PHYSICAL REVIEW A VOLUME 57, NUMBER 2 FEBRUARY 1998

Semiclassical treatment of electron-molecule scattering within the vibron model

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(Received 23 June 1997)

A semiclassical coupled-channels description of electron-molecule scattering is developed within the vibron model of diatomic molecules. The inclusive quasielastic scattering cross section is calculated for a typical system. The effect of the rotational coupling is taken into account by evaluating a rotationally inclusive cross section. [S1050-2947(98)04001-3]

PACS number(s): 34.80.−i

I. INTRODUCTION

In recent years it has been clearly demonstrated that algebraic methods based on group theory provide a general framework to tackle several problems in molecular structure [1–5]. The success of these methods in the study of rotation-vibration spectra of diatomic, triatomic, and multiatomic molecules was demonstrated by extensive comparison with the experimental data. An important test of any theory of the structure of molecules is provided by scattering observables in the simplest possible systems: electron-molecule systems.

Most of the work that has been done on the electron-molecule scattering within the algebraic model relied on the eikonal approximation [6–9]. The use of the eikonal method allows the extension of the algebraic treatment to scattering problems and allows the evaluation of the S matrix with group theoretic methods. However, there are obvious limitations to the use of the eikonal method, even at the intermediate energies (2–50 eV) considered in Refs. [6–9]. An obvious improvement is to use the semiclassical method based on the WKB approximation [10]. Owing to the fact that the rotational final state of the molecule is usually not resolved, one has to use a generalized scheme for the scattering problem based on coupled channels. The combined use of the semiclassical theory, the coupled-channels formalism, and the vibron model of the structure of diatomic molecules such as LiF and KL is the thrust of the present work.

II. THE VIBRON MODEL OF DIATOMIC MOLECULES

In 1981 Iachello introduced a boson model to describe the molecular states of a diatomic molecule [1]. Building blocks of the model are dipole bosons $p_{\mu}^{+}(\mu=1,0,-1)$ and a scalar boson s^{+}. These bosons describe the vibration of the molecule as a whole. Thus the name vibron model (VM). The total number of vibrational quanta (vibrons), N, is conserved by the interactions in the model. In the intrinsic frame, the vibrational wave functions can be parametrized in terms of three geometric variables, a coordinate β and two Euler angles $\Omega=(\phi,\theta,0)$:

$$|N,v,\beta,\Omega\rangle=R(\Omega)|N,v,\beta\rangle, \tag{1}$$

with the basis states $|N,v\beta\rangle$ given by

$$|N,v,\beta\rangle=\frac{1}{\sqrt{V!(N-V)!}}\,(-\beta s^{+}+\sqrt{1-\beta^{2}}p_{0}^{+})^{v} \times(\sqrt{1-\beta^{2}}s^{+}+\beta p_{0}^{+})^{N-v}|0\rangle, \tag{2}$$

where $R(\Omega)$ is a rotation given by

$$R(\Omega)=e^{-i\phi L_{z}}e^{-i\theta L_{y}}. \tag{3}$$

The parameter β is a variational one, determined by minimizing the expectation value of the molecular Hamiltonian in the ground state $|N,v=0,\beta\rangle$. The intrinsic ground state is a condensate of an appropriate linear combination of s^{+} and p^{+} bosons, which depends on β. The vibrational spectrum is generated by promoting v bosons from the condensate to the orthogonal combination.

Within the vibron model, the electron-molecule interaction is taken to be

$$V(r)=-\frac{ed_{0}}{r^{2}+R_{0}^{2}}\,\hat{r}\cdot\hat{D}\equiv\alpha(r)\hat{r}\cdot\hat{T}, \tag{4}$$

where $\hat{D}$ is the dipole operator in the molecular space

$$\hat{D}_{\mu}=(p^{+}s-s^{+}\tilde{p})_{\mu}^{(1)},\quad \hat{T}=d_{0}\hat{D}. \tag{5}$$

d_0 and R_0 are parameters. The operators $\tilde{p}_{\mu}$ is given by

$$\tilde{p}_{\mu}=(-)^{1-\mu}p_{\mu}. \tag{6}$$

In the next section we develop the coupled-channels scheme for the electron-molecule scattering using Eq. (4) as an in-

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teraction. Both rotational and vibrational excitations are taken into account. The rotational states are not resolved and thus a rotationally inclusive cross section has to be calculated. We address this point in the following section.

III. COUPLED-CHANNELS FORMALISM

We take for the Hamiltonian of the electron-molecule system

$$H=T+H_{\mathrm{mol}}+V(\vec{r})+V_c(r), \tag{7}$$

where $V(\vec{r})$ is given by Eq. (4) and

$$H_{\mathrm{mol}}|nIM_I\rangle=\epsilon_{nI}|nIM_I\rangle, \tag{8}$$

n being the vibrational quantum number and I the associated rotational angular momentum.

