

# Quantum theory of inelastic collisions of a diatomic molecule in a $2\Pi$ electronic state with an uncorrugated surface: $\Lambda$ doublet, spinorbit, and polarization effects in NO ( $X\ 2\Pi$ )–Ag (111) scattering

Millard H. Alexander

Citation: *The Journal of Chemical Physics* **80**, 3485 (1984); doi: 10.1063/1.447105

View online: <http://dx.doi.org/10.1063/1.447105>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/80/7?ver=pdfcov>

Published by the AIP Publishing

---

## Articles you may be interested in

[Semiclassical model of  \$\Lambda\$ -doublet states in diatomic molecules](#)

*J. Chem. Phys.* **107**, 5460 (1997); 10.1063/1.474251

[Photodissociation of HOCl: A model for the prediction of the OH  \$\Lambda\$ doublet and Cl spin–orbit product state distributions](#)

*J. Chem. Phys.* **104**, 563 (1996); 10.1063/1.470852

[Quantum scattering studies of inelastic collisions of NH\( \$A\ 3\Pi\$ \) with helium: Finestructure and  \$\Lambda\$ doublet propensities](#)

*J. Chem. Phys.* **95**, 5036 (1991); 10.1063/1.461792

[Inelastic collisions of OH\( \$X\ 2\Pi\$ \) with paraH<sub>2</sub>:  \$\Lambda\$ doublet and hyperfine structure transitions](#)

*J. Chem. Phys.* **88**, 6931 (1988); 10.1063/1.454390

[Inelastic collisions of OH \( \$2\Pi\$ \) with H<sub>2</sub>: Comparison between theory and experiment including rotational, fine structure, and  \$\Lambda\$ doublet transitions](#)

*J. Chem. Phys.* **81**, 5644 (1984); 10.1063/1.447615

---



# Quantum theory of inelastic collisions of a diatomic molecule in a $^2\Pi$ electronic state with an uncorrugated surface: $\Lambda$ -doublet, spin-orbit, and polarization effects in NO ( $X^2\Pi$ )–Ag (111) scattering

Millard H. Alexander

Department of Chemistry, University of Maryland, College Park, Maryland 20742

(Received 1 November 1983; accepted 20 December 1983)

The formalism is developed for scattering of a molecule in a  $^2\Pi$  electronic state by an infinitely massive, uncorrugated surface. A general development of the electrostatic interaction potential is used to obtain matrix elements of the potential between molecular rotational and fine-structure states, described in an intermediate Hund's coupling case. Explicit expressions for the inelastic  $S$ -matrix elements are derived in the energy sudden limit. Semiclassical (high  $J$ ) expressions for the potential matrix elements and sudden  $S$ -matrix elements are obtained. This formal work is then used to make several general predictions for collisions of NO ( $X^2\Pi$ ) with Ag(111), which has been recently studied experimentally. In particular, we predict: (1) for moderate to high values of the final rotational quantum number, the molecules will be scattered so that  $\mathbf{J}$  lies in the plane of the surface, (2) in the energy sudden limit the  $F_1$  and  $F_2$  rotational manifolds will be equally populated by collisions, (3) and, again in the energy sudden limit, preferential population will occur in either the two  $\Lambda$ -doublet levels which are symmetric with respect to reflection of the NO electronic wave function in the plane of rotation or in the two levels which are antisymmetric with respect to this operation.

## I. INTRODUCTION

Over the past decade there has been considerable theoretical interest in inelastic collisions of diatomic molecules with surfaces.<sup>1–18</sup> In all this work the molecules were treated, either explicitly or implicitly, as closed-shell systems. Recently, however, a number of experimental groups have investigated the interaction of NO ( $X^2\Pi$ ) with various surfaces.<sup>19–27</sup> In the particular case of collisions of rotationally cold beams of NO with Ag(111), experiments both by Zare and co-workers at Stanford<sup>21</sup> and Luntz, Kleyn, and Auerbach at IBM<sup>24</sup> have investigated both spin-orbit and  $\Lambda$ -doublet effects in the inelastic scattering, which are direct manifestations of the open-shell character of a  $^2\Pi$  electronic state. In order to understand and analyze the experimental data more completely, it is necessary therefore to develop the formalism for treating the interaction of a  $^2\Pi$  molecule with a surface. This may well be necessary even for the description of experiments in which the spin-orbit states and  $\Lambda$ -doublet levels of NO are not resolved,<sup>19,20,22,23,25–27</sup> since our investigation<sup>28</sup> of gas-phase collisions of NO ( $X^2\Pi$ ) with Ar indicates that treating the molecule as a  $^1\Sigma$  molecule may be an unjustified simplification.

In this paper, we develop the formalism for collisions of a  $^2\Pi$  molecule with an uncorrugated, infinitely massive surface. The work presented will be an extension to molecule-surface collisions of ideas and techniques developed for the description of the gas-phase scattering of open-shell diatomics.<sup>29–33</sup> We will also draw upon the application to molecule-surface collisions by Gerber, Kouri, Schinke, and co-workers<sup>7–10,12–14</sup> of the sudden approximation, in a form used by Secrest<sup>34</sup> and Hunter<sup>35</sup> to describe gas-phase collisions. The organization of the present paper is as follows: In the next section, we present the general scattering formalism.

