories of photoionization⁷ or nuclear reaction¹ angular distributions. The role of these functions in the frame-transformation theory is reviewed in Sec. II. As in the previous work,⁶ we restrict the scope of this work to diatomic molecules in the Σ^+ state, and ignore the electron spin.

The application of this theory to the resonant vibrational excitation of homonuclear molecules is presented in Sec. III. Only a single partial wave l needs to be considered at low energies. The requisite CG coefficients and angular functions are tabulated for $l \leq 3$, and some examples are given to illustrate the utility of the Tables. Thus, one of the objectives of the present work is to provide experimentalists with convenient theoretical angular distributions. Although our derivation and presentation are different from others,^{2,3} the results are identical. However, we are able to show that, because our wave functions are eigenfunctions of parity and total angular momentum, only parity favored transitions⁸ contribute. On the other hand, the results of others contain two terms. Each has parity-unfavored as well as parity-favored components. Upon combining with a suitably³ chosen coefficient (type I or II), the unfavored components cancel out.

The more general case of a heteronuclear diatomic molecule is considered in Sec. IV. Here, even at very low energies, at least two partial waves must be included. In particular, we show that the absence of a second partial wave leads to vanishing cross sections for the strong $\Delta j = \pm 1$ rotational transitions. We extend the previous table to give angular distributions where two different partial waves contribute. However, these tables are no longer sufficient to give unique angular distributions, since the expression now contains a parameter—the mixing parameter in the standard two-channel scattering theory. Nevertheless, the present theory is simpler than that of Read³ which contains two parameters. We show that when the parameter takes on limiting values, our expression for the angular distributions reduces to the case of the homonuclear molecule.

In general, the parameter may be found by fitting to the experimental vibrational-differential cross

section. Then each vibrational-rotational cross section is uniquely determined. Though the vibrational angular distributions are shown to be symmetric about 90° , the individual rotational components are not. In particular, we will show that those with $\Delta j = 0$ will have a forward peak, and those with $\Delta j \neq 0$ a backward peak. Finally, we derive a relationship between the integrated rotational cross sections.

Conclusions are presented in Sec. V. Indications for some future directions are also given.

II. REVIEW OF THE FRAME TRANSFORMATION THEORY

The theory of resonant angular distributions of electrons scattered by molecules can be most conveniently derived from the frame-transformation formulation of Chang and Fano (CF).⁶ This approach differs from others in that the wave functions are always eigenfunctions of total angular momentum J and parity. In particular, the body-frame wave function which describes the (resonating) electron-molecule complex is given by

$$\bar{X}_{j_M}^{(\Lambda\eta)}(\hat{\mathbf{r}}, \hat{\mathbf{R}}) = H_{i, \Lambda}^{(j\eta)}(r, R) X_{j_M}^{(\Lambda\eta)}(\hat{r}, \hat{R}), \quad (1)$$

where

$$\frac{d\sigma}{d\omega}(jv - j_0 v_0) = (2j_0 + 1)^{-1} \sum_{j, j', l_0, l'_0, l, l', \eta, \eta'} (ljv | S^{j\eta} | l_0 j_0 v_0) (l'_0 j'_0 v'_0 | S^{j'\eta'} | l' j' v) \int d\hat{R} \Phi_{j_M}^{(\Lambda\eta)*}(\hat{r}, \hat{R}) \Phi_{j'_M}^{(\Lambda'\eta')}(\hat{r}, \hat{R}), \quad (5)$$

where the $S^{j\eta}$ matrix may be obtained from the asymptotic form of $F_{i, jv}^{(j\eta)}(r)$. The integration over \hat{R} is easily carried out, and as explained previously Eq. (5) may be written as a single sum in the angular momentum transfer j_t ,

$$\frac{d\sigma}{d\Omega}(jv - j_0 v_0) = \pi k_{j_0 v_0}^{-2} (2j_0 + 1)^{-1} \sum_{l_0, l'_0, l, l', j_t} (2l_0 + 1)^{1/2} (2l'_0 + 1)^{1/2} [ljv | \bar{S}(j_t) | l_0 j_0 v_0] [l'_0 j'_0 v'_0 | \bar{S}(j_t) | l' j' v] \Theta(j_t, l'_0, l', \theta). \quad (6)$$

Equation (6) emphasizes the fact that the angular distribution for any process is given by the superposition of the standard angular functions

$$\Theta(j_t, l'_0, l', \theta) = (-1)^{j_t} (2j_t + 1) \frac{(2l + 1)^{1/2} (2l' + 1)^{1/2}}{4\pi} \sum_k \left\{ \begin{matrix} l'_0 & l_0 k \\ l & l' j_t \end{matrix} \right\} (l_0, l'_0 | k 0) (l_0, l'_0 | k 0) P_k(\cos \theta), \quad (7)$$

weighted by elements of the scattering matrix

$$[l' j' v | \bar{S}(j_t) | l_0 j_0 v_0] = \sum_{j\eta} (-1)^{j_0 - l_0 - j} (2J + 1) \left\{ \begin{matrix} l & j & J \\ j_0 & l_0 & j_t \end{matrix} \right\} (ljv | S^{(j\eta)} | l_0 j_0 v_0). \quad (8)$$

