PHYSICAL REVIEW A VOLUME 33, NUMBER 2 FEBRUARY 1986

Algebraic-eikonal approach to electron-molecule scattering: Diatomic molecules

R. Bijker, R. D. Amado, and D. A. Sparrow
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 12 August 1985)

We propose an algebraic-eikonal approach to electron-molecule scattering. In this approach the coupling to both rotational and vibrational molecular states is taken into account simultaneously and to all orders in the coupling strength. We present closed analytic expressions for the transition matrix elements for the two dynamical symmetries of the vibron model for diatomic molecules, the U(3) and O(4) limits. It is shown that the large-N limit of the O(4) result corresponds to the rigid-rotor case. The extension to triatomic and polyatomic molecules is straightforward.

I. INTRODUCTION

The many molecular degrees of freedom complicate the theory of electron-molecule scattering. A close-coupling calculation, even for a diatomic molecule, is a very large undertaking, and the calculation quickly gets out of hand for a more complex molecule.[1] It is also clear that for high-energy electrons, the full power of close coupling is not required by the physics. However, except for the rigid-rotor model of a diatomic molecule, a suitable adiabatic approximation is not available.

In this paper we combine recent work on an algebraic description[2,3] of molecular motion (the vibron model) with the Glauber or eikonal approximation[4] to scattering using the adiabatic approximation. We show that for a diatomic molecule treated in this way, the close-coupling calculation can be done essentially in closed form, treating both elastic scattering and inelastic scattering to rotational and vibrational states. The method makes contact with adiabatic eikonal calculations for the rigid rotor, but goes considerably beyond them.

Since our method is quite simple, it is easily generalized to more complicated molecules. The spectra of triatomic molecules have already been treated in the vibron model.[5,6] Our method can also be applied to other probes and to more sophisticated interactions. In this paper, however, we outline the first steps. We consider high-energy electron scattering from a diatomic molecule and take only dipole coupling. We first review the adiabatic eikonal approximation applied to this problem (Sec. II) and then (Sec. III) review the algebraic or vibron model. In Sec. IV we show how these two approaches are combined to give simple closed-form expressions for the scattering amplitudes with particular emphasis on the two algebraic subgroup chains O(4) and U(3). In Sec. V we present some simple calculations for 5-eV electron scattering from a strongly polar diatomic molecule with a dipole moment of 10 D (e.g., CsCl). We consider elastic scattering, excitation from the ground state to the first rotational state, and excitation of the first 0^+ and first 1^- vibrational states. We see that the effects of channel coupling on all of these cross sections are very significant. We also see that the vibrational coupling cross sections are very sensitive to the molecular dynamics. In Sec. VI we conclude with a discussion of the results and possible extensions.

II. EIKONAL APPROXIMATION

The Hamiltonian for electrons scattering from a molecule is

$$H = T + H_{\text{mol}} + V(\mathbf{r}) , \tag{2.1}$$

where T is the kinetic energy of the incoming electron, H_{mol} describes the molecule and $V(\mathbf{r})$ represents the interaction between the projectile and the molecule. The projectile coordinate $\mathbf{r}$ is measured from the center of mass of the molecule. The initial and final momenta of the projectile are $\mathbf{k}$ and $\mathbf{k}'$, respectively. The z axis is chosen along the direction of the momentum of the incoming electron, $\mathbf{k}$, and impact parameter $\mathbf{b}$ is perpendicular to this direction,

$$\mathbf{r} = \mathbf{b} + z\hat{\mathbf{k}} . \tag{2.2}$$

If the projectile energy is much larger than the strength of the electron-molecule interaction and is also sufficiently large that the projectile wavelength is small compared with the range of potential variation, one may use the eikonal (or Glauber) approximation to describe the scattering.[4] If, in addition, the interaction time of the projectile with the molecule is short compared with the time for molecular excitations, or equivalently the projectile energy is large compared with the molecular excitation energies, one may neglect the excitation energy of the molecule with respect to the projectile energy (adiabatic approximation). This is equivalent to neglecting H_{mol} in Eq. (2.1). Under these two approximations the scattering amplitude for scattering of an electron from a molecule with initial state $|\,i\,\rangle$ to a final state $|\,f\,\rangle$ can be written as

$$A_{fi}(q) = \frac{k}{2\pi i} \int d^2b\, e^{i\mathbf{q}\cdot\mathbf{b}} \langle f \,|\, e^{i\chi(\mathbf{b})} - 1 \,|\, i \rangle , \tag{2.3}$$

where $\mathbf{q}$ is the momentum transfer

$$\mathbf{q} = \mathbf{k}' - \mathbf{k} , \tag{2.4}$$

$k = |\,\mathbf{k}\,|$ and $\chi(\mathbf{b})$ is the phase that the electron acquires as it traverses the molecule

$$\chi(\mathbf{b}) = -\frac{m_e}{\hbar^2 k} \int_{-\infty}^{\infty} dz V(\mathbf{r}) , \tag{2.5}$$

where m_e is the electron mass. In Ref. 7 Ashihara *et al.*

have shown that the small-angle ($\theta \lesssim 50°$) scattering of electrons of a few eV energy from a diatomic nonhomopolar molecule can be approximated by a pure dipole interaction

$$V(\mathbf{r})=\alpha(r)\hat{\mathbf{r}}\cdot\mathbf{T}\ , \tag{2.6}$$

where $\mathbf{T}$ is a dipole operator exciting rotational and vibrational states in the molecule. For this interaction the eikonal phase is

$$\chi(\mathbf{b})=g(b)\hat{\mathbf{b}}\cdot\mathbf{T}\ , \tag{2.7}$$

with

$$g(b)=-\frac{m_e}{\hbar^2 k}\int_{-\infty}^{\infty} dz\alpha(r)\frac{b}{r}\ ,$$
$$r=(b^2+z^2)^{1/2}\ . \tag{2.8}$$

In Sec. V we will discuss the function $\alpha(r)$ in more detail. The transition operator $\exp[i\chi(\mathbf{b})]$ can be simplified by rewriting it as a product of a rotation about an angle $(\hat{\mathbf{b}})=(\phi,\theta=\pi/2,\psi=0)$ to the z axis, a simpler form of the transition operator involving only the z (or m conserving) component of the dipole operator $\mathbf{T}$, and the inverse rotation about $(-\hat{\mathbf{b}})=(0,-\pi/2,-\phi)$

$$e^{i\chi(\mathbf{b})}=R(\hat{\mathbf{b}})e^{ig(b)T_z}R(-\hat{\mathbf{b}})\ . \tag{2.9}$$

Using the properties of the Wigner rotation matrices[8] and writing the molecular states in terms of the internal quantum numbers α, the total angular momentum l and its z-component m, the matrix elements in Eq. (2.3) reduce to

$$\langle \alpha_f,l_f,m_f\,|\,e^{i\chi(\mathbf{b})}-1\,|\,\alpha_i,l_i,m_i\rangle$$
$$=e^{i(m_i-m_f)\phi}\sum_m d^{(l_f)}_{m_f m}\left[\frac{\pi}{2}\right]d^{(l_i)}_{m_i m}\left[\frac{\pi}{2}\right]$$
$$\times\langle \alpha_f,l_f,m\,|\,e^{ig(b)T_z}-1\,|\,\alpha_i,l_i,m\rangle\ . \tag{2.10}$$