This is followed in Sec. III by a detailed analysis of the molecule-surface electrostatic potential and development of a suitable polynomial expansion. Matrix elements of the potential in an intermediate Hund's coupling case are derived in Sec. IV and high  $J$  limits of these matrix elements developed. The energy sudden limit is used in Sec. V to obtain explicit expressions for the inelastic  $S$ -matrix elements. Then in Sec. VI we use the formal work contained in the preceding sections to discuss some possible predictions for polarization effects, fine-structure changing transitions, and  $\Lambda$ -doublet propensities in collisions of NO ( $X^2\Pi$ ) with Ag(111). A brief conclusion follows.

## II. FORMAL COLLISION DYNAMICS

For a  $^2\Pi$  molecule of mass  $\mu$  interacting with an uncorrugated, infinitely massive surface, the Hamiltonian can be written as

$$H(\mathbf{r}_m, \mathbf{r}_s, Z) = -\frac{\hbar^2}{2\mu} \frac{d}{dZ^2} + H_m(\mathbf{r}_m) + H_s(\mathbf{r}_s) + V_{el}(\mathbf{r}_m, \mathbf{r}_s, Z). \quad (1)$$

Here  $Z$  is the perpendicular distance from the center of mass of the molecule to the surface;  $H_s$  and  $H_m$  designate the Hamiltonians of the isolated surface and molecule, respectively, with  $\mathbf{r}_s$  and  $\mathbf{r}_m$  denoting, collectively, the coordinates of all the particles in the surface and the molecule; and  $V_{el}$  designates the electrostatic interaction between the surface and the molecule.

We shall assume that the surface is described by a wave function  $\psi_s(\mathbf{r}_s)$  with eigenvalue  $E_s$  and that the isolated molecule can be described in a Hund's case (a) basis,<sup>36,37</sup> with eigenfunctions given by<sup>37–39</sup>

$$|JMF_1e/f\rangle \equiv |JMF_1\epsilon\rangle = \cos\theta_J |JM, \Omega = \frac{1}{2}, \epsilon\rangle + \sin\theta_J |JM, \Omega = 3/2, \epsilon\rangle, \quad (2)$$

$$|JMF_2e/f\rangle \equiv |JMF_2\epsilon\rangle = -\sin\theta_J |JM, \Omega = \frac{1}{2}, \epsilon\rangle + \cos\theta_J |JM, \Omega = 3/2, \epsilon\rangle, \quad (3)$$

where  $\epsilon = \pm 1$  and<sup>33,37,39,40</sup>

$$|JM\Omega\epsilon\rangle = 2^{-1/2} [ |JM\Omega\rangle |A = 1, \Sigma = \pm \frac{1}{2}\rangle + \epsilon |JM, -\Omega\rangle |A = -1, \Sigma = \mp \frac{1}{2}\rangle ], \quad (4)$$

with the top sign referring to the  $\Omega = \frac{3}{2}$  states and the bottom sign to the  $\Omega = \frac{1}{2}$  states. Here  $J$  is the total angular momentum of the molecule with projections  $M$  and  $\Omega$  along the space- and molecule-fixed  $z$  axes;  $A$  and  $\Sigma$  are the projections along the molecule-fixed  $z$  axis of the electronic and spin angular momenta with  $\Omega = A + \Sigma$ ;  $F_1$  and  $F_2$  designate the lower and higher energy levels; and the  $A$  doublets are labeled<sup>41</sup>  $e$ , with  $\epsilon = +1$ , and  $f$ , with  $\epsilon = -1$ . The total parity of the  $|JMF_i\epsilon\rangle$  states is given by<sup>42</sup>  $\epsilon(-1)^{J-S}$ , where  $S$  is the total spin. The angle  $\theta_J$  can be obtained by diagonalization of a  $2 \times 2$  Hamiltonian.<sup>38</sup> In the case (a) limit<sup>37,38</sup> where  $BJ \ll A$ , with  $B$  and  $A$  designating, respectively, the rotational and spin-orbit constants of the molecule, the angle  $\theta_J$  equals 0 for a regular<sup>36</sup>  ${}^2\Pi$  state ( $A > 0$ ) [as for example NO ( $X^2\Pi$ )] and  $\pi/2$  for an inverted<sup>36</sup>  ${}^2\Pi$  state ( $A < 0$ ). At high  $J$  when  $BJ \gg A$  the case (b) limit is reached, with  $\theta_J = \pi/4$ .<sup>37,39</sup> In the present article, we shall assume that the spin-orbit constant is independent of the distance from the molecule to the surface.

The molecular rotational functions in Eq. (4) are written<sup>40,42</sup>

$$|JM\Omega\rangle = [(2J+1)/4\pi]^{1/2} D_{M\Omega}^{J*}(\alpha\beta, \gamma=0), \quad (5)$$

where  $\alpha$  and  $\beta$  are the Euler angles describing the orientation of the molecule in the space frame, and we use active rotations<sup>42</sup> following Brink and Satchler.<sup>43</sup> For a diatomic molecule, it is possible without loss of generality to set the third Euler angle  $\gamma = 0$ <sup>37,40,42</sup>; the normalization factor in Eq. (5) has been adjusted accordingly. With  $\gamma = 0$  the molecule frame  $y$  axis lies in the space frame  $XY$  plane, which in the present application is the plane of the surface. The space-frame Cartesian coordinates are designated by upper case letters; the body-frame coordinates by lower case letters. Note that the diatomic molecule is taken to lie along the  $z$  axis. For simplicity, we have not included the vibrational motion of the diatomic in Eqs. (2)–(4). This degree of freedom could be easily added to the present analysis.