Applying a transformation to the body frame, one obtains

$$(ljv | S^{(j\eta)} | l_0 j_0 v_0) = -i^{l_0 - l} \sum_{\alpha\Lambda} U_{i, \Lambda}^{(j\eta)} \int dR \chi_v(R) C_{i\alpha}^{(\Lambda)} e^{2i\delta_{\alpha\Lambda}(R)} \bar{C}_{\alpha l_0}^{(\Lambda)} \chi_{v_0}(R) \tilde{U}_{\Lambda}^{(l_0 j_0 \eta)}, \quad (9)$$

where U is the unitary matrix given by

$$U_{i, \Lambda}^{(j\eta)} = \left(\frac{2j + 1}{2J + 1} \right)^{1/2} (l\Lambda, j_0 | j\Lambda) \frac{1 + \eta(-1)^{j-j-l}}{[2(1 + \delta_{\Lambda 0})]^{1/2}}. \quad (10)$$

The body-frame description is particularly appropriate for a resonance, since the electron spends an appreciable amount of time near the molecule and it is this interaction which determines $\delta_{i, \Lambda}(R)$. Using an

$$X_{j_M}^{(\Lambda\eta)}(\hat{r}, \hat{R}) = \left(\frac{2J + 1}{8\pi(1 + \delta_{\Lambda 0})} \right)^{1/2} \times [Y_{i, \Lambda}(\vartheta', \varphi') D_{\Lambda M}^{(j)}(\theta, \phi) + \eta Y_{i, -\Lambda}(\vartheta', \varphi') D_{-\Lambda M}^{(j)}(\theta, \phi)], \quad (2)$$

while the laboratory-frame wave function which describes the asymptotic region is given by

$$\bar{\Phi}_{j_M}^{(j)}(\hat{\mathbf{r}}, \hat{\mathbf{R}}) = F_{i, jv}^{(j\eta)}(r) \chi_v(R) \Phi_{j_M}^{(j)}(\hat{r}, \hat{R}), \quad (3)$$

where

$$\Phi_{j_M}^{(j)}(\hat{r}, \hat{R}) = \sum_m (l m, j M - m | J M) \times Y_{lm}(\vartheta, \varphi) Y_{j M - m}(\theta, \phi). \quad (4)$$

For these equations, the Y 's are the ordinary spherical harmonics, (θ, ϕ) are the angles of the molecular axis, while (ϑ, φ) are electronic angles with primed terms indicating body frame coordinates and unprimed terms indicating laboratory frame coordinates. $D_{\Lambda M}^{(j)}$ are symmetric top functions and $(\dots, \dots | \dots)$ are CG coefficients.

The differential cross section for the transition $(jv - j_0 v_0)$ without resolving internal states of the electron-molecule complex is given by

identity of Racah algebra⁹ as in CF, we may combine Eqs. (8), (9), and (10) to yield¹⁰

$$(ljv|\bar{S}(j_t)l_0j_0v_0) = -i^{l_0-l}(-1)^{j_0+j_t}(2l_0+1)^{-1/2}(2j_0+1)^{1/2}(j_00, j_t0|j_0) \\ \times \sum_{\Lambda} \frac{2}{1+\delta_{\Lambda 0}} (\Lambda, j_t0|l_0\Lambda) \int_0^{\infty} dR \chi_v(R) \sum_{\alpha} (C_{i\alpha}^{(\Lambda)} e^{2i\delta_{\alpha\Lambda}(R)} \bar{C}_{\alpha l_0}^{(\Lambda)} \chi_{v_0}(R)). \quad (11)$$

Note that in (11) the first CG coefficient requires that $(\Delta j - j_t) = \text{even}$, where $\Delta j \equiv j - j_0$; but the second does not require $(\Delta l - j_t) = \text{even}$, where $\Delta l \equiv l - l_0$, unless $\Lambda = 0$. However, we will see that consideration of parity favoredness⁸ does require $(\Delta l - j_t) = \text{even}$. Resonant scattering implies strong domination by only one value of Λ in the cross sections, therefore the summation over Λ in Eq. (9) is superfluous. Furthermore, at low energies, very few values of l contribute significantly. We will see that Eq. (6) is quite tractable in Secs. III and IV.

III. HOMONUCLEAR DIATOMIC MOLECULES

In homonuclear molecules, consideration of nuclear symmetry requires $\Delta j = \text{even}$, and hence $j_t = \text{even}$. As discussed previously,⁶ that in turn requires $\Delta l = \text{even}$; so only alternate values of l contribute, and at low energies we may include only l_r , the lowest value of l consistent with the symmetry of the resonance $\Lambda_{g/u}$. The C matrix in Eq. (11) simply becomes the unit matrix. In most experimental data, rotational states are not resolved so one is usually interested in the total differential cross section for vibrational excitation, given by

$$\frac{d\sigma}{d\Omega}(v \leftarrow v_0) = 4\pi \bar{\sigma}_{v,v_0}(\Lambda) \\ \times \sum_{\text{even } j_t} (\Lambda, j_t0|\Lambda)^2 \Theta(j_t; lll\theta), \quad (12)$$

where

$$\bar{\sigma}_{v,v_0}(\Lambda) = \left(\frac{1}{4k_{j_0v_0}^2} \right) \left(\frac{2}{1+\delta_{\Lambda 0}} \right)^2 \\ \times \left| \int_0^{\infty} dR \chi_v(R) e^{2i\delta_{i\Lambda}(R)} \chi_{v_0}(R) \right|^2. \quad (13)$$

Equation (12) reiterates the fact that the angular distribution is the superposition of angular functions Θ , weighted by a squared CG coefficient which contains the body-frame information in Λ .