If we neglect spin-orbit interaction, one can forget the electron spin. Treat the problem as a zero-spin particle scattering off the molecules. The conserved quantities are the total angular momentum $\vec{J}$ and its Z projection M. We use as an ansatz the total wave function (for fixed J and M)

$$\Psi_{JM}(\vec{r},\xi)=\sum_{nLI}\mathcal{U}^J_{nLI}(r)\Phi^M_{nLI}(\hat{r},\xi), \tag{9}$$

where ξ represents the internal variable of the molecule. $\mathcal{U}^J_{nLI}(r)$ are the relative wave functions of the electron and the molecule for a given total angular momentum I. When the molecule is in the state $|nIM_I\rangle$, the "channel" wave function $\Phi^M_{nLI}(\hat{r},\xi)$ is defined as

$$\Phi^M_{nLI}(\hat{r},\xi)=\sum_{M_LM_I}\langle LM_LIM_I|JM\rangle Y_{LM_L}(\hat{r})|nIM_I\rangle. \tag{10}$$

We are interested in low-energy electron-molecule scattering. We thus shall not use the Glauber (eikonal) approximation but will start with traditional coupled-channels equations. These are obtained by using the equation

$$(H-E)\Psi_{JM}=0 \tag{11}$$

and projecting onto the "channel" wave functions

$$(\Phi^{JM}_{nLI}|(H-E)\Psi_{JM})=0. \tag{12}$$

In Eq. (13), the parentheses indicate that the integral is only over the angular coordinates $\hat{r}$ and over the target internal variables. Using the orthogonality of the channel functions

$$(\phi^{JM}_{nLI}|\Phi^{JM}_{n'L'I'})=\int d\hat{r}\int d\xi\Phi^{JM}_{nLI}(\hat{r},\xi)\Phi^{JM}_{n'L'I'}(\hat{r},\xi)$$
$$=\delta_{nn'}\delta_{LL'}\delta_{II'}, \tag{13}$$

Eq. (13) reduces to the set of coupled (radial) equations

$$(K_L+V_c(r)+\epsilon_{nI}-E)\mathcal{U}^J_{nLI}(r)$$
$$=\sum_{n'L'I'}V^J_{nLI;n'L'I'}(r)\mathcal{U}^J_{n'L'I'}(r). \tag{14}$$

We shall consider an even molecule with ground-state spin of zero. Equation (14) then has to be solved subject to the boundary condition

$$\mathcal{U}^J_{nLI}(r)\xrightarrow[r\to\infty]{}\frac{e^{i\sigma_L(\epsilon_{00})}}{2i}[I_L(k_0r)\delta_{n0}\delta_{I0}\delta_{LJ}$$
$$-S^J_{nLI;0J0}O_L(k_{nI}r)], \tag{15}$$

where σ_L is the Coulomb phase shift, I_L and O_L are the ingoing and outgoing Coulomb wave functions, and $S^J_{nLI;0J0}$ is the scattering matrix element for a transition from the ground state $|L=J,\ J=0\rangle$ to the final state $|nLIJ\rangle$ of the system.

The coupling potential $V_{nLI;n'L'I'}(r)$ is explicitly of the form

$$V^J_{nLI;n'L'I'}(r)=(\Phi^{JM}_{nLI}|\alpha(r)\hat{r}\cdot\vec{T}|\Phi^{JM}_{n'L'I'})$$
$$=\alpha(r)\int d\hat{r}\int d\xi\Phi^{JM*}_{nLI}(\hat{r},\xi)\hat{r}\cdot\vec{T}\Phi^{JM}_{n'L'I'}(\hat{r},\xi), \tag{16}$$

where the operator $\vec{T}$ is a dipole operator that acts only on the internal states of the molecule. Using Racah algebra, one can explicitly express the matrix element as (see Brink and Satchler)

$$V^J_{nLI;n'L'I'}(r)=\alpha(r)(-)^{L'+I'-I}$$
$$\times[(2L+1)(2I+1)]^{1/2}\langle L010|IL'0\rangle$$
$$\times\langle nI\|T\|n'I'\rangle W(LIL'I';J1). \tag{17}$$

Because of the dipole approximation, it can be seen that only states with $L'=L\pm1$ can be excited in the reaction (i.e., successive transitions between opposite parity states). The reduced matrix element $\langle nI\|T\|n'I'\rangle$ is determined by the model used to describe the molecule. Before discussing this, let us consider two possible approximations.

A. Adiabatic approximation

If we assume that the excitation energies of the target are still small compared to the projectile energy, so that we can set $\epsilon_{nI}=0$, then the operator on the left-hand side of Eq. (9) becomes independent of the target angular momentum. Thus, we could hope to reduce the system of coupled equations. On the right-hand side we have the reduced matrix elements $\langle nI\|T\|n'I'\rangle$ in the target space. If we can find a transformation that will diagonalize this, one would eliminate any dependence on the target spins and the coupled equations will describe the scattering of an electron by a deformed field of the molecule.