The total wave function for the molecule-surface system can be expanded in terms of the products of the wave functions for the isolated molecule and surface, namely

$$\Psi(\mathbf{r}_m, \mathbf{r}_s, Z) = \sum_{JMF_i\epsilon} C_{JMF_i\epsilon}(Z) |\psi_s\rangle |JMF_i\epsilon\rangle. \quad (6)$$

The expansion coefficients satisfy the close-coupled equations for scattering of a molecule from an uncorrugated surface, presented by Gerber, Kouri, and co-workers.<sup>7-9</sup> We have

$$\left[ \frac{d^2}{dZ^2} + k_{J'F_i'\epsilon}^2 \right] C_{J'M'F_i'\epsilon}(Z) = \frac{2\mu}{\hbar^2} \sum_{JMF_i\epsilon} V_{J'M'F_i'\epsilon, JMF_i\epsilon}(Z) C_{JMF_i\epsilon}(Z), \quad (7)$$

where the wave vectors are defined by

$$k_{JF_i\epsilon}^2 = \hbar^{-1} [2m(E - E_{JF_i\epsilon})]^{1/2}. \quad (8)$$

Here  $E$  is the total energy,  $E_{JF_i\epsilon}$  designates the molecular energy (rotational plus spin orbit). For collisions with an infinitely massive, uncorrugated surface, only specular scattering occurs and the effective translational energy is proportional to the square of the normal component of the total translational velocity.<sup>7-9</sup> The potential matrix elements in Eq. (7) are defined by

$$V_{J'M'F_i'\epsilon, JMF_i\epsilon}(Z) = \langle J'M'F_i'\epsilon | \psi_s | V_{el}(\mathbf{r}_m, \mathbf{r}_s, Z) | JMF_i\epsilon \psi_s \rangle, \quad (9)$$

and will be discussed in more detail in the next section.

The solutions to the CC equations must satisfy the boundary conditions<sup>7-9</sup>

$$\lim_{Z \rightarrow -\infty} C_{JMF_i\epsilon}(Z) = 0 \quad (10a)$$

and

$$\lim_{Z \rightarrow \infty} C_{JMF_i\epsilon}(Z) = \delta_{JJ'} \delta_{MM'} \delta_{F_i F_i'} \delta_{\epsilon \epsilon'} \times \exp(-ik_{J'M'F_i'\epsilon} Z) + (k_{J'F_i'\epsilon}/k_{JF_i\epsilon})^{1/2} \times S_{J'M'F_i'\epsilon, JMF_i\epsilon} \exp(ik_{JMF_i\epsilon} Z). \quad (10b)$$

The transition probability for the  $JMF_i\epsilon \rightarrow J'M'F_i'\epsilon'$  transition can be written

$$P_{JMF_i\epsilon \rightarrow J'M'F_i'\epsilon'} = |S_{J'M'F_i'\epsilon', JMF_i\epsilon}|^2. \quad (11)$$

### III. INTERACTION POTENTIAL

The matrix elements of the electrostatic interaction potential in Eq. (9) can be formally written as

$$V_{J'M'F_i'\epsilon', JMF_i\epsilon}(Z) = \langle J'M'F_i'\epsilon' | \psi_s | \sum_{ij} r_{ms_{ij}}^{-1} | JMF_i\epsilon \psi_s \rangle, \quad (12)$$

where for convenience we have suppressed the electronic charge;  $r_{ms} \equiv |\mathbf{r}_m - \mathbf{r}_s|$  designates the distance between any two charged particles in the molecule and surface; and the sum runs over all particles in the surface and the molecule. The inverse distance  $r_{ms}^{-1}$  can be expanded in the usual multipolar series<sup>44</sup>

$$r_{ms_{ij}}^{-1} = \sum_{l_1 l_2} (l_1 l_1 m_1 | l_2 m_2) A_{l_1 l_2}(\mathbf{r}_{m_1}, \mathbf{r}_{s_j}, R) \times C_{l_m}(\hat{\mathbf{r}}_{m_1}) C_{l_1 m_1}(\hat{\mathbf{r}}_{s_j}) C_{l_2 m_2}^*(\hat{\mathbf{R}}), \quad (13)$$

where  $(\dots | \dots)$  is a Clebsch-Gordan coefficient,<sup>43</sup>  $C_{l_m}(\hat{\mathbf{r}})$  designates an unnormalized spherical harmonic,<sup>43</sup> and the vector

$\hat{R}$  designates the distance between the origins of two space-frame coordinate systems: One fixed in the surface and one fixed in the molecule.

We take  $\mathbf{R} = \mathbf{Z}$  and restrict  $m_1$  to zero, since for an uncorrugated surface the wave function of the surface is both translationally and rotationally symmetric in the  $XY$  plane. Because  $C_{l_2 m_2}(\hat{\mathbf{Z}}) = \delta_{m_2, 0}$ ,<sup>43</sup> Eq. (13) reduces to

$$r_{m_s j}^{-1} = \sum_{l_1 l_2} (l_1 0 l_1 0 | l_2 0) A_{l_1 l_2}(r_{m_1}, r_{s_j}, \mathbf{Z}) C_{l_1 0}(\hat{r}_{m_1}) C_{l_2 0}(\hat{r}_{s_j}). \quad (14)$$

Since the electronic wave function of the molecule is usually expressed in the molecule frame, it will be convenient to transform the dependence on  $\hat{r}_{m_1}$  in Eq. (14) into this frame to give

$$r_{m_s j}^{-1} = \sum_{l_1 l_2} (l_1 0 l_1 0 | l_2 0) A_{l_1 l_2}(r_{m_1}, r_{s_j}, \mathbf{Z}) \times D_{0\mu}^{l_2}(\alpha\beta 0) C_{l_1 \mu}(\hat{\rho}_{m_1}) C_{l_2 0}(\hat{r}_{s_j}), \quad (15)$$

where  $\hat{\rho}_{m_1}$  designates the orientation of  $\hat{r}_{m_1}$  in the molecule frame.