These standard functions Θ and the CG coefficients for values of l up to 3 are presented in Table I. The first line shows the trivial result that $\Theta = 1$ and $d\sigma/d\Omega = 1$ for the s wave. The second line shows that for p -wave scattering with no angular momentum transferred ($j_t = 0$), $\Theta = \cos^2\theta$, a well-known result for $d\sigma/d\Omega$ in electron-atom scattering, e.g., e -He at 20.45 eV.¹¹

For the $p\sigma$ wave which is responsible for vibrational excitation via the ${}^2\Sigma_u^+$ resonance in H_2^- at 4 eV,¹² the angular distribution is found by multiplying the σ column and then summing over j_t ,

$$\frac{d\sigma}{d\Omega} = \bar{\sigma}_{v,v_0}(1,0) \sum_{j_t} (10, j_t0|10)^2 \Theta(j_t; 1111\theta) \\ = \bar{\sigma}_{v,v_0}(1,0) [\cos^2\theta + 0.4(1.5 + 0.5\cos^2\theta)] \\ = 0.6\bar{\sigma}_{v,v_0}(1,0) (1 + 2\cos^2\theta). \quad (14)$$

Similarly for the ${}^2\Pi_u$ resonance ($p\pi$ wave),

TABLE I. Angular distributions for homonuclear molecules. For the resonance Λ , the angular distributions are found by going to the block $l_0 = l'_0 = l = l'_r$. One multiplies the column Λ by the standard angular functions Θ expressed as a sum of powers of $\cos\theta$ with the given coefficients. Then one adds up these products within the appropriate block.

l_0	l_0	l	l'	j_t	Λ	$(\Lambda, j_t0 l_0\Lambda)^2$				$(4\pi)\Theta(j_0, l_0l'_0l'_r, \theta)$				
						σ	π	δ	ϕ	1	$\cos^2\theta$	$\cos^4\theta$	$\cos^6\theta$	
0	0	0	0	0		1				1				
1	1	1	1	0		1	1			0	1			
				2		0.4	0.1			1.5	0.5			
				4		0.286	0.071	0.286		1.429	-3.214	3.214		
2	2	2	2	0		1	1	1		0.25	-1.5	2.25		
				2		0.286	0.071	0.286		1.429	-3.214	3.214		
				4		0.286	0.127	0.008		1.446	0.965	0.161		
3	3	3	3	0		1	1	1	1	0	2.25	-7.5	6.25	
				2		0.267	0.15	0	0.417	0.062	8.563	-20.313	13.021	
				4		0.182	0.005	0.247	0.045	2.045	-3.989	1.023	2.557	
				6		0.233	0.131	0.021	0.001	1.392	1.051	0.540	0.047	

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \bar{\sigma}_{v,v_0}(1,1) \sum_{j_t} (11, j_t 0 | 11)^2 \Theta(j_t; 1111 \theta) \\ &= \bar{\sigma}_{v,v_0}(1,1) [\cos^2 \theta + 0.1(1.5 + 0.5 \cos^2 \theta)] \\ &= 0.15 \bar{\sigma}_{v,v_0}(1,1) (1 + 7 \cos^2 \theta). \end{aligned} \quad (15)$$

It should be noted that Table I contains only even values of j_t , corresponding to parity-favored transitions. These must satisfy the condition that $(l - l_0 + j_t)$ is an even integer.⁸ An example of a parity-unfavored angular distribution is $l_0 = l'_0 = l = l' = 1$ and $j_t = 1$, so that $(l - l_0 + j_t) = \text{odd}$. The corresponding values in completing Table I are 0 under σ and 0.5 under π , with 1.5 under 1 and -1.5 under $\cos^2 \theta$. Note that $\Theta(1; 1111, 0^\circ \text{ or } 180^\circ) = 0$ as predicted by Fano for all parity-unfavored transitions. These transitions are known to occur only in a more complex model (e.g., such as when one includes the spin-orbit interaction), but not in the present single-configuration model (ignoring spin). We therefore exclude these from Table I to avoid causing confusion.

We note in passing that the contribution from each vibrational-rotational cross section can be recovered from (12). All one needs to do is to multiply the right-hand side by the squared CG coefficient $(j_0 0, j_t 0 | j_0)^2$.

Next we compare our results to those found by O'Malley and Taylor² and Read.³ Instead of Eq. (12), Read has

$$\frac{d\sigma}{d\Omega} \propto \sum_k A_k P_k(\cos \theta), \quad (16)$$

where

$$A_k(l, \Lambda) = (2k+1) \left[\begin{pmatrix} l & l & k \\ \Lambda & -\Lambda & 0 \end{pmatrix}^2 + p \begin{pmatrix} l & l & k \\ \Lambda & \Lambda & -2\Lambda \end{pmatrix}^2 \right]. \quad (17)$$

In (17), $\begin{pmatrix} \dots \end{pmatrix}$ is the Wigner 3- j symbol, and p has the interesting property of having a value of 0.5 for $\Lambda = 0$ (type II) and of 1.0 for $\Lambda \neq 0$ (type I).