Finally combining Eqs. (2.10) and (2.3) and writing the ϕ integral in terms of a Bessel function, the scattering amplitude can be expressed in terms of a one-dimensional integral over the impact parameter b,

$$A_{fi}(q)=iki^{|m_f-m_i|}\int b\,db\,J_{|m_f-m_i|}(qb)\left[\delta_{fi}-\sum_m d^{(l_f)}_{m_f m}\left[\frac{\pi}{2}\right]d^{(l_i)}_{m_i m}\left[\frac{\pi}{2}\right]\langle \alpha_f,l_f,m\,|\,e^{ig(b)T_z}\,|\,\alpha_i,l_i,m\rangle\right]\ . \tag{2.11}$$

The differential cross section for scattering from electron momentum $\mathbf{k}$ to $\mathbf{k}'$ is given in terms of $A_{fi}(q)$ of Eq. (2.11) by

$$\frac{d\sigma(\alpha_i,l_i,m_i\rightarrow\alpha_f,l_f,m_f;q)}{d\Omega}=\frac{2k'}{k}\,|A_{fi}(q)|^2\ , \tag{2.12}$$

where the factor of 2 comes from summing over final electron spin states (here assumed unobserved). In the adiabatic approximation $k'\simeq k$. If no molecular spin substates are known, Eq. (2.13) then becomes

$$\frac{d\sigma(\alpha_i,l_i\rightarrow\alpha_f,l_f;q)}{d\Omega}=\frac{2}{2l_i+1}\sum_{m_i,m_f}|A_{fi}(q)|^2\ . \tag{2.13}$$

This is the formula we will use to calculate cross sections. For the calculation of the transition matrix element

$$\langle \alpha_f,l_f,m\,|\,e^{ig(b)T_z}\,|\,\alpha_i,l_i,m\rangle \tag{2.14}$$

we will use the vibron model,[2,3] which is an algebraic approach for describing molecular excitations. In the next section we will review the main properties of the vibron model for diatomic molecules and in Sec. IV we will show that the transition matrix elements of Eq. (2.12) can be derived in the framework of the vibron model exactly to all orders in the coupling strength $g(b)$. This is equivalent to doing a complete close-coupling calculation in the adiabatic approximation.

III. VIBRON MODEL

Traditionally, rotation-vibration spectra in molecules have been studied in terms of a Born-Oppenheimer potential approach, in which one has to solve the Schrödinger equation to obtain the energy spectrum. For diatomic molecules it has been shown that a simple Morse potential is a valid approximation to the interaction potential and provides a good description of the experimental spectra. More recently, an algebraic approach[2,3] called the vibron model has been proposed as an alternative method for describing the properties of rotation-vibration states in diatomic molecules. Such an algebraic approach becomes particularly useful in the treatment of the following two problems. Firstly, the vibron model can easily be generalized to triatomic and polyatomic molecules. In Refs. 5 and 6 this extended version has been applied to the rotation-vibration spectra of both linear and nonlinear triatomic molecules as well as to linear tetraatomic molecules. Secondly, in processes such as electron-molecule scattering one has to calculate transition probabilities, which in general involve a complicated sum over intermediate states. Using the algebraic properties of the vibron model and the adiabatic approximation these quantities can be derived exactly to all orders in the coupling strength. This last property will be used extensively in Secs. IV and V to treat electron scattering from diatomic molecules.

In the remainder of this section we will outline some basic properties of the vibron model as it was proposed originally for nonhomopolar diatomic molecules.[2,3] Rotation-vibration spectra in diatomic molecules arise from the $n=3$ dipole degrees of freedom, which can be chosen as the interatomic distance, r, and two angles, θ and ϕ, characterizing the orientation of the molecule. In the vibron model the energy spectra of the bound states are generated by a dynamic algebra of the unitary group in $n+1=4$ dimensions, U(4). The algebra is realized in terms of four boson, or vibron, creation (annihilation) operators, divided into a scalar boson with $L^{\pi}=0^{+}$, $s^{\dagger}$ (s), and the three components of a vector boson with $L^{\pi}=1^{-}$, $p_{\mu}^{\dagger}$ (p_{μ}), $\mu=-1,0,1$. The generators of the U(4) algebra are the $4^2=16$ possible bilinear products of a vibron creation operator ($s^{\dagger},p_{\mu}^{\dagger}$) and a vibron annihilation (s,p_{μ}) operator. The most general Hamiltonian which is invariant under the dynamical group U(4) can be written in terms of an expansion in these generators. Keeping only terms which are at most quadratic in the generators and imposing spherical symmetry and parity invariance, the vibron Hamiltonian is given by

$$H=H_0+a_1\hat{n}_p+a_2\hat{n}_p\hat{n}_p+a_3\hat{L}\cdot\hat{L}+a_4\hat{D}\cdot\hat{D} \ , \tag{3.1}$$

where

$$\begin{aligned}\hat{n}_p&=p^{\dagger}\cdot\tilde{p}=-\sqrt{3}(p^{\dagger}\tilde{p})^{(0)} \ ,\\ \hat{L}_{\mu}&=\sqrt{2}(p^{\dagger}\tilde{p})_{\mu}^{(1)} \ ,\\ \hat{D}_{\mu}&=(s^{\dagger}\tilde{p}+p^{\dagger}s)_{\mu}^{(1)} \ ,\end{aligned} \tag{3.2}$$

with $\tilde{p}_{\mu}=(-1)^{\mu}p_{-\mu}$. In the above equations (3.1) and (3.2) $\hat{n}_p$ is the number operator for p vibrons, $\hat{L}$ is the angular momentum operator, and $\hat{D}$ is a dipole operator. By construction, the Hamiltonian of Eq. (3.1) conserves the total number of vibrons,

$$[H,\hat{N}]=0 \ , \tag{3.3}$$

where $\hat{N}$ is the number operator

$$\hat{N}=\hat{n}_s+\hat{n}_p=s^{\dagger}s+p^{\dagger}\tilde{p} \tag{3.4}$$

Therefore, all eigenstates of H can be labeled by $[N]$, the symmetric representations of U(4). The first term in Eq. (3.1) contains all terms that only contribute to the binding energy and not the excitation energies. It can therefore only depend on the number operator $\hat{N}$:

$$H_0=a_0+a_0'\hat{N}+a_0''\hat{N}^2 \ . \tag{3.5}$$

Given N and H the energy spectrum can be obtained by diagonalizing H in an appropriate basis. It is interesting to note that the vibron model Hamiltonian has two dynamical symmetries, which are related to two different chains of subgroups of U(4),

$$\mathrm{U}(4)\supset\mathrm{U}(3)\supset\mathrm{O}(3)\supset\mathrm{O}(2) \ , \tag{3.6a}$$

$$\mathrm{U}(4)\supset\mathrm{O}(4)\supset\mathrm{O}(3)\supset\mathrm{O}(2) \ . \tag{3.6b}$$

In a dynamical symmetry the Hamiltonian is written in terms of only invariants of the subgroups appearing in the corresponding group chains and as such represents a special case of the more general Hamiltonian of Eq. (3.1). The advantage of these dynamical symmetries is that it is possible to derive analytic expressions for the energy spectra, transition probabilities, etc., which can be used easily to analyze the experimental data.

To calculate electromagnetic transition rates for dipole ($E1$) radiation one has to express the $E1$ operator in terms of vibron operators. In Ref. 3 the following form of the $E1$ operator was suggested,

$$\begin{aligned}T_{\mu}^{(1)}=&\,d_1\hat{D}_{\mu}+d_2(\hat{n}_p\hat{D}+\hat{D}\,\hat{n}_p)_{\mu}^{(1)}\\ &+d_3(\hat{L}\,\hat{D}+\hat{D}\,\hat{L})_{\mu}^{(1)}+d_4(\hat{Q}\,\hat{D}+\hat{D}\,\hat{Q})_{\mu}^{(1)}+\cdots \ ,\end{aligned} \tag{3.7}$$

where the ellipsis represent higher-order terms and $\hat{Q}$ is a quadrupole operator

$$\hat{Q}_{\mu}=(p^{\dagger}\tilde{p})_{\mu}^{(2)} \ . \tag{3.8}$$

We discuss the dipole operator in more detail in the next section.