We see from Eqs. (2)–(4) that the matrix elements in Eq. (7) can be expressed in terms of matrix elements involving the  $|JM\Omega\rangle |A\Sigma\rangle$  functions. With the help of Eq. (5) these will be given by

$$\begin{aligned} & \langle J'M'\Omega'A'\Sigma'\psi_s | \sum_{ij} r_{m_s j}^{-1} | JM\Omega A \Sigma \psi_s \rangle \\ &= \frac{[(2J+1)(2J'+1)]^{1/2}}{4\pi} \sum (l_1 0 l_1 0 | l_2 0) \\ & \int D_{M'\Omega'}^{J'\Sigma'} \times (\alpha\beta 0) D_{M\Omega}^{J\Sigma} (\alpha\beta 0) D_{0\mu}^{l_2}(\alpha\beta 0) \sin \beta d\beta d\alpha \int d\tau_{m_1} d\tau_{s_j} \\ & \times \langle \psi_s | \langle A' \Sigma' | A_{l_1 l_2}(r_{m_1}, r_{s_j}, \mathbf{Z}) C_{l_1 \mu}(\hat{\rho}_{m_1}) C_{l_2 0}(\hat{r}_{s_j}) | A \Sigma \rangle | \psi_s \rangle, \end{aligned} \quad (16)$$

where the summation extends over the indices  $l_1, l_2, i, j$  and  $\mu$ . Because of the integration over spin, these matrix elements will vanish unless  $\Sigma' = \Sigma$ . A  $^2\Pi$  electronic state can correspond to a singly filled  $\pi$  orbital outside of closed shells [as in the case of  $\text{CH}(X^2\Pi)$  or  $\text{NO}(X^2\Pi)$ ] or a triply filled  $\pi$  orbital [as in the case of  $\text{OH}(X^2\Pi)$ ]. In both cases, the open-shell component of these wave functions can be built from Slater determinants containing these  $\pi$  molecular orbitals.<sup>37</sup> Since the dependence of the  $\pi$  orbitals on the molecule frame azimuthal angle is equivalent to that of a spherical harmonic  $Y_{L\pm 1}$ ,<sup>37</sup> one can show that the only values of  $\mu$  which will give nonvanishing contributions to Eq. (16) are  $\mu = A' - A = 0, \pm 2$ . Furthermore, since  $\Sigma' = \Sigma$  we have  $\Omega' - \Omega = A' - A = \mu$ .

Thus we see that Eq. (16) can be equally well written as

$$\begin{aligned} & \langle J'M'\Omega'A'\Sigma'\psi_s | \sum_{ij} r_{m_s j}^{-1} | JM\Omega A \Sigma \psi_s \rangle \\ &= \delta_{\Sigma\Sigma'} \frac{[(2J+1)(2J'+1)]^{1/2}}{4\pi} \int_0^{2\pi} d\alpha \\ & \times \int_0^\pi D_{M'\Omega'}^{J'\Sigma'}(\alpha\beta 0) D_{M\Omega}^{J\Sigma}(\alpha\beta 0) V_{A'A}^{\text{eff}}(\beta, \mathbf{Z}) \sin \beta d\beta, \end{aligned} \quad (17)$$

where

$$V_{A'A}^{\text{eff}}(\beta, \mathbf{Z}) = (-1)^{A-A'} \sum_l V_{l, A-A'}(\mathbf{Z}) d_{0, A-A'}^l(\beta) \quad (18)$$

and

$$\begin{aligned} V_{l\mu}(\mathbf{Z}) &= \sum_{l_1 l_2} (l_1 0 l_1 0 | l_2 0) \sum_{i,j} \int d\tau_{m_1} d\tau_{s_j} \\ & \times \langle \psi_s | \langle A' \Sigma' | A_{l_1 l_2}(r_{m_1}, r_{s_j}, \mathbf{Z}) \\ & \times C_{l_1 \mu}(\hat{\rho}_{m_1}) C_{l_2 0}(\hat{r}_{s_j}) | A \Sigma \rangle | \psi_s \rangle. \end{aligned} \quad (19)$$

We observe that  $V_{A'A}^{\text{eff}}(\beta, \mathbf{Z})$  is just a matrix element of the electrostatic Hamiltonian in the basis of molecular electronic wave functions  $|A\rangle$  with the orientation of the molecule fixed with respect to the surface. We show in the Appendix that the  $V_{l\mu}(\mathbf{Z})$  coefficients are independent of the sign of  $\mu$ . Because of the equivalence between the  $d_{0\mu}^l$  rotation matrix elements and Legendre polynomials,<sup>43</sup> we can write Eq. (18) in the perhaps more familiar form

$$\begin{aligned} V_{A'A}^{\text{eff}}(\beta, \mathbf{Z}) &= \sum_l V_{l, A-A'}(\mathbf{Z}) \\ & \times \left[ \frac{(l+A-A')!}{(l-A+A')!} \right]^{1/2} P_{l, A-A'}(\cos \beta). \end{aligned} \quad (20)$$

The reader should observe that the above development is completely independent of the form chosen for the surface wave function in Eq. (19), provided that it have the translational and rotational symmetry of a flat surface. In particular, we could include interactions between the molecule and electron-hole pairs, in which case Eq. (19) would be modified to include a sum over the various contributing surface states.