From simple Racah algebra⁹ we derive the following in Appendix A:

$$\begin{aligned} \begin{pmatrix} l_0 & l & k \\ \Lambda & \Lambda & 0 \end{pmatrix}^2 &= \sum_{j_t} (-1)^{k+j_t} (2j_t+1) \\ &\quad \times \begin{pmatrix} l_0 & l & j_t \\ \Lambda & -\Lambda & 0 \end{pmatrix}^2 \begin{Bmatrix} l_0 & l & j_t \\ l_0 & l & k \end{Bmatrix} \end{aligned} \quad (18a)$$

and

$$\begin{aligned} \begin{pmatrix} l_0 & l & k \\ \Lambda & \Lambda & -2\Lambda \end{pmatrix}^2 &= \sum_{j_t} (2j_t+1) \\ &\quad \times \begin{pmatrix} l_0 & l & j_t \\ \Lambda & -\Lambda & 0 \end{pmatrix}^2 \begin{Bmatrix} l_0 & l & j_t \\ l_0 & l & k \end{Bmatrix}. \end{aligned} \quad (18b)$$

Left-hand sides are contained in Eq. (17), while the right-hand sides appear in Eqs. (7) and (12) of the present work. In the case at hand, $l_0 = l$ and $k = \text{even}$ in (18), and j_t takes on all values, so parity-unfavored as well as favored terms are included. However, after summing with $p=1$ in Eq. (17), the parity-unfavored terms cancel because they enter Eqs. (18a) and (18b) with opposite signs. For $\Lambda = 0$, such addition is not necessary as parity-unfavored terms automatically vanish. Thus the present formulation differs from the others by excluding parity-unfavored contributions at the start, rather than by judicious subtraction (or addition) later. It can certainly be argued that as long as both approaches yield the same results, no one method should be preferred over another. We will see in Sec. IV that incorrect results can be obtained in the approach disregarding parity.

IV. HETERONUCLEAR DIATOMIC MOLECULES

In our previous treatment of homonuclear molecules, we have derived only ($\Delta j = \text{even}$) cross sections from one partial wave. Conversely, the assumption of only one partial wave allows even- Δj transitions and forbids odd- Δj transitions. Hence, at least two (adjacent) partial waves are required for the case of heteronuclear molecules. At low energies, we expect that the two lowest values l_0 and $l = (l_0 + 1)$ consistent with molecular symmetry Λ are sufficient. In this "two channel" model, the C matrix in Eq. (11) may be written

$$\underline{C}^{(\Lambda)} = \begin{pmatrix} \cos \beta & \sin \beta \\ -\sin \beta & \cos \beta \end{pmatrix}. \quad (19)$$

In normal situations where the Born-Oppenheimer approximation is valid, β and the eigenphases $\delta_{\alpha\Lambda}$ are slowly varying functions of the internuclear distance R . However at a resonance, one eigenphase (the resonant one labeled 1) varies rapidly with R as well as with the energy. We may represent this eigenphase near the resonance in a Taylor series,

$$\delta_{1\Lambda}(R) \approx \frac{1}{2}\pi + \delta'_{1\Lambda}(R - R_0) + \dots \quad (20a)$$

The first term is standard for a resonance, the second is the primary cause for vibrational excitation, and the higher-order terms are neglected here for simplicity, since they only complicate Eq. (22) below, which is treated as a normalization factor. The nonresonant eigenphase and the mixing parameter are simply approximated by

$$\delta_{2\Lambda}(R) \approx \delta_{2\Lambda}(R_0) \quad (20b)$$

and

$$\beta(R) \approx \beta(R_0) = \beta. \quad (20c)$$

Substituting Eqs. (20) into Eqs. (11) and (6), one obtains after some manipulation

$$\frac{d\sigma}{d\Omega}(jv \rightarrow j_0v_0) = 4\pi\bar{\sigma}_{j_0v_0}(\Lambda) \left(\sum_{\text{even } j_t} (j_00, j_t0 | j0)^2 [(1 + \cos 2\beta)^2 (l_0\Lambda, j_t0 | l_0\Lambda)^2 \Theta(j_t; l_0l_0l_0\theta) + (1 - \cos 2\beta)^2 (l\Lambda, j_t0 | l\Lambda)^2 \Theta(j_t; lll\theta) + 2(1 + \cos 2\beta)(1 - \cos 2\beta)(l_0\Lambda, j_t0 | l_0\Lambda)(l\Lambda, j_t0 | l\Lambda) \Theta(j_t; l_0l_0l\theta)] + \sum_{\text{odd } j_t} (j_00, j_t0 | j0)^2 [2 \sin^2 2\beta (l\Lambda, j_t0 | l_0\Lambda)^2 \Theta(j_t; l_0l_0ll\theta) - 2 \sin^2 2\beta (l_0\Lambda, j_t0 | l\Lambda)(l\Lambda, j_t0 | l_0\Lambda) \Theta(j_t; l_0ll_0\theta)] \right), \quad (21)$$

where

$$\bar{\sigma}_{j_0v_0}(\Lambda) = \frac{1}{4k^2 j_0 v_0} \left(\frac{2}{1 + \delta_{\Lambda 0}} \right)^2 \left| \delta'_{l_0\Lambda} \int_0^\infty dR \chi(R)(R - R_0) \chi_{v_0}(R) \right|^2. \quad (22)$$

In (21), l_0 and l are the two lowest values of the orbital angular momentum consistent with the symmetry Λ . The terms fall into two groups because of the requirement of parity-favored character. The first must have $j_t = \text{even}$ (and $\Delta j = \text{even}$) as for homonuclear molecules, while the second must have $j_t = \text{odd}$ (and $\Delta j = \text{odd}$) and are new. It can be seen that Eq. (21) contains only one parameter—the mixing parameter β —but describes all rotational-vibrational cross sections via the resonance Λ . One observes that $\cos 2\beta = \pm 1$ corresponds to the homonuclear case, with one value for *gerade* and the other for *ungerade* symmetry. For a heteronuclear molecule we must have $|\cos 2\beta| < 1$.