IV. TRANSITION MATRIX ELEMENTS IN THE VIBRON MODEL

The transition matrix elements, Eq. (2.14) can be evaluated in the context of the vibron model by using explicitly its algebraic properties. For the excitation of low-lying states in diatomic molecules, it is a reasonably good approximation to keep only the first term in the dipole operator,[3,9] Eq. (3.7),

$$T_{\mu}^{(1)}=d\hat{D}_{\mu}=d(s^{\dagger}\tilde{p}+p^{\dagger}s)_{\mu}^{(1)} \ . \tag{4.1}$$

Since the dipole operator in Eq. (4.1) is linear in the generators of U(4), the transition operator of Eq. (2.14),

$$\begin{aligned}\hat{U}(\epsilon)&=e^{i\epsilon\hat{D}_{\mu=0}} \ ,\\ \epsilon&=\epsilon(b)=dg(b) \ ,\end{aligned} \tag{4.2}$$

can be regarded as a U(4) transformation and the transition matrix element

$$U_{fi}=\langle f\mid\hat{U}(\epsilon)\mid i\rangle \ , \tag{4.3}$$

as a U(4) representation matrix. The representation matrix for many bosons (vibrons) can be derived from a transformation of the single bosons,

$$\begin{aligned}\hat{U}(\epsilon)s^{\dagger}\hat{U}(-\epsilon)&=s^{\dagger}+i\epsilon[\hat{D}_0,s^{\dagger}]\\ &\qquad+\frac{1}{2!}(i\epsilon)^2[\hat{D}_0,[\hat{D}_0,s^{\dagger}]]+\dots\\ &=(\cos\epsilon)s^{\dagger}+i(\sin\epsilon)p_0^{\dagger} \ ,\\ \hat{U}(\epsilon)p_0^{\dagger}\hat{U}(-\epsilon)&=i(\sin\epsilon)s^{\dagger}+(\cos\epsilon)p_0^{\dagger} \ ,\\ \hat{U}(\epsilon)p_{\mu}^{\dagger}\hat{U}(-\epsilon)&=p_{\mu}^{\dagger}, \ \ \mu\neq 0 \ .\end{aligned} \tag{4.4}$$

In general the transition matrix element can be expressed in terms of a three-dimensional integration.[10] However, using the symmetry properties of the transition operator of Eq. (4.2) we show in the Appendix that in this case the general expression for the transition matrix element can be simplified to a single integral. If the Hamiltonian has a dynamical symmetry, it is possible to derive closed analytic expressions for the transition matrix elements. In the next two parts of this section we will present the results for the U(3) and the O(4) chains of (3.6a) and (3.6b), respectively.

A. U(3) limit

The U(3) limit arises if we take $a_4=0$ in the Hamiltonian Eq. (3.1). The ground state then contains only s bosons while the excited states are labeled by the number of p bosons, n,

$$n=0,1,\dots,N\;. \tag{4.5}$$

For a given value of n there is a multiplet of states with different values of the angular momentum, l,

$$l=n,n-2,\dots,1,\text{ or }0\;, \tag{4.6}$$

and its third component, m,

$$m=-l,-l+1,\dots,l\;. \tag{4.7}$$

The eigenstates in the U(3) limit are monomials of rank N-n in the s bosons and of rank n in the p bosons,

$$|\,[N],n,l,m\,\rangle=A^N_{nl}(s^\dagger)^{N-n}(p^\dagger\cdot p^\dagger)^{1/2(n-l)}\,|\,[l],l,l,m\,\rangle\;, \tag{4.8}$$

where A^N_{nl} is a normalization constant

$$A^N_{nl}=\left[\frac{(2l+1)!!}{(N-n)!(n+l+1)!!(n-l)!!}\right]^{1/2}, \tag{4.9}$$

and $|\,[l],l,l,m\,\rangle$ is proportional to a solid harmonic in $p^\dagger$

$$\begin{aligned}|\,[l],l,l,m\,\rangle&=\left[\frac{4\pi}{(2l+1)!!}\right]^{1/2}\mathcal{Y}_{lm}(p^\dagger)\,|\,0\rangle\;,\\ \mathcal{Y}_{lm}(p^\dagger)&=\left[\frac{2l+1}{4\pi}\right]^{1/2}\frac{\sqrt{(l+m)!(l-m)!}}{l!2^l}\\ &\quad\times\sum_{k=0}^{l-|m|}{}'\begin{bmatrix}l\\k\end{bmatrix}\begin{bmatrix}l-k\\\frac{1}{2}(l-k)\end{bmatrix}2^{(l+k)/2}\\ &\quad\times(p_0^\dagger)^k(p_{-1}^\dagger)^{1/2(l-k-m)}(p_1^\dagger)^{1/2(l-k+m)}\;.\end{aligned} \tag{4.10}$$

For the present we assume that the molecule is excited from its ground state, $n=l=m=0$. The action of the transition operator on the ground state is

$$\begin{aligned}\hat{U}(\epsilon)\,|\,[N],n=l=m=0\rangle\\ =\frac{1}{\sqrt{N!}}[(\cos\epsilon)s^\dagger+i(\sin\epsilon)p_0^\dagger]^N\,|\,0\rangle\;.\end{aligned} \tag{4.11}$$

Taking the overlap with an arbitrary final state the transition matrix element in the U(3) limit is

$$\begin{aligned}U^N_{nlm}(\epsilon)&=\langle[N],n,l,m\,|\,\hat{U}(\epsilon)\,|\,[N],n'=l'=m'=0\rangle\\ &=\delta_{m,0}\left[\frac{N!(2l+1)}{(N-n)!(n+l+1)!!(n-l)!!}\right]^{1/2}\\ &\quad\times(\cos\epsilon)^{N-n}(i\sin\epsilon)^n\;.\end{aligned} \tag{4.12}$$

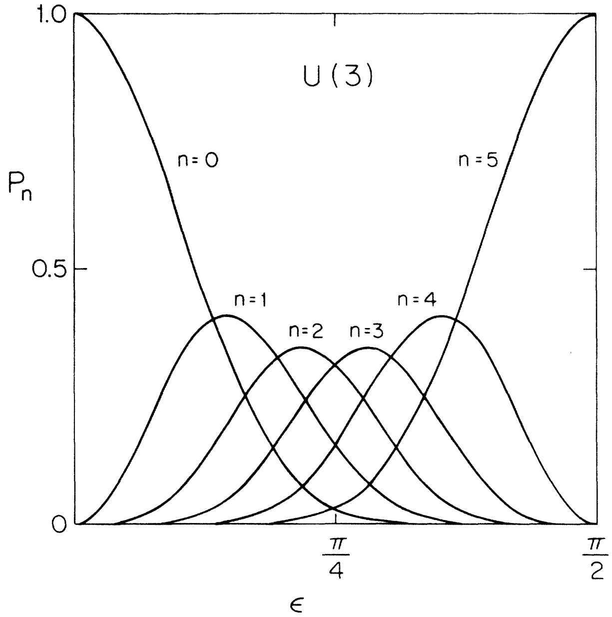

FIG. 1. Probability, $P_n(\epsilon)$, of exciting a state belonging to the vibrational multiplet, n, in the U(3) limit as a function of the strength parameter ϵ. The number of bosons is $N=5$.