In principle, information on the  $\beta$  and  $\mathbf{Z}$  dependence of the potential could be obtained from an *ab initio* calculation of the molecule-surface interaction. Usually this type of calculation would be performed in terms of real electronic wave functions for the molecule which can be written as

$$|A\eta\rangle = 2^{-1/2} [ |A\rangle + \eta | -A \rangle ], \quad (21)$$

where  $\eta = \pm 1$ . In the molecule frame the symmetry of the  $|A\rangle$  wave functions with respect to reflection in the  $yz$  plane is given by  $\sigma_v(yz)|A\rangle = | -A \rangle$ ,<sup>37,38,42</sup> so that

$$\sigma_v(yz)|A\eta\rangle = \eta |A\eta\rangle. \quad (22)$$

Since the molecule frame is obtained by an Euler rotation with  $\gamma = 0$ , for  $\beta = \pi/2$  the  $yz$  plane will lie in the plane of the surface. Thus we see from Eq. (22) that for orientations where the molecular axis is parallel to the surface, the  $\eta = +1$  wave function is symmetric, and the  $\eta = -1$  wave function antisymmetric with respect to reflection in a plane parallel to the surface. In the case of  $\text{NO}(X^2\Pi)$  the electron occupancy corresponds to one electron in an unfilled  $\pi$  orbital. Thus in the  $\eta = +1$  wave function this orbital lies in the plane of the surface, again when the  $z$  axis is parallel to the surface, while in the  $\eta = -1$  wave function the unfilled  $\pi$  orbital points toward the surface.

We can determine matrix elements of the electrostatic Hamiltonian in this  $|A\eta\rangle$  basis from Eq. (18), keeping in mind that  $V_{l\mu}(\mathbf{Z})$  is independent of the sign of  $\mu$  (see the Appendix) as is the rotation matrix element  $d_{0\mu}^l(\beta)$  (for  $\mu$  even, which is what we are dealing with here). We find

$$V_{\Lambda\eta',\Lambda\eta}^{\text{eff}}(\beta, Z) = \delta_{\eta\eta'} \sum_{\gamma} [V_{l0}(Z) d_{00}^{\gamma}(\beta) + \eta V_{l2}(Z) d_{0,-2}^{\gamma}(\beta)]. \quad (23)$$

Thus we see, exactly as in the case of collisions between a  $^2\Pi$  molecule and an atom,<sup>45</sup> that the  $V_{l0}(Z)$  terms represent the expansion of the average of the effective potentials for  $\eta = 1$  and  $\eta = -1$ , and the  $V_{l2}(Z)$  terms represent the expansion of one-half the difference between these two effective potentials.

We observe from Eqs. (7) and (10) that to within an arbitrary phase factor, the solutions to the CC equations will be independent of a shift in the  $Z$  origin. Since a phase difference will not affect the transition probabilities [Eq. (11)], we could without loss of generality take the independent variable in the CC equations to be the distance from the minimum in the molecule-surface interaction, rather than the distance from the surface. A similar transformation is also possible even in the presence of surface corrugations, as discussed by Wolken.<sup>1</sup> Thus any experimental measurement of the inelastic scattering of molecules from a rigid surface will yield information only about the *relative*  $Z$  dependence of the molecule-surface interaction, but not about the true location of the potential well.

#### IV. POTENTIAL MATRIX ELEMENTS

The matrix elements of the interaction potential in the  $|JM\Omega\Lambda\Sigma\psi_s\rangle$  basis can be evaluated by integrating over the Euler angles in Eq. (17). We find, with Eq. (23)

$$\begin{aligned} \langle J'M'\Omega'\Lambda'\Sigma'\psi_s | \sum_{\eta} r_{m\eta}^{-1} | JM\Omega\Lambda\Sigma\psi_s \rangle \\ = \delta_{\Sigma\Sigma'} \delta_{MM'} (-1)^{M-\Omega} \sum_{\mu} \delta_{\mu,\Lambda'-\Lambda} V_{l,-\mu}(Z) \\ \times \begin{pmatrix} J' & J & l \\ M & -M & 0 \end{pmatrix} \begin{pmatrix} J' & J & l \\ \Omega' & -\Omega & -\mu \end{pmatrix}, \quad (24) \end{aligned}$$

where  $(\dots)$  is a  $3j$  symbol.<sup>43</sup> With Eqs. (2)-(4), one can show that the matrix elements in the  $|JMF_i e/f\rangle$  basis [Eqs. (2) and (3)] are given by

$$\begin{aligned} \langle J'M'F_i e' | V_{el} | JMF_i e \rangle = \delta_{MM'} (-1)^M \sum_{\epsilon} \\ \times \frac{i}{2} [1 - \epsilon\epsilon' (-1)^{J+J'+l}] \begin{pmatrix} J' & J & l \\ M & -M & 0 \end{pmatrix} \\ \times \left\{ V_{l0}(Z) \left[ A_l(J'F_i e', JF_i e) \begin{pmatrix} J' & J & l \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \right. \right. \\ \left. \left. + B_l(J'F_i e', JF_i e) \begin{pmatrix} J' & J & l \\ \frac{3}{2} & -\frac{3}{2} & 0 \end{pmatrix} \right] \right. \\ \left. + \epsilon V_{l2}(Z) \left[ C_l(J'F_i e', JF_i e) \begin{pmatrix} J' & J & l \\ \frac{3}{2} & \frac{1}{2} & -2 \end{pmatrix} \right. \right. \\ \left. \left. + D_l(J'F_i e', JF_i e) \begin{pmatrix} J' & J & l \\ \frac{1}{2} & \frac{3}{2} & -2 \end{pmatrix} \right] \right\}, \quad (25) \end{aligned}$$

where the  $A_l$ ,  $B_l$ ,  $C_l$ , and  $D_l$  coefficients are given in Table I.