Strictly, this approximation would be reasonable only for the lowest vibron states we consider dipole excitations. One can set up the matrix $\langle nI\|I\|n'I'\rangle$ and diagonalize the potential in a truncated base, 0^+, 1^-, 2^+, 3^-,...,$I_{\max}$. This will determine a transformation operator $\hat{O}$ such that

$$\sum_{??I^2} \hat{O}^{JK}_{nLI}\langle nLIJ|\hat{r}\cdot I|n'L'I'J\rangle. \tag{18}$$

If we now define new functions

$$\mathcal{U}^{JK}_{L}(r)=\sum_{nI} \hat{O}^{JK}_{nLI}\mathcal{U}^{J}_{nLI}(r), \tag{19}$$

these functions are solutions of the coupled equations

$$[K_L+V_c(r)-E]\mathcal{U}^{JK}_{nLI}(r)=\alpha(r)\sum_{L'} \Gamma^{JK}_{LL'}\mathcal{U}^{JK}_{L'}(r). \tag{20}$$

A new quantum number K now appears as a ‘‘conserved’’ quantum number.

B. Isocentrifugal approximation

The other approximation is the isocentrifugal approximation (this may be the easier one to evaluate). In this, one makes the centrifugal kinetic energy $K_L=K_J$. Then we have

$$(K_J+V_c(r)+\epsilon_{nI}-E)\mathcal{U}^{J}_{nLI}(r)=-\sum V^{J}_{nLI;n'L'I'}\mathcal{U}^{J}_{n'L'I'}(1). \tag{21}$$

Since the operator on the left is independent of L, one can reduce the dimensionality of the coupled equations. One can show that the new functions

$$\mathcal{U}^{J}_{nI}(r)=\sum_{L} \langle I0J0|L0\rangle\mathcal{U}^{J}_{nLI}(r) \tag{22}$$

are solutions of coupled equations

$$\begin{aligned}[K_J+V_c(r)+\epsilon_{ni}-E]&\mathcal{U}^{J}_{nI}(r)\\ &=-\alpha(r)\sum_{n'I'} \langle nI0|T_{10}|n'I'0\rangle\mathcal{U}^{J}_{n'I'}(r).\end{aligned} \tag{23}$$

These are a small number of coupled equations depending upon the number of states (nI) of the molecule one wishes to consider. The *vibron model* can be used in the evaluation of the dipole coupling matrix elements

$$\langle nI0|T_{10}|n'I'0\rangle. \tag{24}$$

The equations are to be solved subject to the boundary condition

$$\mathcal{U}^{J}_{nI}(r)=[\delta_{n0}\delta_{I0}I_J(k_0r)-S^{J}_{nI;00}O_J(k_{nI}r)]. \tag{25}$$

The ‘‘dipole’’ S matrix element will be given by

$$S^{J}_{nLI;0J0}=\langle I0J0|L0\rangle S^{J}_{nI;00} \tag{26}$$

and the scattering amplitude for transition to the state $|nIM_I\rangle$,

$$\begin{aligned}A_{nIM_I;000}(0,\phi)\propto\sum_{JL} &\langle LM_LIM_I|L0\rangle\sqrt{(2L+1)}Y_{LM_L}(0,\phi)\\ &\times[S^{J}_{nLI;0J0}-\delta_{n0}\delta_{LJ}\delta_{I0}],\end{aligned} \tag{27}$$

where the Coulomb phases are introduced at the correct energies and orbital angular momenta.

Equation (23) can be further simplified if one assumes that the rotational states in a given vibration (n) are degenerate. In this case the excitation energy ϵ_{nI} does not depend upon the spin I. Then one can further reduce the coupled equations by diagonalizing the coupling matrix elements $\langle nI0|T_{10}|n'I'0\rangle$,

$$\sum_{I} G^{\lambda}_{nI}\langle nI0|T_{10}|n'I'0\rangle=\Gamma^{\lambda}_{nn'}G^{\lambda}_{n'I'}. \tag{28}$$

Now defining new functions

$$W^{J\lambda}_{n}(r)=\sum_{I} G^{\lambda}_{nI}\mathcal{U}^{J}_{nI}(r), \tag{29}$$

we have the coupled equations

$$(K_J+\epsilon_n-E)W^{J\lambda}_{n}(r)=-\alpha(r)\sum_{n'} \Gamma^{\lambda}_{nn'}W^{J\lambda}_{n'}(r). \tag{30}$$

These functions satisfy the boundary conditions

$$W^{J\lambda}_{n}(r)=[\delta_{n0}I_J(k_0r)-S^{J\lambda}_{n0}O_J(k_nr)], \tag{31}$$

where

$$\begin{aligned}k_0^2&=\frac{2\mu(E-\epsilon_0)}{\hbar^2},\\ k_n^2&=\frac{2\mu(E-\epsilon_n)}{\hbar^2}.\end{aligned} \tag{32}$$

Equations (30) describe the coupling between vibrational states and the dimension of the coupled equations is equal to that of the number of vibrations one includes in the calculation.