Usually, as in Sec. III, we are interested in the total vibrational cross section (summed over rotational levels). We find

$$\frac{d\sigma}{d\Omega}(v \rightarrow v_0) = 4\pi\bar{\sigma}'_{v_0}(\Lambda) \left(\sum_{\text{even } j_t} [(1 + \cos 2\beta)^2 (l_0\Lambda, j_t0 | l_0\Lambda)^2 \Theta(j_t; l_0l_0l_0\theta) + (1 - \cos 2\beta)^2 (l\Lambda, j_t0 | l\Lambda)^2 \Theta(j_t; lll\theta)] + \sum_{\text{odd } j_t} 2 \sin^2 2\beta (l\Lambda, j_t0 | l_0\Lambda)^2 \Theta(j_t; l_0l_0ll\theta) \right). \quad (23)$$

Note that the third and the last terms of Eq. (21) cancel out exactly when summed over j .¹³ Consequently Eq. (23) is always symmetric about 90° . In contrast, Read's expression³ predicts asymmetry about 90° in general, with the amount of asymmetry

determined by a second parameter.

In the first two terms of (23), the angular functions and CG coefficients have already been given in Table I. The remaining terms require additional quantities found in Table II. An example will

TABLE II. Angular distributions for heteronuclear molecules. Usage is similar to Table I. However, here one does not obtain a unique expression, but one with a parameter. The expression is given by Eq. (23), and instructions for using Table II in conjunction with Table I is given in the text.

l_0	l'_0	l	l'	j_t	Λ	$(l\Lambda, j_t0 l_0\Lambda)(l'\Lambda, j_t0 l'_0\Lambda)$			$(4\pi)\Theta(j_t; l_0l_0l'_0\theta)$						
						σ	π	δ	1	$\cos\theta$	$\cos^2\theta$	$\cos^3\theta$	$\cos^4\theta$	$\cos^5\theta$	
0	0	1	1	1		0.333			3						
0	1	0	1	0		1				1					
0	1	1	0	1		-0.577				-1.732					
1	1	2	2	1		0.4	0.3		0.5		1.5				
				3		0.257	0.086		2.0		1.0				
1	2	1	2	0		1	1			-0.5		1.5			
				2		0.338	-0.085			0.423		1.268			
1	2	2	1	1		-0.516	-0.387			1.936		-3.486			
				3		-0.332	-0.111			-1.936		-0.387			
2	2	3	3	1		0.429	0.238	0.238	0.45		-0.9		2.25		
				3		0.190	0.024	0.238	2.217		-5.6		5.25		
				5		0.216	0.108	0.011	1.708		1.25		0.375		
2	3	2	3	0		1	1	1		9.493		-3.5		3.75	
				2		0.276	0.207	0		-0.611		10.101		10.229	
				4		0.228	-0.025	-0.044		-0.384		1.795		0.641	
2	3	3	2	1		-0.507	-0.451	-0.282		-1.901		9.889		-9.508	
				3		-0.225	-0.028	-0.282		-0.740		2.859		-3.698	
				5		-0.256	-0.128	-0.013		-1.897		-0.446		-0.528	

illustrate the utility of Table II in conjunction with Table I in Eq. (23).

Consider the ${}^2\Sigma^+$ resonance, for example, in the vibrational excitation of HF or HCl in the experiment of Rohr and Linder.¹⁴ The first two terms in Eq. (23) are obtained from Table I, rows 1 to 3, and the last from Table II, row 1, as follows:

$$\begin{aligned} \frac{d\sigma}{d\Omega}(v \rightarrow v_0) &= \bar{\sigma}'_{v_0}(0) \{1 + \cos 2\beta\}^2 [(1)(1)] + (1 - \cos 2\beta)^2 \\ &\quad \times [(1)(\cos^2 \theta) + (0.4)(1.5 + 0.5 \cos^2 \theta) \\ &\quad + 2 \sin^2 2\beta (0.333)(3)]. \end{aligned} \quad (24)$$

Equation (24) can be rearranged to give

$$\begin{aligned} \frac{d\sigma}{d\Omega}(v \rightarrow v_0) &= \bar{\sigma}'_{v_0}(0) [4 - 0.4(1 - \cos 2\beta)^2 \\ &\quad + 1.2(1 - \cos 2\beta)^2 \cos^2 \theta] \end{aligned} \quad (25)$$

which is symmetric about 90° . Note that Eq. (25) is isotropic only when $\cos 2\beta = +1$ which correspond to the ${}^2\Sigma_g^+$ symmetry. In the case under consideration, ${}^2\Sigma_g^+$ symmetry, $\cos 2\beta < 1$, and the angular distributions *cannot* be isotropic. (However, the amount of anisotropy is small even for $\cos 2\beta = 0$, only a difference of 25% between 0° and 90° .) Ordinarily, fitting (25) to the experimental data enables us to find $\cos 2\beta$. Unfortunately, the error bars in the data of Rohr and Linder are too large to determine $\cos 2\beta$ uniquely, except that $0.2 \lesssim \cos 2\beta < 1$. Further details are published elsewhere.¹⁵

Fortunately, the case of the ${}^2\Pi$ resonance in CO provides an excellent illustration of the present theory. The data there^{16a} are sufficiently accurate to determine $\cos 2\beta$, and an excellent fit of the theory to experiment has been found.^{16b}

Returning to Eq. (21), we note that it gives the individual rotational-vibrational cross sections in terms of still only one parameter. The differential cross sections with $\Delta j = \text{even}$ are given by the first three terms only, and those with $\Delta j = \text{odd}$ by the last two only. Now these expressions are no longer symmetric about 90° , as is evident from the entries with odd powers of $\cos \theta$ in Table II, which correspond to the third and last terms of (21). In Appendix B, we prove that the last term is positive definite when $\theta = 0^\circ$ (and negative when $\theta = 180^\circ$). Therefore, differential cross sections with $\Delta j = \text{odd}$ will peak in the backward direction with a corresponding dip in the forward direction. For the $\Delta j = \text{even}$ differential cross section, we show in Appendix B that the elastic transition ($\Delta j = 0$) will always have a forward peak and backward dip. However, the situation for other transitions ($\Delta j = \text{even} \neq 0$) is less clear in general. We know that all rotationally elastic cross sections have forward peaks, and all rotationally inelastic ones examined have backward peaks. It is conjectured that in fact all inelastic cross sections have backward peaks. Experimental data with resolution of some rotational levels will be most useful in confirming this aspect of the present theory.