It will be useful in the ensuing discussion to determine simplified expressions for the coupling coefficients in Eq. (25) which will be valid whenever  $J$  and  $J'$  are large with respect to the values of  $l$  which make a significant contribution to the summation. To do so, we make use of three asymptotic relations between the  $3j$  symbols in Eq. (25), namely<sup>33</sup>

$$\lim_{J,J' \gg l} \begin{pmatrix} J' & J & l \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} = - \lim_{J,J' \gg l} \begin{pmatrix} J' & J & l \\ \frac{3}{2} & -\frac{3}{2} & 0 \end{pmatrix}, \quad (26)$$

$$\lim_{J,J' \gg l} \begin{pmatrix} J' & J & l \\ \frac{3}{2} & \frac{1}{2} & -2 \end{pmatrix} = - \lim_{J,J' \gg l} \begin{pmatrix} J' & J & l \\ \frac{1}{2} & \frac{3}{2} & -2 \end{pmatrix}, \quad (27)$$

and

$$\lim_{J,J' \gg l} \begin{pmatrix} J' & J & l \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} = 0 \quad \text{unless } (J + J' + l) = \text{odd}. \quad (28)$$

We first use these expressions to investigate the situation where  $J$  and  $J'$  are both large compared to  $l$ , but still small enough that a pure case (a) description of the rotational states is valid. For example, for NO ( $X^2\Pi$ ) where  $\theta_j = 0$  in the case (a) limit, at  $J = 15.5$   $\theta_j$  is only  $12.5^\circ$ , so that  $\cos \theta_j / \sin \theta_j = 4.5$ . In this situation ( $J, J'$  large but  $\sin \theta_j \ll \cos \theta_j$ ) the potential matrix elements for  $F_i' = F_i$  ( $i = 1, 2$ ) are given by

$$\begin{aligned} \langle J'M'F_i e' | V_{el} | JMF_i e \rangle \simeq \delta_{MM'} \delta_{e'e} (-1)^{M+1} \sum_{\epsilon} \\ \times \frac{i}{2} [1 - (-1)^{J+J'+l}] \\ \times \begin{pmatrix} J' & J & l \\ M & -M & 0 \end{pmatrix} \begin{pmatrix} J' & J & l \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} V_{l0}(Z), \quad (29) \end{aligned}$$

and, for  $F_i' \neq F_i$

TABLE I. Potential matrix elements, intermediate coupling basis.<sup>a</sup>

	$F_1$	$F_2$
$A_l(J'F_i e', JF_i e)$		
$F_1'$	$-\cos \theta_j' \cos \theta_j$	$\cos \theta_j' \sin \theta_j$
$F_2'$	$\sin \theta_j' \cos \theta_j$	$-\sin \theta_j' \sin \theta_j$
$B_l(J'F_i e', JF_i e)$		
$F_1'$	$\sin \theta_j' \sin \theta_j$	$\sin \theta_j' \cos \theta_j$
$F_2'$	$\cos \theta_j' \sin \theta_j$	$\cos \theta_j' \cos \theta_j$
$C_l(J'F_i e', JF_i e)$		
$F_1'$	$\sin \theta_j' \cos \theta_j$	$-\sin \theta_j' \sin \theta_j$
$F_2'$	$\cos \theta_j' \cos \theta_j$	$-\cos \theta_j' \sin \theta_j$
$D_l(J'F_i e', JF_i e)$		
$F_1'$	$-\cos \theta_j' \sin \theta_j$	$-\cos \theta_j' \cos \theta_j$
$F_2'$	$\sin \theta_j' \sin \theta_j$	$\sin \theta_j' \cos \theta_j$

<sup>a</sup> See Eq. (25).

$$\begin{aligned} \langle J'M'F_i\epsilon'|V_{el}|JMF_i\epsilon\rangle &\simeq \epsilon\delta_{MM'}(-1)^{M+1}\sum_T \\ &\times \frac{i}{2}[1-\epsilon\epsilon'(-1)^{J+J'+I}] \\ &\times \begin{pmatrix} J' & J & I \\ M & -M & 0 \end{pmatrix} \begin{pmatrix} J' & J & I \\ \frac{1}{2} & \frac{1}{2} & -2 \end{pmatrix} V_{I2}(Z). \end{aligned} \quad (30)$$

It is also worthwhile to determine analytic expressions for the potential matrix elements when both  $J$  and  $J'$  are very large, so that a pure case (b) description of the rotational states ( $\theta_J = \pi/4$ ) is appropriate. We find, for  $F'_i = F_i$ :

$$\begin{aligned} \langle J'M'F_i\epsilon'|V_{el}|JMF_i\epsilon\rangle &\simeq \delta_{MM'}(-1)^{M+1}\sum_T \\ &\times \frac{i}{2}[1-\epsilon\epsilon'(-1)^{J+J'+I}] \begin{pmatrix} J' & J & I \\ M & -M & 0 \end{pmatrix} \\ &\times \left[ \delta_{\epsilon\epsilon'} \begin{pmatrix} J' & J & I \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} V_{I0}(Z) \right. \\ &\left. \pm \epsilon \begin{pmatrix} J' & J & I \\ \frac{1}{2} & \frac{1}{2} & -2 \end{pmatrix} V_{I2}(Z) \right], \end{aligned} \quad (31)$$