In Fig. 1 we show the probability, $P_n(\epsilon)$, that a state belonging to a vibrational multiplet characterized by the quantum number n can be excited,

$$\begin{aligned}P_n(\epsilon)&=\sum_l|\,U^N_{nlm=0}(\epsilon)\,|^2\\ &=\begin{bmatrix}N\\n\end{bmatrix}(\cos^2\epsilon)^{N-n}(\sin^2\epsilon)^n\;,\end{aligned} \tag{4.13}$$

as a function of ϵ. For $\epsilon=0$ of course only the ground state ($n=0$) can be excited. With increasing ϵ all excited states will be populated until for $\epsilon=\pi/2$ only the states belonging to the highest vibrational multiplet ($n=N$) can be excited. In Fig. 1 we only show $P_n(\epsilon)$ for the interval $0\le\epsilon\le\pi/2$. Since $P_n(\epsilon)$ is symmetric around $\epsilon=\pi/2$ and is a periodic function with period π,

$$P_n(\epsilon)=P_n(\pi\pm\epsilon)\;, \tag{4.14}$$

implying that for $\epsilon=\pi$ all strength again is concentrated in the ground state. This behavior is an artifact of the finiteness of the model space of the vibron model. However, if ϵ is sufficiently small with respect to π, it is still a good approximation to use the vibron model and the final result will not be influenced by the finite number of states. In the next section, where we will discuss some applications of this approach, we will come back to this point.

For large N the energy spectrum of the U(3) limit of the vibron model corresponds to that of a three-dimensional harmonic oscillator[9,11] and the transition matrix elements become even simpler functions of ϵ. In taking this limit we have to take into account the fact that the strength of the dipole operator, d, Eq. (4.1), scales with the reduced matrix element of the dipole operator,

$$d=\frac{\bar{d}}{\langle[N],1,1||\hat{D}||[N],0,0\rangle}=\frac{\bar{d}}{\sqrt{3N}}\;. \tag{4.15}$$

Similarly, we introduce a reduced ϵ by $\epsilon=\bar{\epsilon}/\sqrt{3N}$ with

$$\bar{\epsilon}=\bar{d}g(b)\ . \tag{4.16}$$

For N large, ϵ becomes small while $\bar{\epsilon}$ remains finite. Assuming further that $n/N \ll 1$, the large-N limit of the transition matrix element in the U(3) limit is

$$\lim_{N\to\infty} U^N_{nl0}(\epsilon)=i^n\left[\frac{2l+1}{(n+l+1)!!(n-l)!!}\right]^{1/2} \times\left[\frac{\bar{\epsilon}}{\sqrt{3}}\right]^n e^{-\bar{\epsilon}^2/6} \tag{4.17}$$

for $\bar{\epsilon} \ll \sqrt{3N}$ and $n \ll N$.

B. O(4) limit

The Hamiltonian, Eq. (3.1), has O(4) symmetry if we take $a_1=a_2=0$. The energy spectrum in the O(4) limit is characterized by a series of bands that are labeled by the quantum number σ,

$$\sigma=N,N-2,\ldots,1 \textit{ or } 0\ . \tag{4.18}$$

For a given value of σ the allowed values of the angular momentum l are

$$l=0,1,\ldots,\sigma\ . \tag{4.19}$$

The eigenstates in the O(4) limit are

$$|\,[N],\sigma,l,m\,\rangle=B^N_\sigma(s^\dagger s^\dagger-p^\dagger\cdot p^\dagger)^{1/2(N-\sigma)}\,|\,[\sigma],\sigma,l,m\,\rangle\ , \tag{4.20}$$

where B^N_σ is a normalization constant

$$B^N_\sigma=\left[\frac{(2\sigma+2)!!}{(N+\sigma+2)!!(N-\sigma)!!}\right]^{1/2} \tag{4.21}$$

and the state with $N=\sigma$ can be written

$$|\,[\sigma],\sigma,l,m\,\rangle=\sum_{k=0}^{[1/2(\sigma-l)]} F_k(\sigma,l)(s^\dagger)^{\sigma-l-2k}(s^\dagger s^\dagger-p^\dagger\cdot p^\dagger)^k \times|\,[l],l,l,m\,\rangle \tag{4.22}$$

with

$$F_k(\sigma,l)=\left[\frac{2^\sigma(\sigma-l)!(2l+1)!!}{\sigma!(\sigma+l+1)!}\right]^{1/2} \times(-\tfrac{1}{4})^k\frac{(\sigma-k)!}{(\sigma-l-2k)!k!}\ . \tag{4.23}$$

As before, the state $|\,[l],l,l,m\,\rangle$ is proportional to the solid harmonics in $p^\dagger$, Eq. (4.10). In Eqs. (4.20) and (4.22) we have introduced the operator

$$I^\dagger=s^\dagger s^\dagger-p^\dagger\cdot p^\dagger\ . \tag{4.24}$$

Since $I^\dagger$ commutes with all generators of O(4), including the dipole operator $\hat{D}_\mu$ of Eq. (4.1),

$$[\hat{D}_\mu,I^\dagger]=0\ , \tag{4.25}$$

it is invariant under the action of the transition operator $\hat{U}(\epsilon)$:

$$\hat{U}(\epsilon)I^\dagger\hat{U}(-\epsilon)=I^\dagger\ . \tag{4.26}$$

Again, we assume that the molecule is excited from its ground state $\sigma=N,l=m=0$. Since the dipole operator is a generator of O(4), it cannot connect different representations of O(4). Therefore, only states belonging to the ground-state band, $\sigma=N$, can be excited. The action of the transition operator on the ground state is

$$\hat{U}(\epsilon)\,|\,[N],\sigma=N,l=m=0\rangle =\sum_{k=0}^{[N/2]} F_k(N,0)[(\cos\epsilon)s^\dagger+i(\sin\epsilon)p_0^\dagger]^{N-2k}(I^\dagger)^k\,|\,0\rangle\ . \tag{4.27}$$

Taking the overlap of Eq. (4.27) with an arbitrary final state we obtain, after some algebra, the following expression for the transition matrix element

$$U^N_{\sigma lm}(\epsilon)=\langle\,[N],\sigma,l,m\,|\,\hat{U}(\epsilon)\,|\,[N],\sigma'=N,l'=m'=0\rangle =\delta_{\sigma,N}\delta_{m,0}\left[\frac{2^N N!(2l+1)}{(N+1)(2l+1)!!}\right]^{1/2}(i\sin\epsilon)^l \times\sum_{k=0}^{[1/2(N-l)]}F_k(N,l)(\cos\epsilon)^{N-2k-l}\ . \tag{4.28}$$

This expression can be rewritten in terms of ultraspherical (Gegenbauer) polynomials[12]

$$U^N_{Nlm=0}(\epsilon)=\left[\frac{(2l+1)(N-l)!}{(N+1)(N+l+1)!}\right]^{1/2}(i\sin\epsilon)^l l!2^l \times C^{(l+1)}_{N-l}(\cos\epsilon)\ , \tag{4.29}$$

or equivalently in terms of hypergeometric functions[12]

$$U^N_{Nlm=0}(\epsilon)=\left[\frac{(2l+1)(N+l+1)!}{(N+1)(N-l)!}\right]^{1/2}(i\sin\epsilon)^l l!2^l\frac{1}{(2l+1)!}\,{}_2F_1(-\tfrac{1}{2}(N-l),\tfrac{1}{2}(N+l+2);l+\tfrac{3}{2};\sin^2\epsilon)\ . \tag{4.30}$$