The cross section for the scattering of an electron of initial momentum $\vec{k}_i$ into a final momentum $\vec{k}_f$ off a diatomic molecule, leaving it in an excited vibrational state, is given by

$$\frac{d\sigma_{fi}(\theta)}{d\Omega}=\frac{2}{2l_i+1}\sum_{m_i}\sum_{l_f,m_f}|A_{fi}(\theta)|^2, \tag{33}$$

where an average over the initial magnetic quantum number m_i and a sum over the final rotional states (l_f,m_f) is indicated.

The coupled-channel (CC) formalism presented above allows for the calculation of $d\sigma_{fi}/d\Omega$. This has been partly done [10]. In what follows we use a simplified version of the CC that has embedded in it the adiabatic nature of the vibrational excitation and the ‘‘sudden’’ nature of the rotational excitation. This CC calculation has been done in using the Glauber-eikonal approximation. Here we use instead the WKB approximation for the partial-wave phase shifts.

IV. THE SEMICLASSICAL-ALGEBRAIC METHOD

We start by considering the usual [11] near-far decomposition of the semiclassical transition operator, namely,

$$\hat{A}^{\pm}(\theta)=\frac{1}{\sqrt{2\pi k^{2}\sin\theta}}\int^{\infty}\tfrac{1}{2}d\lambda\lambda^{1/2}\times\exp\left[2i\hat{\delta}(\lambda)\mp i\left(\lambda\theta-\frac{\pi}{4}\right)-\frac{i\pi}{2}\right],\qquad(34)$$

where ± refers to the near (far) components and use has been made of the asymptotic form of the Legendre polynomials, valid for large $\lambda=l+1/2$. The phase operator $\hat{\delta}$ responsible for the vibrational transitions is given by

$$2\hat{\delta}(\lambda,E)=\frac{\sqrt{2\mu}}{\hbar}\lim_{R\to\infty}\left[\int_{r_0(V)}^{R}dr\left(E-\frac{\hbar^{2}\lambda^{2}}{2\mu r^{2}}-\hat{V}(r)\right)^{1/2}-\int_{r_0(0)}^{R}dr\left(E-\frac{\hbar^{2}\lambda^{2}}{2\mu r^{2}}\right)^{1/2}\right],\qquad(35)$$

where $\hat{V}(r)$ is the operator (4) describing the dipole interaction between electron and molecule. The scattering amplitude for scattering of an electron from a molecule with initial state $|i\rangle$ to a final state $|f\rangle$ is then given by the sum

$$A_{fi}(\theta)=A_{fi}^{+}(\theta)+A_{fi}^{-}(\theta),\qquad(36)$$

where $A_{fi}^{\pm}(0)$ can be written as

$$A_{fi}^{\pm}(\theta)=\frac{1}{\sqrt{2\pi k^{2}\sin\theta}}\int_{0}^{\infty}d\lambda\times\lambda^{1/2}\left\langle f\left|\exp\left[2i\hat{\delta}(\lambda)\mp i\left(\lambda\theta-\frac{\pi}{4}\right)-\frac{i\pi}{2}\right]\right|i\right\rangle.\qquad(37)$$

These expectation values cannot be evaluated as they are, but if we assume the dipole interaction between electron and molecule to be sufficiently small we can substitute the phase-shift operator $\hat{\delta}$ by its eikonal approximation

$$\hat{\delta}\simeq-\frac{1}{\hbar}\int_{-\infty}^{\infty}\hat{V}[r(t)]dt\qquad(38)$$

and use the technique described in Refs. [6,7] to write these amplitudes as

$$A_{fi}^{\pm}(0)=\frac{1}{\sqrt{2\pi k^{2}\sin\theta}}\int_{0}^{\infty}d\lambda\lambda^{1/2}\exp\left[\mp i\left(\lambda\theta-\frac{\pi}{4}\right)-\frac{i\pi}{2}\right]\times\langle\alpha_f,l_f,m_f|\exp[igT_z]|\alpha_i,\ell_i,m_i\rangle,\qquad(39)$$

where the transition matrix elements

$$3\langle\alpha_f,\ell_f,m|\exp[igT_z]|\alpha_i,\ell_i,m\rangle\qquad(40)$$

are calculated using the vibron model for describing the molecular excitations. In the case that we are interested in only the rotational bands are excited and in the limit of large number N we have

$$\langle\alpha_f,\ell_f,m|\exp[ig(\epsilon)T_z]|\alpha_i,\ell_i,m\rangle=i^{\ell}\sqrt{2\ell+1}j_{\ell}(\epsilon),\qquad(41)$$

where

$$\epsilon(\lambda)=-\frac{d}{\hbar v_0}\int_{-\infty}^{\infty}\alpha(r)dz.\qquad(42)$$