where the  $+$  sign refers to the  $F_1 \rightarrow F_1$  coupling matrix elements and the  $-$  sign, to the  $F_2 \rightarrow F_2$  matrix elements. For  $F'_i \neq F_i$  we find

$$\langle J'M'F_i\epsilon'|V_{el}|JMF_i\epsilon\rangle = 0. \quad (32)$$

## V. ENERGY SUDDEN APPROXIMATION

Let us suppose that the total energy  $E$  is large compared to  $\Delta E$ , and the effective collision time short compared to  $\hbar/\Delta E$ , where  $E$  is a typical spacing between initial and final levels. In this case the  $S$ -matrix elements between the  $|JMF_i\epsilon\psi_s\rangle$  states which, by reason of Eqs. (2)–(4) and Eq. (6), are linear combinations of the  $|JM\Omega\Lambda\Sigma\psi_s\rangle$  states, can be written as linear combinations of  $S$ -matrix elements between these  $|JM\Omega\Lambda\Sigma\psi_s\rangle$  states. Since the rotation matrix elements with half-integer  $J$  provide a complete set of eigenfunctions for a symmetric top with even multiplicity,<sup>43</sup> they satisfy the closure relation<sup>46</sup>

$$\begin{aligned} \sum_{JMM'} [(2J+1)/8\pi^2] D_{MM'}^{J*}(\alpha\beta\gamma) D_{MM'}^J(\alpha'\beta'\gamma') \\ = \delta(\alpha - \alpha')\delta(\beta - \beta')\delta(\gamma - \gamma')/\sin\beta. \end{aligned} \quad (33)$$

Thus we can adopt the development originally presented by Secrest<sup>34</sup> and Hunter<sup>35</sup> for gas-phase collisions of  $^1\Sigma$  molecules, and then later applied by Gerber *et al.*<sup>7,8</sup> to collisions of  $^1\Sigma$  molecules with surfaces, and by Alexander<sup>33</sup> to gas-phase collisions of  $^2\Pi$  molecules. The  $S$ -matrix elements in the  $|JM\Omega\Lambda\Sigma\psi_s\rangle$  basis can be written in a form equivalent to Eq. (17), namely,

$$S_{J'M'\Omega'\Lambda'\Sigma'\psi_s, JM\Omega\Lambda\Sigma\psi_s} = \delta_{\Sigma\Sigma'} \frac{1}{4\pi} [(2J+1)(2J'+1)]^{1/2}$$

$$\times \int_0^{2\pi} d\alpha \int_0^\pi D_{M'\Omega'}^{J'}(\alpha\beta 0) D_{M\Omega}^{J*}(\alpha\beta 0) S_{\Lambda'\Lambda}(\beta) \sin\beta d\beta, \quad (34)$$

where  $S_{\Lambda'\Lambda}(\beta)$  is the sudden  $S$  function.

This latter quantity is obtained by solving a scattering problem in which the orientation of the diatomic molecule with respect to the surface normal (the angle  $\beta$ ) is fixed during the time of the strongest interaction with the surface, so that the potential coupling the various  $|JM\Omega\Lambda\Sigma\psi_s\rangle$  channels is given by  $V_{\Lambda'\Lambda}^{\text{eff}}(\beta, Z)$  [Eq. (18)]. Equivalently, the fixed orientation problem can be solved in a basis labeled by  $JM\Lambda\eta\psi_s$ , with a coupling potential given by  $V_{\Lambda'\Lambda\eta}^{\text{eff}}(\beta, Z)$  [Eq. (23)]. In both cases the  $S$  functions can be expanded, following Eqs. (18) and (23), as

$$S_{\Lambda'\Lambda}(\beta) = \sum_I S_{I, \Lambda - \Lambda'} d_{0, \Lambda - \Lambda'}^I(\beta) \quad (35)$$

and

$$S_{\Lambda\eta', \Lambda\eta}(\beta) = \delta_{\eta\eta'} \sum_I [S_{I0} d_{00}^I(\beta) + \eta S_{I2} d_{0, -2}^I(\beta)]. \quad (36)$$

From these two equations and the discussion following Eq. (23), we see that the  $S_{I0}$  terms represent the coefficients in an expansion in Legendre polynomials [since  $[d_{00}^I(\beta) = P_I(\cos\beta)]$ ] of the average of the fixed-orientation  $S$  functions corresponding to the scattering of the molecules with the electronic wave function chosen to be symmetric with respect to reflection in the plane of the surface when  $\beta = \pi/2$  ( $\eta = +1$ ) and with the electronic wave functions chosen to be antisymmetric with respect to the same operation ( $\eta = -1$ ). The  $S_{I2}$  terms represent the coefficients in an expansion in associated Legendre polynomials [since<sup>43</sup>  $d_{0, -2}^I(\beta) \sim P_{I2}(\cos\beta)$ ] of one-half the difference of the  $S$  functions for the  $\eta = +1$  and  $\eta = -1$  electronic wave functions.

The reader should note that this dynamical limit should properly be called an energy-sudden<sup>47</sup> or “coordinate representation”<sup>7,8</sup> sudden limit, but not an “infinite-order-sudden”<sup>34,35,48</sup> limit. The latter was developed for atom-molecule collisions and involves an additional centrifugal decoupling which is irrelevant for molecule-surface scattering, where there is no orbital angular momentum.