As an illustration, we show in Fig. 2 the probability, $P_l(\epsilon)$ that a state with angular momentum l belonging to the ground-state band $\sigma=N$, can be excited,

$$P_l(\epsilon)=|\,U^N_{Nlm=0}(\epsilon)\,|^2\ . \tag{4.31}$$

Again we see that with increasing ϵ all states in the ground-state band are successively populated until for $\epsilon=\pi/2$ the state with maximum angular momentum $l=N$ has the highest probability. The probability function, $P_l(\epsilon)$, Eq. (4.31), has the same symmetry properties

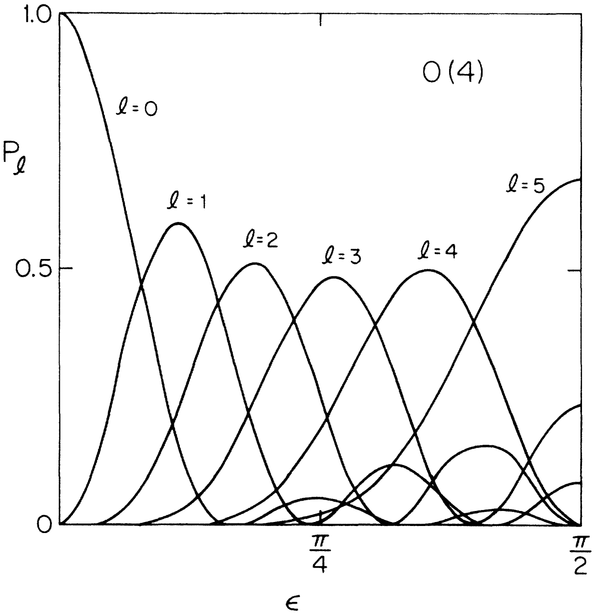

FIG. 2. Probability, $P_l(\epsilon)$, of exciting a state with angular momentum, l, belonging to the ground-state band $\sigma=N$ of the O(4) limit, as a function of ϵ. The number of bosons is $N=5$.

as $P_n(\epsilon)$ in the U(3) limit, Eq. (4.14).

For large N the energy spectrum of the O(4) limit of the vibron model corresponds to that of a Morse oscillator.[9,11] In taking this limit again we introduce the reduced ϵ by

$$\epsilon=\frac{\bar{\epsilon}}{\langle[N],N,1\|\hat{D}\|[N],N,0\rangle}=\frac{\bar{\epsilon}}{\sqrt{N(N+2)}} . \tag{4.32}$$

Assuming that for large N, $\bar{\epsilon}$ remains finite and $l/N \ll 1$, the transition matrix element can be expressed in terms of a spherical Bessel function

$$\lim_{N\to\infty} U^N_{Nl0}(\epsilon)=i^l\sqrt{2l+1}\,j_l(\bar{\epsilon}) \tag{4.33}$$

for $\bar{\epsilon} \ll N$ and $l \ll N$. We note that the scattering amplitude Eq. (2.11) for the large-N limit of the O(4) case is identical to that in the classical "rotor" calculation of Ashihara *et al.*[7]

V. APPLICATIONS

In this section we will discuss some schematic calculations in the algebraic-eikonal approach to electron scattering from a diatomic molecule. These calculations are meant primarily to be exploratory and to illustrate the method. To be concrete we choose as an example the scattering of 5-eV electrons from a strongly polar diatomic molecule with a dipole moment of $\bar{d}=10$ D$=2.08$ e Å (e.g., CsCl has $\bar{d}=10.42$ D). We will present the results for three different cases: (a) the U(3) limit (three-dimensional harmonic oscillator), (b) the O(4) limit (Morse oscillator), and (c) a mixed case. The total number of bosons, N, can be determined by the number of vibrational bands.[2,3] For example, the spectrum of H_2 $({}^1\Sigma_g^+)$ was described in Refs. 2 and 3 in terms of the O(4) limit of the vibron model with $N=29$. In the following we have chosen $N=20$. We note that the results for elastic scattering (ground state to ground state) and for the excitation of the low-lying rotational ($l \ll N$) and vibrational ($n \ll N$) states do not depend on N [see Eqs. (4.17) and (4.33)]. Next we have to specify the form of $\alpha(r)$ of Eq. (2.6). A pure dipole form $\alpha(r)\approx 1/r^2$ makes no sense physically since the actual atomic and molecular structure will remove the singularity at small r. We therefore take

$$\alpha(r)=\frac{e}{r^2+R_0^2} . \tag{5.1}$$

For 5-eV electrons and a dipole moment of 10 D, there is little sensitivity to R_0 so long as it is in the range 0.2 Å $\lesssim R_0 \lesssim 0.75$ Å. For the present schematic calculations we take $R_0=0.50$ Å. With this choice for $\alpha(r)$ the coefficient ϵ of Eq. (4.2) becomes

$$\epsilon=\epsilon_0 f\left[\frac{b}{R_0}\right] , \tag{5.2a}$$

$$\epsilon_0=\frac{m_e e d}{\hbar^2 k R_0}=\frac{m_e e\bar{d}}{\hbar^2 k R_0\langle 1_1^-\|\hat{D}\|0_1^+\rangle} , \tag{5.2b}$$

$$f(x)=\frac{x}{(1+x^2)^{1/2}}\ln\left[\frac{(1+x^2)^{1/2}+1}{(1+x^2)^{1/2}-1}\right] . \tag{5.2c}$$

For the molecular Hamiltonian we take

$$H'_{\rm mol}=a_1\hat{n}_p+a_4\hat{D}\cdot\hat{D} , \tag{5.3}$$

with $a_1>0$, $a_4=0$ in the U(3) limit and $a_1=0$, $a_4<0$ in the O(4) limit. For the mixed case, $a_1>0$ and $a_4<0$. In Table I we show the value of the parameters a_1 and a_4, the corresponding value of ϵ_0, Eq. (5.2b) and the excitation energies of the 1_1^-, 0_2^+, and 1_2^- states. We note that for this realistic choice of the parameters the effect of the band cutoff on the differential cross sections is negligible.

After having specified all parameters we now study elastic scattering ($0_1^+\to 0_1^+$), the excitation of the first rotational state ($0_1^+\to 1_1^-$) and the excitation of the first vibrational states ($0_1^+\to 0_2^+, 1_2^-$). In contrast with the classical rigid-motor model,[7] in the algebraic approach the coupling to vibrational states is taken into account automatically when $a_1\neq 0$. The calculation of the scattering amplitude, Eq. (2.11) is numerically sensitive because of the long range of the dipole interaction. To improve the convergence we first subtract the terms up to fourth order in the coupling parameter ϵ [Eqs. (5.2) and (4.2)] from the integrand of Eq. (2.11) and later add the contributions of these terms to the scattering amplitude.

In Fig. 3 we show the calculation of the cross section for elastic scattering ($0_1^+\to 0_1^+$) and for the excitation of the first 0^+ vibrational state ($0_1^+\to 0_2^+$) for the U(3) case. Also shown is the lowest-order contribution for the elastic scattering. Since in our model there is no diagonal electron-molecule coupling, the lowest-order contribution is of second order (quadratic) in the coupling strength ϵ of Eq. (5.2). The significant difference between this lowest-order contribution and the full calculation shows the importance of the multiple scattering or equivalently of the

TABLE I. Values of the parameters in H'_{mol}, Eq. (5.3). The corresponding value of ϵ_0 and the excitation energies of the 1_1^-, 0_2^+, and 1_2^- states in units of A_i, $i=1,2,3$. The results for the cross sections are independent of A_i. The number of bosons is $N=20$.