The cross section is given in terms of the amplitudes $A_{fi}^{\pm}(\theta)$ by

$$\frac{d\phi_{fi}(\theta)}{d\Omega}=2|A_{fi}^{+}(\theta)+A_{fi}^{-}(\theta)|^{2},\qquad(43)$$

where the factor of 2 takes into account the sum over final electron spin states. On one hand, in order to make a comparison with experimental data we have to consider that in the available sets of data the individual rotational transitions are not observed. So, we consider the cross section summed over the final ℓ states given by

$$\frac{d\sigma(\theta)}{d\Omega}=2\sum_{\ell}|A_{\ell}^{+}(\theta)+A_{\ell}^{-}(\theta)|^{2}.\qquad(44)$$

If we use the expressions for the amplitudes (39) with the transition matrix elements given by Eq. (41) and expand the square of the modulus, we can make use of the addition theorem [12]

$$\sum_{\ell}(2\ell+1)j_{\ell}[\epsilon(\lambda)]j_{\ell}[\epsilon(\lambda')]=j_0[\epsilon(\lambda)-\epsilon(\lambda')]\qquad(45)$$

to perform the ℓ sum. By further using the Bessel function integral representation

$$j_0(z)=\frac{1}{2}\int_{0}^{\pi}\exp(iz\cos\xi)\sin\xi d\xi\qquad(46)$$

we can write

$$\frac{d\sigma(\theta)}{d\Omega}=\frac{1}{2\pi k^2\sin\theta}\frac{1}{2}\int_0^{\pi}d\xi\,\sin\xi\left|\int_0^{\infty}d\lambda\lambda^{1/2}\exp\left[i\epsilon(\lambda)\cos\xi-i\left(\lambda\theta-\frac{\pi}{4}\right)\right]\right.$$
$$\left.+\int_0^{\infty}d\lambda\lambda^{1/2}\exp\left[i\epsilon(\lambda)\cos\xi+i\left(\lambda\theta-\frac{\pi}{4}\right)\right]\right|^2. \tag{47}$$

This expression can be further reduced if we observe that the two integrals have stationary phase contributions in different domains of the angle ξ. Thus, if we split the integration into a sum of two integrals, from 0 to $\pi/2$ and from $\pi/2$ to π, we can rewrite the above equation asymptotically as

$$\frac{d\sigma(\theta)}{d\Omega}=\frac{1}{2\pi k^2\sin\theta}\frac{1}{2}\int_0^{\pi/2}d\xi\,\sin\xi\left\{\left|\int_0^{\infty}d\lambda\lambda^{1/2}\exp\left[-i\epsilon(\lambda)\cos\xi-i\left(\lambda\theta-\frac{\pi}{4}\right)\right]\right|^2\right.$$
$$\left.+\left|\int_0^{\infty}d\lambda\lambda^{1/2}\exp\left[i\epsilon(\lambda)\cos\xi+i\left(\lambda\theta-\frac{\pi}{4}\right)\right]\right|^2\right\} \tag{48}$$

or

$$\frac{d\sigma(\theta)}{d\Omega}=\frac{1}{2}\int_0^1 dx\left[\frac{d\sigma^{\text{near}}(\theta,x)}{d\Omega}+\frac{d\sigma^{\text{far}}(\theta,x)}{d\Omega}\right]. \tag{49}$$

The double integration makes this formula inadequate to do the numerical calculation. Actually, it is more practical to calculate each individual ℓ contribution and sum them. Only a few terms are necessary in order to have convergence as we are going to show below. However, the above expressions have a nice physical interpretation. The angle ξ may be associated with the arbitrary orientation of the molecule during the collision. Thus, in the summed cross section we are making an average over these possible orientations. We can see that the above expression is an incoherent sum of the near and the far sides of the scattering amplitude and as a result it will give rise a smooth function of the scattering angle even if the individual contributions are oscillatories.