Next, we examine the integrated cross sections given by¹⁷

$$\sigma_{v_j \leftarrow v_0 j_0}(\Delta j \text{ even}) = \sum_{\text{even } j_t} (j_0 0, j_t 0 | j_0)^2 [(l_0 \Lambda, l_0 - \Lambda | j_t 0)^2 (1 + \cos 2\beta)^2 + (l_0 + 1 \Lambda, l_0 + 1 - \Lambda | j_t 0)^2 (1 - \cos 2\beta)^2] \quad (26a)$$

and

$$\sigma_{v_j \leftarrow v_0 j_0}(\Delta j \text{ odd}) = \sum_{\text{odd } j_t} (j_0 0, j_t 0 | j_0)^2 (l_0 + 1 \Lambda, l_0 - \Lambda | j_t 0)^2 2 \sin^2 2\beta. \quad (26b)$$

The first CG coefficients are simply given by¹⁸

$$(j_0 0, j_t 0 | j_0)^2 = \frac{(2j + 1)(j_0 + j_t - j)! (j_t + j - j_0)! (j + j_0 - j_t)!}{(j_0 + j_t + j + 1)!} \left(\frac{\frac{1}{2}(j + j_t + j_0)!}{\frac{1}{2}(j_0 + j_t - j)! \frac{1}{2}(j_t + j - j_0)! \frac{1}{2}(j + j_0 - j_t)!} \right)^2. \quad (27)$$

The others have already appeared in Tables I and II for $l_0 \leq 3$.

An interesting relation can be derived from Eqs. (26) for the sums of the two types of cross sections. Summing over j , the first squared CG coefficients in both Eqs. (26a) and (26b) become unity by the usual sum rule. Further summation over j_t gives a value of $\frac{1}{2}$ for each remaining squared CG coefficient, using the half-sum rule derived in Appendix C. Thus,

$$\sigma_{v \leftarrow v_0}(\Delta j \text{ even}) = \frac{1}{2}(1 + \cos 2\beta)^2 + \frac{1}{2}(1 - \cos 2\beta)^2 \quad (28a)$$

and

$$\sigma_{v \leftarrow v_0}(\Delta j \text{ odd}) = \sin^2 2\beta. \quad (28b)$$

Finally, the ratio of Eqs. (28a) to (28b) is

$$\sigma(\Delta j \text{ even})/\sigma(\Delta j \text{ odd}) = 1 + 2 \cot^2 2\beta \geq 1. \quad (29)$$

Equation (29) states that the ratio of the sum of

these two kinds of cross sections must exceed unity. The minimum value 1 corresponds to $\beta = \frac{1}{4}\pi$ which may be approached in highly polar molecules. On the other hand, the other limit is reached when the denominator vanishes, as β becomes 0 or $\frac{1}{2}\pi$ in homopolar molecules.

V. CONCLUSIONS

We have derived the angular distributions for electrons scattered by resonant angular distributions by a diatomic in the Σ^+ state. Results are also presented in tabular form for convenient usage, without having to read through the details of the theory and to look up the requisite coupling coefficients. For homonuclear diatomic molecules, Table I suffices for this purpose as long as ($l, \Lambda \leq 3$). However, for heteronuclear molecules, one needs both Tables I and II in conjunction with the one-parameter expression in Eq. (23).

From a theoretical viewpoint, our results are derived with conservation of angular momentum and parity. Our expressions contain only parity-favored contributions, while those of others may contain parity-unfavored contributions. For the homonuclear case, these parity-unfavored contributions cancel out upon addition of certain squared CG coefficients, and all results become identical. Since our theory does not assume that the molecular axis is held fixed during the lifetime of the resonance as in other theories, it might be argued that correction for the rotation of the axis⁴ is superfluous. For the heteronuclear case, our results are different from those of Read³ in that expressions contain only one parameter while his contain two parameters. Further, we show that each vibrational-rotational cross section can be obtained using the value of the parameter fitted to the vibrational data. Finally we prove a relation on these vibrational-rotational cross sections.

The present theory is limited to diatomic target molecules in the Σ^+ state. It also assumes that rotational and vibrational states of the resonance are not resolved although the initial and the final states may well be resolved. In practice, the vibrational states of the resonance are usually resolved,¹⁵ this has no effect on the angular distribution, but further work is required in the present framework to understand the resultant structures in the energy dependence of the cross section, understood in terms of the boomerang model.¹⁹ In some high-resolution experiment²⁰ on H_2 , even the rotation levels in the resonant state are resolved. The corresponding angular distributions can be found by extending this work. Future extensions of the present theory are considered for electronic excitation of the target and for polyatomic molecules.