				E_{ex}/A_i		
	a_1	a_4	ϵ_0	1_1^-	0_2^+	1_2^-
U(3)	A_1	0	0.887	1	2	3
O(4)	0	$-A_2$	0.327	2	80	82
Mixed	$76A_3$	$-A_3$	0.571	31.7	82.0	130.4

channel coupling.

In Fig. 4 we show the $0_1^+ \to 0_1^+$ cross section in the O(4) limit. In this limit the dipole operator can only excite states belonging to the ground-state rotational band. The excitation of vibrational states, e.g., $0_1^+ \to 0_2^+$ is forbidden in this case. The lowest-order contribution to the cross section is the same as for the U(3) case since it only depends on the dipole moment $\bar{d}$. Again the full result differs very significantly from the lowest-order contribution showing the importance of channel coupling. The cross section for elastic scattering is very similar in the U(3) and O(4) limits, indicating that it is controlled almost entirely by the value of the dipole moment.

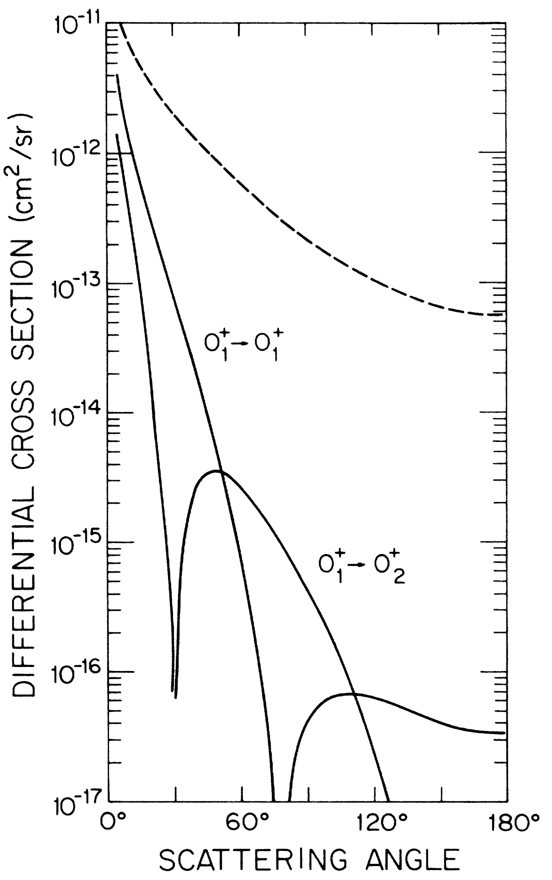

FIG. 3. Differential cross section for elastic scattering ($0_1^+ \to 0_1^+$) and the excitation of the first vibrational 0^+ state ($0_1^+ \to 0_2^+$) in the U(3) limit [$a_1 > 0$, $a_4 = 0$ in Eq. (5.3)]. The dashed curve shows the lowest-order ($\sim \epsilon^2$) contribution to the differential cross section for elastic scattering. The parameters used in the calculation are discussed in the text and Table I. The number of bosons is $N=20$.

Fig. 5 shows the mixed case for elastic scattering and for the $0_1^+ \to 0_2^+$ transition. The lowest-order contribution to the elastic cross section is, by construction, the same as in the two previous cases (see Figs. 3 and 4). The cross section for the excitation of the first 0^+ vibrational state is very different, since it depends on the details of the mixing.

In Fig. 6 we show the cross sections for excitation of the first and second excited 1^- states in the U(3) limit. Also shown is the Born approximation for the first excited 1^- state. In this case the Born amplitude is of first order in the coupling parameter ϵ, and the first-order eikon-

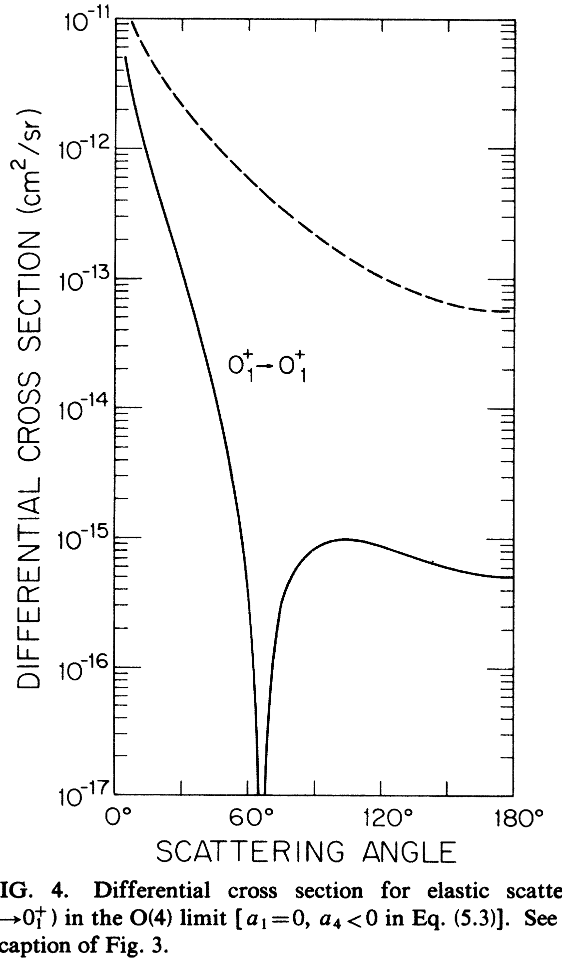

FIG. 4. Differential cross section for elastic scattering ($0_1^+ \to 0_1^+$) in the O(4) limit [$a_1 = 0$, $a_4 < 0$ in Eq. (5.3)]. See also the caption of Fig. 3.

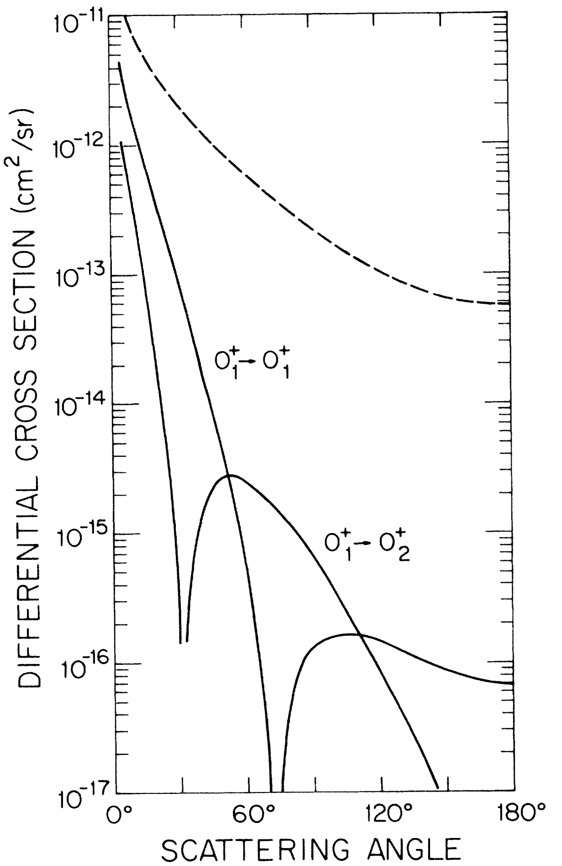

FIG. 5. Differential cross section for elastic scattering $(0_1^+ \rightarrow 0_1^+)$ and the excitation of the first vibrational 0^+ state $(0_1^+ \rightarrow 0_2^+)$ for a general case $[a_1 > 0,\ a_4 < 0$ in Eq. (5.3)]. See also the caption of Fig. 3.