The next step in the semiclassical approximation is to evaluate asymptotically the above integrals using the stationary phase method. To do this we first write the Bessel function as

$$j_{\ell}(z)=\sqrt{\pi/2z}M_{\ell+1/2}\cos\phi_{\ell+1/2}, \tag{50}$$

where the modulus and the phase are given respectively by

$$M_{\ell+1/2}=\sqrt{J_{l+1/2}^2+Y_{\ell+1/2}^2} \tag{51}$$

and

$$\phi_{\ell+1/2}=\arctan\left(\frac{Y_{\ell+1/2}}{J_{\ell+1/2}}\right). \tag{52}$$

Using these relations we can then write the following expressions for the two amplitudes $A_{fi}^{\pm}$:

$$A_{\ell}^{\pm}(\theta)=\frac{i^l\sqrt{2\ell+1}}{\sqrt{2k^2\sin\theta}}\int_0^{\infty}\frac{d\lambda}{2\epsilon}\lambda^{1/2}M_{\ell+1/2}$$
$$\times\exp\left[\mp i\phi_{\ell+1/2}(\epsilon)\mp i\left(\lambda\theta-\frac{\pi}{4}\right)-\frac{i\pi}{2}\right], \tag{53}$$

since we can consistently neglect the branch of the cosine without stationary points. We remark also that the above phase $\epsilon(\lambda)$ leads to a deflection function that extends, for small angular momenta, to angles larger than π, which is physically unacceptable. In order to correct this we substitute in the argument of the phase $\phi_{\ell+1/2}$ the quantity ϵ as

$$\epsilon=\mp 2\delta^{\pm}(\lambda), \tag{54}$$

where $\delta^{\pm}$ are the semiclassical phase shifts given by Eq. (35) with a real repulsive (attractive) interaction. Making this identification, the stationary angular momenta are now obtained as the solutions of the equation

$$\Theta_{\ell}(\lambda)=\Theta_0(\lambda)\,\frac{d\phi_{\ell+1/2}}{d\epsilon}(\lambda)=\mp\theta, \tag{55}$$

where Θ_0 is the classical elastic deflection function in the attractive and repulsive dipole interaction and $\Theta_l(\lambda)$ is the effective deflection function for the inelastic process that excites the l rotational state of the molecule. The derivative of the phase ϕ (we omit the label) with respect to its argument is given by

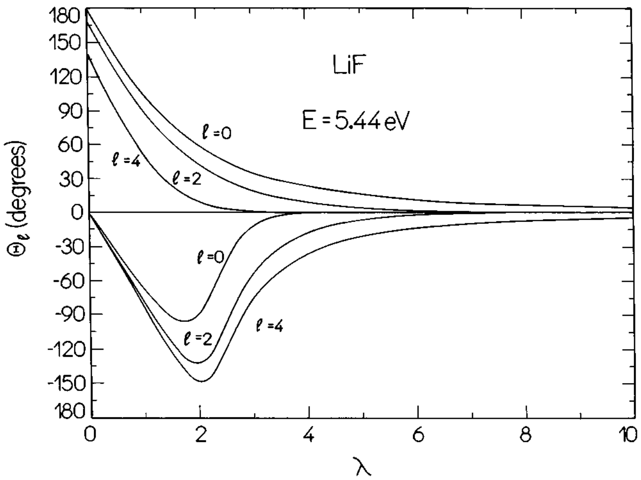

FIG. 1. The classical deflection function for e+LiF at E = 5.44 eV (see text for details).