Notes added in proof

(a) I am grateful to P. G. Burke for clarifying the assumption embodied in Eqs. (20) in the more familiar formalism of W. Brenig and R. Haag, [Fortschr. Phys. 7, 183 (1959)]. Accordingly,

$$\underline{S} = \underline{S}_0^{1/2} \left[\underline{I} - \frac{i\Gamma\gamma^\dagger \times \gamma}{E - E_r + \frac{1}{2}i\Gamma} \right] \underline{S}_0^{1/2},$$

where \underline{S}_0 is assumed to be the unit matrix, i.e., no background scattering in the present work. Hence my $\underline{C}^{(\Lambda)}$ is the matrix which diagonalizes $\gamma^\dagger \times \gamma$ yielding $\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$. Consequently, the resonance is described by only one eigenphase; my β , given by Eq. (19), is energy independent; and the angular distributions are constant within the broad resonance in accordance with observations.

(b) It has been brought to my attention that Eq. (25) has been explicitly derived by F. Fiquet-Fayard [J. Phys. B 8, 2880 (1975)] with a different formalism but similar assumptions. The thrust of her paper is on target molecules not in the $^1\Sigma^+$ state.

APPENDIX A

We derive here several formulas based on Racah algebra in the text. The fundamental equation is found in Rotenberg *et al.*⁹, Eq. (2.19), which is

$$\sum_{m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & j_3 \\ n_1 & n_2 & -m_3 \end{pmatrix} = \sum_{l_3 n_3} (-1)^{j_3 + l_3 + m_1 + n_1} (2l_3 + 1) \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix} \begin{pmatrix} l_1 & j_2 & l_3 \\ n_1 & m_2 & n_3 \end{pmatrix} \begin{pmatrix} j_1 & l_2 & l_3 \\ m_1 & n_2 & -n_3 \end{pmatrix}. \quad (A1)$$

Let $j_1 = l_1 = l_0$, $j_2 = l_2 = l$, $j_3 = k$, $l_3 = j_t$, $m_1 = n_1 = \Lambda$, and $m_2 = n_2 = -\Lambda$. Equation (A1) becomes

$$\begin{pmatrix} l_0 & l & k \\ \Lambda & -\Lambda & 0 \end{pmatrix}^2 = \sum_{j_t} (-1)^{k + j_t + 2\Lambda} (2j_t + 1) \begin{Bmatrix} l_0 & l & k \\ l_0 & l & j_t \end{Bmatrix} \begin{pmatrix} l_0 & l & j_t \\ \Lambda & -\Lambda & 0 \end{pmatrix}^2. \quad (A2)$$

Equation (A2) is the same as Eq. (18a) if one notes that $(-1)^{2\Lambda} = 1$ and that columns of the 6- j symbol may be inverted.

Next, we return to (A1) and let $j_1 = l_1 = l_0$, $j_2 = l_2 = l$, $j_3 = k$, $l_3 = j_t$, $m_1 = m_2 = \Lambda$, and $n_1 = n_2 = -\Lambda$. We obtain

$$\begin{pmatrix} l_0 & l & k \\ \Lambda & \Lambda & -2\Lambda \end{pmatrix} \begin{pmatrix} l_0 & l & k \\ -\Lambda & -\Lambda & 2\Lambda \end{pmatrix} = \sum_{j_t} (-1)^{k+j_t} (2j_t+1) \begin{Bmatrix} l_0 & l & k \\ l_0 & l & j_t \end{Bmatrix} \begin{pmatrix} l_0 & l & j_t \\ -\Lambda & \Lambda & 0 \end{pmatrix} \begin{pmatrix} l_0 & l & j_t \\ \Lambda & -\Lambda & 0 \end{pmatrix}. \quad (\text{A3})$$

Equation (A3) is identical to Eq. (18b) if we make use of the well-known property of 3- j symbols:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \quad (\text{A4})$$

APPENDIX B

In Eq. (21), the first, second, and fourth terms are symmetric about 90° , however the third and the last are not. We will show that the last term is positive definite when $\theta = 0^\circ$, and so is the third when $j = j_0$. With the aid of Eq. (7), we write the last term as

$$\begin{aligned} \bar{\sigma}'_{vv_0}(\Lambda) \sum_{\text{odd } j_t} (j_0 0, j_t 0 | j_0)^2 2 \sin^2 2\beta (l_0 \Lambda, j_t 0 | l \Lambda) (l \Lambda, j_t 0 | l_0 \Lambda) (-1)^{j_t} (2j_t+1) \\ \times (2l_0+1)^{1/2} (2l+1)^{1/2} \sum_k \begin{Bmatrix} l & l_0 & k \\ l & l_0 & j_t \end{Bmatrix} (l_0, l_0 | k 0) (l_0 0, l_0 | k 0) P_k(1), \end{aligned} \quad (\text{B1})$$

with $P_k(1) = 1$. Making use of (A1), we obtain from (B1),

$$\bar{\sigma}'_{vv_0}(\Lambda) \sum_{\text{odd } j_t} (j_0 0, j_t 0 | j_0)^2 2 \sin^2 2\beta (l_0 \Lambda, j_t 0 | l \Lambda)^2 (2l_0+1) (2j_t+1) \begin{pmatrix} l_0 & l & j_t \\ 0 & 0 & 0 \end{pmatrix}^2. \quad (\text{B2})$$

In (B2), every quantity is positive definite, therefore the entire expression is positive definite. This implies that for $l = l_0 + 1$ and $\Delta j = \text{odd}$ transitions, the differential cross sections will have a forward dip (and a backward peak), taking into account of the negative sign in Eq. (21).