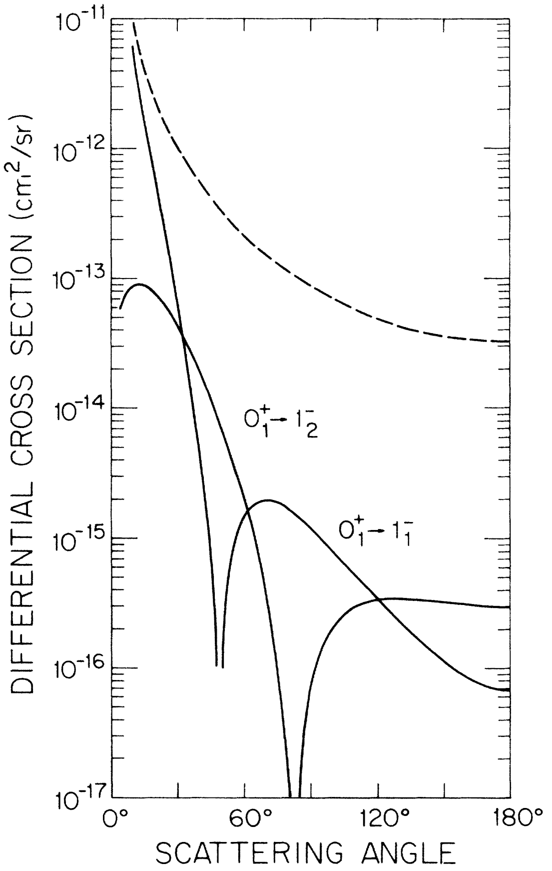

FIG. 6. Differential cross section for the excitation of the first and second excited 1^- states $(0_1^+ \rightarrow 1_{1,2}^-)$ in the U(3) limit $[a_1 > 0,\ a_4 = 0$ in Eq. (5.3)]. The dashed curve shows the lowest-order $(\sim\epsilon)$ contribution to the $0_1^+ \rightarrow 1_1^-$ transition. See also the caption of Fig. 3.

al and true Born approximation are identical. Again we see that except for the smallest angles (most peripheral collisions), the effects of channel coupling are very important.

In Fig. 7 we show the corresponding O(4) result. The excitation of the first vibrational 1^- state is forbidden. The 1_1^- cross section differs a bit in detail from that in the U(3) limit, but both are still largely controlled by the dipole moment.

Fig. 8 shows the 1_1^- and 1_2^- excitation cross section in the mixed case. The 1_1^- cross section is little changed, as we expect, but the 1_2^- cross section is very sensitive to the mixing. In particular, since the effect of mixing is to mix some of the 1_1^- state into the 1_2^-, the 1_2^- cross section has the same strong forward peak as the 1_1^-.

In Figs. 3–8 we have shown the cross sections for $0° \leq \theta < 180°$ although we realize that strictly speaking the eikonal approximation is only valid for small angles. In Ref. 7, Ashihara *et al.* studied electron scattering from CsCl in a rigid-rotor model assuming a pure dipole interaction for the electron-molecule interaction. Since our approach contains the rigid-rotor model as a limiting case [O(4) symmetry and large N), we obtain similar agreement with what experimental data exist for CsCl.

VI. SUMMARY AND OUTLOOK

We have proposed a new algebraic method describing electron scattering off diatomic molecules. Our approach is to combine the Glauber or eikonal adiabatic approximation and the recently introduced vibron model for the description of the molecular states. In the vibron model the transition matrix elements have been derived in closed form and to all orders in the coupling constants, using algebraic techniques. This is equivalent to performing a complete close-coupling calculation in the adiabatic approximation.

Beyond its inherent simplicity, this approach has the advantage that molecular vibrational states can be treated on the same footing as rotational states. This clearly cannot be done in the classical rigid-rotor case. We have presented a series of schematic calculations for the cross sections for elastic scattering and the excitation of both rotational and vibrational states. In these calculations we have made a number of simplifying assumptions. We have taken only a pure dipole coupling and used a rather simple form for the radial part of this coupling. Both of these assumptions can easily be relaxed. In particular, since the algebraic-eikonal approach gives wave functions,

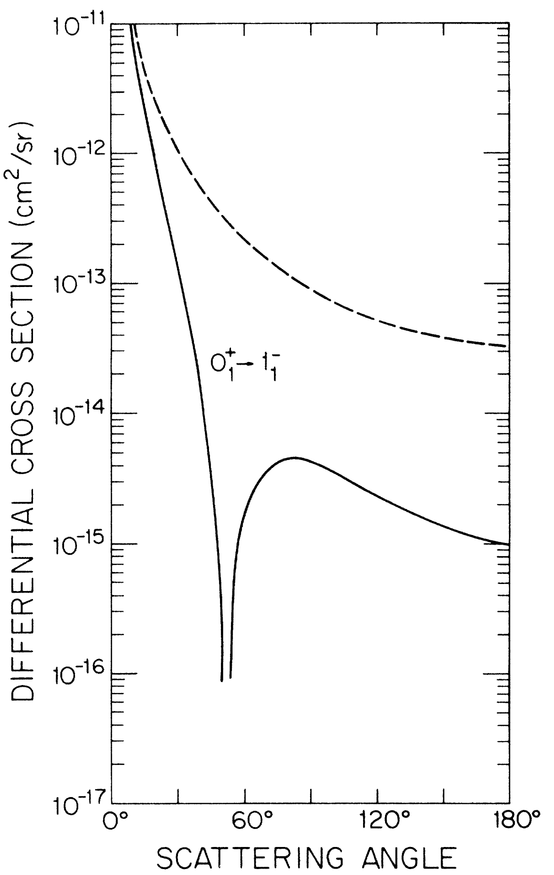

FIG. 7. Differential cross section for the excitation of the first excited 1^- state ($0_1^+ \rightarrow 1_1^-$) in the O(4) limit [$a_1=0$, $a_4<0$ in Eq. (5.3)]. See also the caption of Fig. 6.

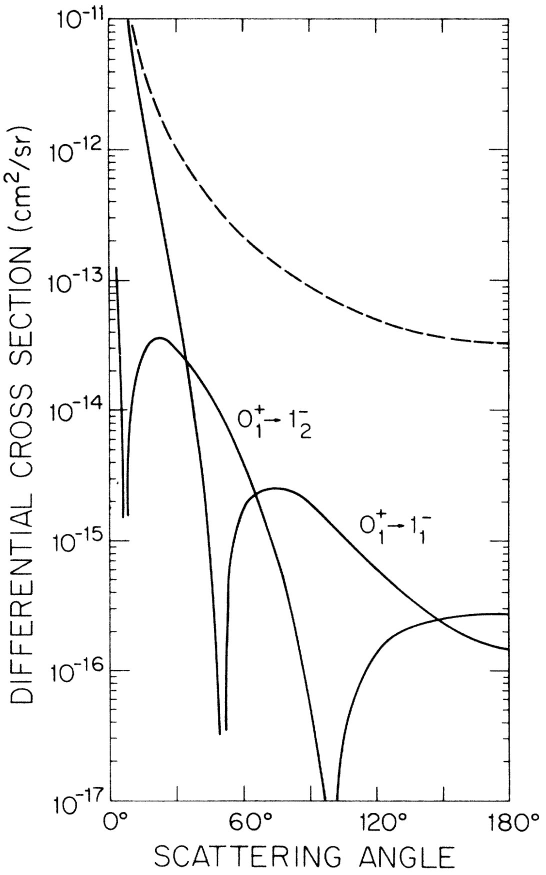

FIG. 8. Differential cross section for the excitation of the first and second excited 1^- states ($0_1^+ \rightarrow 1_{1,2}^-$) for a general case [$a_1>0$, $a_4<0$ in Eq. (5.3)]. See also the caption of Fig. 6.

correction terms can easily be included either exactly or in perturbation theory. Furthermore, we have used the adiabatic approximation. That is, we have neglected the molecular Hamiltonian. Especially for processes which are dominated by long-range interaction, the inclusion of nonadiabatic effects may become important. We are presently working on a method to incorporate these effects and will report on them separately.