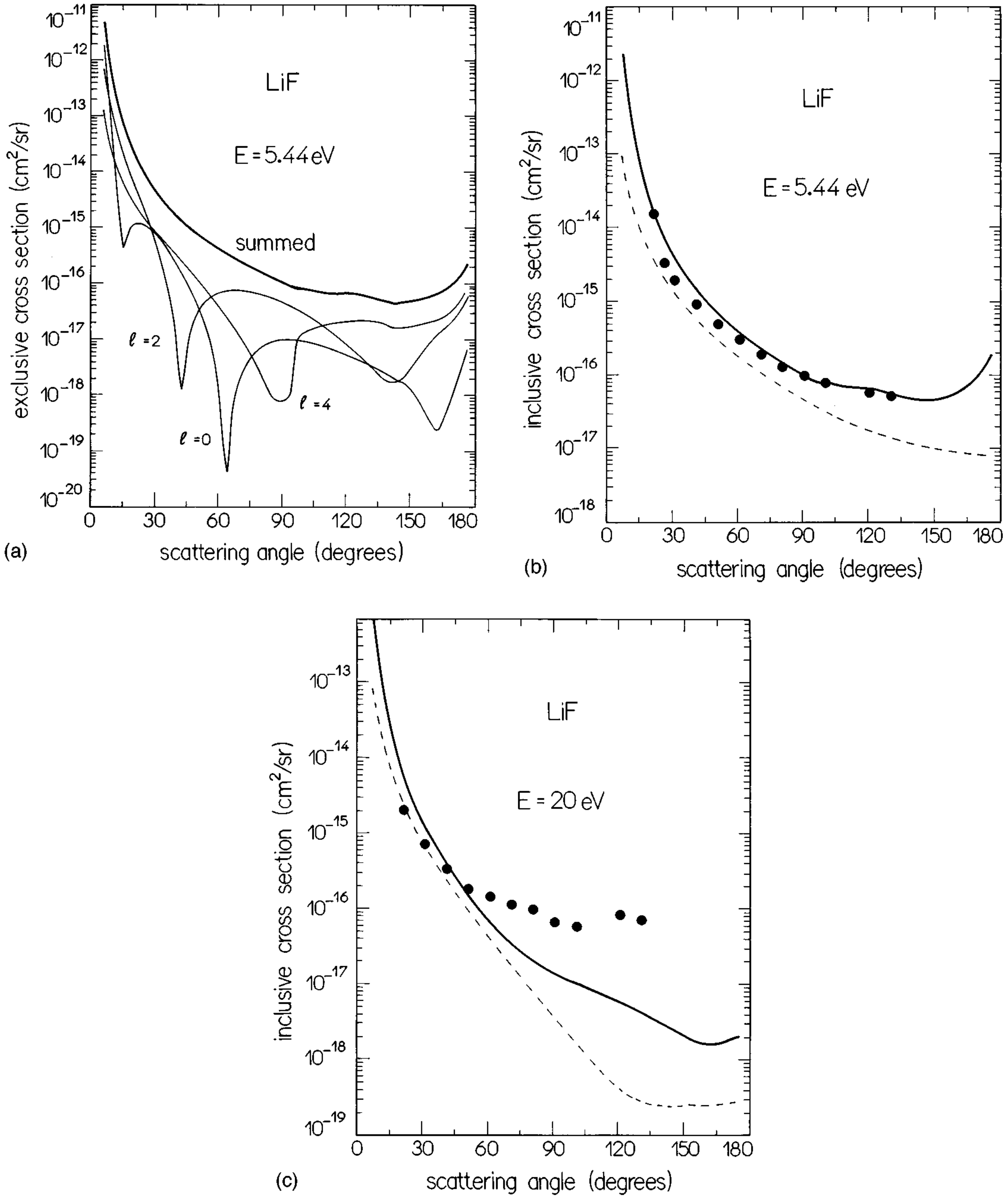

FIG. 2. (a) The rotationally exclusive cross sections for the system of Fig. 1 (see text for details). (b) The inclusive cross section (solid line) for the system of Fig. 1. (c) Same as (b) at $E=20$ eV. The dashed curves in these last two figures correspond to the eikonal result of Refs. [6,7].

$$\frac{d\phi_{\ell+1/2}}{d\epsilon}=\frac{2}{\pi M^2_{\ell+1/2}\epsilon}. \tag{56}$$

Denoting by λ_ℓ the corresponding solutions of Eq. (55) the near-side amplitude can be written as

$$A^+_\ell(\theta)=\frac{i^\ell\sqrt{2\ell+1}}{\sqrt{2k^2\sin\theta}}\,\frac{1}{2\epsilon}\,\lambda^{1/2}M_{\ell+1/2}\left(\frac{2\pi}{\Theta'_\ell(\lambda_\ell)}\right)^{1/2}\times\exp\left[-i\phi_{\ell+1/2}(\lambda_\ell)-i\left(\lambda\theta-\frac{\pi}{4}\right)-\frac{i\pi}{2}\right]. \tag{57}$$

For the far-side amplitude that is dominated by a rainbow we have the uniform asymptotic expressions

$$A^-_\ell(\theta)=\frac{i^\ell\sqrt{2\ell+1}}{\sqrt{2k^2\sin\theta}}\,\frac{1}{2\epsilon}\,2\pi\,\exp(iA)[p_0\mathrm{Ai}(x)-iq_0\mathrm{Ai}'(x)], \tag{58}$$

where $\mathrm{Ai}(x)$ and $\mathrm{Ai}'(x)$ are Airy function and its derivative and $A(\theta),x(\theta)$ are given by

$$A(\theta)=\frac{\phi_{\ell+1/2}(\lambda_1)-\lambda_1\theta+\phi_{\ell+1/2}(\lambda_2)-\lambda_2\theta}{2} \tag{59}$$

and

$$x(\theta)=\left\{\frac{3}{4i}\left[\phi_{\ell+1/2}(\lambda_1)-\lambda_1\theta-\phi_{\ell+1/2}(\lambda_2)+\lambda_2\theta\right]\right\}^{2/3}. \tag{60}$$

In these equations $\lambda_{1,2}$ are the two roots of Eq. (55) corresponding to the angular momenta of the semiclassical trajectories. Finally, p_0 and q_0 are given by

$$p_0=\tfrac{1}{2}(G_1F_1'+G_2F_2'), \tag{61}$$

$$q_0=\frac{1}{\sqrt{-x}}\,(G_1F_1'-G_2F_2'), \tag{62}$$

where $F=\phi_{\ell+1/2}$ and $G=\lambda^{1/2}M_{\ell+1/2}/\epsilon$ and the indices denote the order of derivative.