Clearly, the third term must largely behave in the opposite manner so that it will cancel the asymmetry about 90° produced by the last term when summed. The third term is

$$\begin{aligned} \bar{\sigma}'_{vv_0}(\Lambda) \sum_{\text{even } j_t} (j_0 0, j_t 0 | j_0)^2 2(1 - \cos^2 2\beta) (l_0 \Lambda, j_t 0 | l_0 \Lambda) (l \Lambda, j_t 0 | l \Lambda) \\ \times (-1)^{j_t} (2j_t+1) (2l_0+1)^{1/2} (2l+1)^{1/2} \sum_k \begin{Bmatrix} l & l_0 & k \\ l_0 & l & j_t \end{Bmatrix} (l_0 0, l_0 | k 0)^2 P_k(1). \end{aligned} \quad (\text{B3})$$

Using (A1), the sum in k may be performed, and we have

$$\bar{\sigma}'_{vv_0}(\Lambda) 2 \sin^2 2\beta \sum_{\text{even } j_t} (j_0 0, j_t 0 | j_0)^2 (l_0 \Lambda, j_t 0 | l_0 \Lambda) (l \Lambda, j_t 0 | l \Lambda) (l_0 0, j_t 0 | l_0 0) (l_0, j_t 0 | l_0). \quad (\text{B4})$$

In contrast to (B2), quantities in (B4) are not necessarily positive, and (B4) need not be positive definite for all values of j and j_0 (subject to the condition $j - j_0 = \text{even}$). However, the first term in (B4) with $j_t = 0$ is simply $\delta_{j_0 j}$, and is clearly the dominating term when $j = j_0$. Therefore, the rotationally elastic differential cross section is expected to have a large forward peak. For the inelastic process, the situation is less clear, since we need the examine terms in (B4) with $j_t = 2, 4$, etc. In the case of a Π resonance as in CO, we have shown^{16b} that (B4) is negative for $j_t = 2$. Therefore the angular distributions for the rotational transition $j = j_0 \pm 2$ will have a backward peak.

APPENDIX C

We wish to show that the well-known sum rule for CG coefficients

$$\sum_{j_3} (j_1 m, j_2 - m | j_3 0)^2 = 1 \quad (\text{C1})$$

is composed of two equal half-sum rules when $m \neq 0$, namely,

$$\begin{aligned} \sum_{\text{even } j_3} (j_1 m, j_2 - m | j_3 0)^2 \\ = \sum_{\text{odd } j_3} (j_1 m, j_2 - m | j_3 0)^2 = \frac{1}{2}. \end{aligned} \quad (\text{C2})$$

Equation (C2) holds for both integral and half-integral values of j_1 and j_2 .

Defining a new coefficient

$$C_{m,n}^{j_1 j_2 j_3} = 2^{-1/2} [(j_1 m, j_2 - m | j_3 0) + n(j_1 - m, j_2 m | j_3 0)], \quad (\text{C3})$$

where $n = \pm 1$; and using (A4), one finds

$$C_{m,n}^{j_1 j_2 j_3} = 2^{-1/2} [1 + n(-1)^{j_1 + j_2 + j_3}] \times (j_1 m, j_2 - m | j_3 0). \quad (\text{C4})$$

Clearly, $C_{m,n}^{j_1 j_2 j_3}$ vanishes whenever n and $(-1)^{j_1 + j_2 + j_3}$ have opposite signs. In other words, for fixed values of n , j_1 , and j_2 , only alternate values of j_3 yield a nonvanishing result for $C_{m,n}^{j_1 j_2 j_3}$. Thus, in the sum

$$\sum_{j_3} (C_{m,n}^{j_1 j_2 j_3})^2 = \frac{1}{2} \left(\sum_{j_3} [2 + 2n(-1)^{j_1 + j_2 + j_3}] \times (j_1 m, j_2 - m | j_3 0)^2 \right), \quad (\text{C5})$$

only alternate values of j_3 contribute, as is evident from the square bracket. Indeed the first term in (C5) sums to one by (C1), and the second vanishes since

$$\sum_{j_3} (j_1 m, j_2 - m | j_3 0)(j_1 - m, j_2 m | j_3 0) = 0, \quad (\text{C6})$$

except when $m = 0$. Therefore, we have shown that

$$\sum_{j_3} (C_{m,n}^{j_1 j_2 j_3})^2 = 1 + n\delta_{m,0}. \quad (\text{C7})$$

For $m \neq 0$, (C5) and (C7) show that if $n = (-1)^{j_1 + j_2}$, then

$$\frac{1}{2} \sum_{\text{even } j_3} 4(j_1 m, j_2 - m | j_3 0)^2 = 1, \quad (\text{C8})$$

and if $n = (-1)^{j_1 + j_2 + 1}$, then

$$\frac{1}{2} \sum_{\text{odd } j_3} 4(j_1 m, j_2 - m | j_3 0)^2 = 1. \quad (\text{C9})$$

Equations (C8) and (C9) are clearly equivalent to Eq. (2) which is referred as the half-sum rule.

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¹⁰Equation (11) differs from CF(58) by the factor $(-1)^{l+l_0+j_1}$ which is +1 for parity-favored transitions.

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$$\sum_k (2l_0 + 1)(l_0 \Lambda, k 0 | l \Lambda)^2 (l_0 0, l 0 | k 0)^2 P_k(\cos \theta).$$

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¹⁷Note that

$$\int \Theta(j_1' l_0 l_0' l_0' \theta) \sin \theta d\theta d\phi = \frac{2j_1 + 1}{2l_0 + 1}.$$

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