In this paper we have restricted ourselves to diatomic molecules. The algebraic approach may become particular useful in the treatment of more complex molecules. The vibron model has already been generalized to describe the energy spectra of triatomic and polyatomic molecules.[5,6] It is straightforward to extend the algebraic-eikonal approach to electron scattering from these more complex molecules. This will be the subject of the next paper in this series. Another possible extension is to molecular collisions with other probes (protons, atoms, etc.)

Finally we wish to point out that a similar algebraic approach[13] has been applied to multistep processes in hadron-nucleus scattering[14–16] and in electromagnetic excitation of nuclei.[17] In conclusion, algebraic methods may provide a useful alternative to the coupled channels approach to multiple-step processes in both molecular and nuclear processes.

ACKNOWLEDGMENTS

We are grateful to Dr. O. S. van Roosmalen for providing a program to calculate the transition matrix elements and to Dr. W. Reinhardt for encouraging discussions. This work was supported in part by a grant from the National Science Foundation.

APPENDIX

In general, the U(4) representation matrices can be expressed in terms of a three-dimensional integral.[10] However, in Sec. II we have shown that for a dipole interaction, Eq. (2.6), the transition operator $\hat{U}(\epsilon)$ only depends on the z component of the dipole operator, Eq. (2.10)

$$\hat{U}(\epsilon)=\exp(i\epsilon\hat{D}_{\mu=0}) , \qquad (A1)$$

where we have used the notation of Eq. (4.2). In the following we will show by explicitly using the symmetry properties of $\hat{D}_0$, that the matrix elements of $\hat{U}(\epsilon)$ can be expressed in terms of a one-dimensional integral only.

Since the transition operator of (A1) is an O(4) group element, it is diagonal in the O(4) basis and its matrix elements do not depend on the number of vibrons, N. In addition it is diagonal in the magnetic substates, m,

$$\langle [N],\sigma,l,m \mid \hat{U}(\epsilon) \mid [N],\sigma',l',m' \rangle = \delta_{\sigma\sigma'}\delta_{mm'}\langle [\sigma],\sigma,l,m \mid \hat{U}(\epsilon) \mid [\sigma],\sigma,l',m \rangle \; . \tag{A2}$$

The matrix elements on the right-hand side of Eq. (A2) can be evaluated using three properties of coherent states[18]

$$\mid [\sigma],\alpha_\mu \rangle = \frac{1}{\sqrt{\sigma!}}[(1-\mid\alpha\mid^2)^{1/2}s^\dagger + \alpha\cdot p^\dagger]^\sigma \mid 0 \rangle \; . \tag{A3}$$

Firstly, O(4) basis states with $N=\sigma$ can be projected out from the coherent state

$$\mid [\sigma],\sigma,l,m \rangle = \frac{1}{\sigma!}\left[\frac{(\sigma+l+1)!(\sigma-l)!}{4\pi}\right]^{1/2} \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\varphi \, Y_{lm}(\theta,\varphi) \mid [\sigma],\alpha_\mu(\chi=0,\theta,\varphi) \rangle \; . \tag{A4}$$

with

$$\alpha_\mu(\chi,\theta,\varphi) = \frac{1}{\sqrt{2}} e^{i\chi} D^{(1)}_{\mu 0}(\varphi,\theta,0) \; . \tag{A5}$$

Secondly, the action of $\hat{U}(\epsilon)$ on the coherent state is

$$\hat{U}(\epsilon) \mid [\sigma],\alpha_\mu \rangle = e^{i\beta\sigma} \mid [\sigma],\alpha'_\mu \rangle \; , \tag{A6}$$

and thirdly the overlap of (A3) with an O(4) basis state is given by [cf. Eq. (4.22)]

$$\langle [\sigma],\sigma,l,m \mid [\sigma],\alpha_\mu \rangle = \sqrt{\sigma!} \sum_{k=0}^{[1/2(\sigma-l)]} F_k(\sigma,l)(1-\mid\alpha\mid^2)^{1/2(\sigma-l-2k)}(1-\mid\alpha\mid^2-\alpha\cdot\alpha)^k \left[\frac{4\pi}{(2l+1)!!}\right]^{1/2} \mathcal{Y}^*_{lm}(\alpha) \; . \tag{A7}$$

Combining Eqs. (A1) and (A4)—(A7) we obtain the following expression for the matrix element of Eq. (A2):

$$\begin{aligned} &\langle [\sigma],\sigma,l,m \mid \hat{U}(\epsilon) \mid [\sigma],\sigma,l',m \rangle \\ &\quad = 2\pi \left[\frac{2^\sigma(\sigma+l'+1)!(\sigma-l')!}{(\sigma+l+1)!(\sigma-l)!}\right]^{1/2} e^{i\beta\sigma} \int_{-1}^{1} d(\cos\theta) Y_{l'm}(\theta,\varphi=0)(1-\mid\alpha'\mid^2)^{1/2(\sigma-l)} \mathcal{Y}^*_{lm}(\alpha') \; , \\ &\qquad \alpha' = \alpha'(\chi=0,\theta,\varphi=0,\epsilon) \; . \end{aligned} \tag{A8}$$

By expanding the eigenstates of the most general one- and two-body vibron Hamiltonian, Eq. (3.1) in the O(4) basis as

$$\mid [N],v,l,m \rangle = \sum_\sigma a^v_\sigma(l) \mid [N],\sigma,l,m \rangle \; , \tag{A9}$$

the matrix elements of $\hat{U}(\epsilon)$ between eigenstates of H are given by

$$\begin{aligned} \langle [N],v,l,m \mid \hat{U}(\epsilon) \mid [N],v',l',m' \rangle &= 2\pi\delta_{mm'} \sum_\sigma a^v_\sigma(l) a^{v'}_\sigma(l') \left[\frac{2^\sigma(\sigma+l'+1)!(\sigma-l')!}{(\sigma+l+1)!(\sigma-l)!}\right]^{1/2} e^{i\beta\sigma} \\ &\quad \times \int_{-1}^{1} d(\cos\theta) Y_{l'm}(\theta,\varphi=0)(1-\mid\alpha'\mid^2)^{1/2(\sigma-l)} \mathcal{Y}^*_{lm}(\alpha') \; , \\ &\qquad \alpha' = \alpha'(\chi=0,\theta,\varphi=0,\epsilon) \; . \end{aligned} \tag{A10}$$

Furthermore, the integral over $\cos\theta$ can be replaced by a $(N+1)$-point Gaussian summation due to the fact that the eigenstates of the vibron Hamiltonian are polynomials in the boson operators of order N. In the numerical calculations presented in Sec. V we have used (A10) to evaluate the transition matrix elements.

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