The above expressions for the far-side amplitudes are valid in the so-called bright side of the rainbow, i.e., for angles below the rainbow angle. In the dark side, which corresponds to the classical forbidden region they are analytically continued through a parabolic approximation of the deflection function. In the next section we apply our theory to the scattering of electrons from the molecules LiF and KI.

V. APPLICATIONS AND DISCUSSION

As an application of the above formalism we consider the case of scattering of the 15.7-eV electrons by KI molecules discussed in Ref. [7]. We show in Fig. 1 the elastic ($\ell=0$) and the effective inelastic deflection functions for several values of the rotational angular momentum ℓ. It is seen that the far side, i.e., the region of negative angles, is dominated by rainbows that becomes shallower as ℓ increases. In the near-side, positive angles, we have a typical repulsive deflection function whose maximum angle of deflection become smaller for larger ℓ.

The corresponding cross sections are shown in Fig. 2 together with the summed cross section. It is seen that although the cross section for the excitation of a given rotational state of the molecule is oscillatory, the inclusive cross section is a smooth function of the angle. This result corroborates the discussion following Eq. (49). In Fig. 2(b) we show a comparison between our results (solid line) and those of Refs. [6, 7]. As expected, our cross section is a bit higher than that of the pure eikonal one. In Fig. 2(c) the results for the same system at $E=5$ eV are also shown. Here our results come very close to the data. Finally, in Figs. 3(a) and 3(b) we show the calculation for the system $e+\mathrm{KI}$ at $E=15.7$ eV and 6.74 eV. We see here a trend similar to that of the previous case, although the lower-energy case comes out much worse. This may be an indication that the adiabatic approximation is not a very good one for the KI molecule.

The fact that the experimental data show a conspicuous rise and a hint of an oscillation, thus contradicting the calculation, may indicate the presence of a quasistationary, resonant state in the electron-molecule system, as Refs. [6,7] asserted.

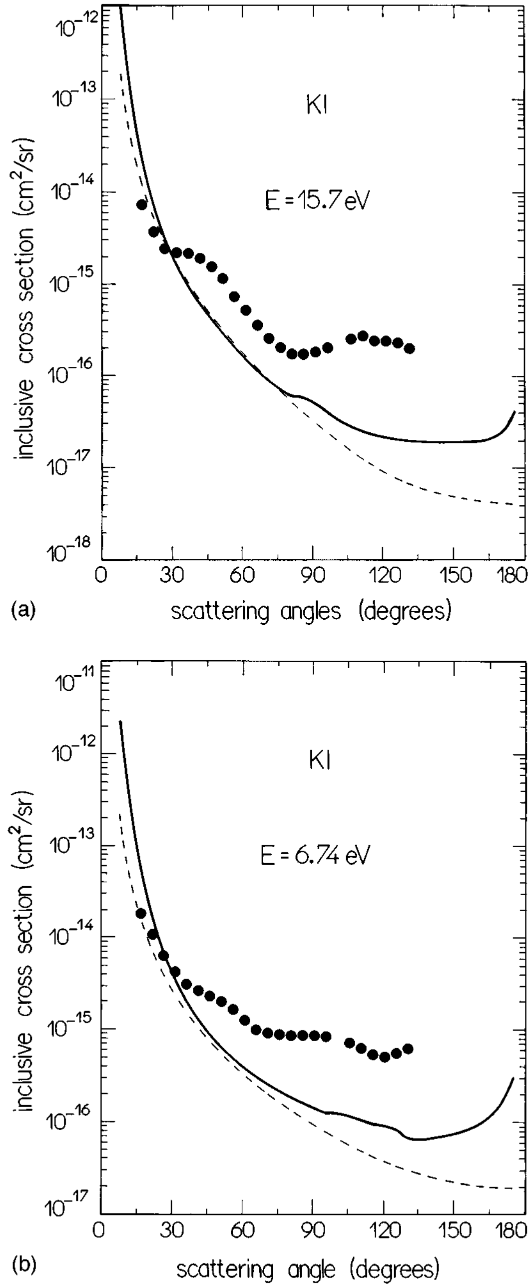

FIG. 3. Same as Figs. 2(b) and 2(c) for the system $e+\mathrm{KI}$ at (a) $E=15.7$ eV and (b) 6.74 eV.

In conclusion, we have presented in this paper an improved eikonal treatment of the electron-molecule scattering. The diatomic molecule is treated within the vibron model. We found that, though more accurate than the theory of Refs. [6,7], our treatment still fails to reproduce fully the rotational inclusive cross section.

ACKNOWLEDGMENTS

One of us (M.P.P.) appreciates the kind hospitality of the ECT where part of this work was done. M.S.H. was supported by FAPESP (Brazil), by funds provided by the U.S. Department of Energy (DOE) under Grant No. DE-IC02–94ER40818, and by the National Science Foundation (NSF). M.P.P. was supported in part by FAPESP (Brazil).

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