In this energy sudden limit the  $S$ -matrix elements in the  $|JMF_i\epsilon\psi_s\rangle$  basis can be obtained from Eqs. (34) and (35) by means of Eqs. (2)–(4) and Eq. (6). The expressions are *entirely equivalent* to the expressions derived in Secs. III and IV for the potential coupling matrix elements of the electrostatic potential [Table I and Eqs. (29)–(32)] with the  $V_{I0}(Z)$  and  $V_{I2}(Z)$  terms replaced by the  $S_{I0}$  and  $S_{I2}$  coefficients, respectively.

It will be useful in the discussion in the next section to derive explicitly from Table I sudden limit expressions for the  $S$ -matrix elements when the initial rotational level at low  $J$  can be described in the case (a) limit with  $\theta_J = 0$  and the final level at high  $J'$  can be described in the case (b) limit with  $\theta'_J = \pi/4$ . We find, for transitions out of an  $F_i$  level:

$$\begin{aligned}
S_{J'M'F'_i\epsilon', JMF_1\epsilon} &= \delta_{MM'} (-1)^{M+1} \\
&\times \sum_l \frac{i}{2^{3/2}} [1 - \epsilon\epsilon' (-1)^{J'+J'+l}] \\
&\times \left[ \begin{pmatrix} J' & J & l \\ M & -M & 0 \end{pmatrix} \left[ \pm S_{l0} \begin{pmatrix} J' & J & l \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix} \right. \right. \\
&\left. \left. + \epsilon S_{l2} \begin{pmatrix} J' & J & l \\ \frac{3}{2} & \frac{1}{2} & -2 \end{pmatrix} \right] \right], \quad (37)
\end{aligned}$$

where the plus sign refers to  $F'_i = F_1$  and the minus sign to  $F'_i = F_2$ . Similarly, for transitions out of an  $F_2$  level, we find

$$\begin{aligned}
S_{J'M'F'_i\epsilon', JMF_2\epsilon} &= \delta_{MM'} (-1)^M \\
&\times \sum_l \frac{i}{2^{3/2}} [1 - \epsilon\epsilon' (-1)^{J'+J'+l}] \\
&\times \left[ \begin{pmatrix} J' & J & l \\ M & -M & 0 \end{pmatrix} \left[ S_{l0} \begin{pmatrix} J' & J & l \\ \frac{3}{2} & -\frac{3}{2} & 0 \end{pmatrix} \right. \right. \\
&\left. \left. \pm \epsilon S_{l2} \begin{pmatrix} J' & J & l \\ \frac{1}{2} & \frac{3}{2} & -2 \end{pmatrix} \right] \right], \quad (38)
\end{aligned}$$

where the plus sign refers to  $F'_i = F_2$  and the minus sign to  $F'_i = F_1$ .

## VI. IMPLICATIONS FOR COLLISIONS OF NO( $X^2\Pi$ ) WITH Ag(111)

Obviously, a complete understanding of inelastic processes in collisions of a  $^2\Pi$  molecule with a surface can come only from a full solution of the CC equations with an *ab initio* description of the various terms in the potential. Several qualitatively different potentials have been developed to describe collisions of NO with Ag(111),<sup>14,17,49</sup> but these potentials correspond only to the  $V_{l0}(Z)$  terms in Eq. (18). Unfortunately, no information is available as yet on the variation of the interaction with the orientation of the unfilled  $\pi$  orbital, which would determine the important  $V_{l2}(Z)$  terms.

Nevertheless, some useful insights into possible trends in the inelastic scattering of NO by Ag(111) can be gained by examination of both the potential matrix elements and sudden limit  $S$ -matrix elements. We shall look, in turn, at polarization effects, fine-structure changing transitions, and  $\Lambda$ -doublet propensities.

### A. Polarization effects

Due to the presence of the Kronecker delta in Eq. (24), we observe that the projection of the molecular angular momentum along the surface normal will be rigorously conserved. It was Gerber, Kouri, and co-workers<sup>8-10</sup> who originally demonstrated this selection rule for collisions of  $^1\Sigma$  molecules with uncorrugated surfaces. This implies that inelastic scattering with the surface will populate only  $M$  states with  $M < J_{\max}$ , where  $J_{\max}$  is the highest rotational level present in the initial beam. If this latter is produced in a supersonic expansion, as in some of the published experiments on NO-Ag(111) scattering,<sup>20-24</sup> then  $J_{\max}$  will be small, so we might expect that the high  $J$  final states will be highly polarized, with significant populations only in the low  $M$  levels. This will correspond to finding the  $\mathbf{J}$  vectors of the scattered molecules oriented preferentially perpendicular to

the surface normal  $\mathbf{Z}$ . This prediction is independent of the exact form of the potential but does depend critically on the assumption of a flat surface. This  $M$  selection rule for NO-Ag(111) collision has also been justified, using both classical and quantum arguments, by Barker and Hurst and their co-workers.<sup>17,18</sup> Kleyn *et al.*<sup>21</sup> have observed this predicted polarization of the scattered NO molecules for  $J'$  levels beyond the rotational rainbow, except at the highest values of  $J'$ , where the polarization is seen to decrease. Also, McCurdy and co-workers<sup>51</sup> have recently discussed rotational polarization in NO-Ag(111) collisions.

### B. Fine-structure changing transitions

A transition from an initial  $J$  to a final  $J'$  can be imagined to take place as a direct process, coupled by terms in the potential with  $l \geq |J' - J|$ , or, as a series of virtual transitions, in the sense of a Born series.<sup>50</sup> Transitions from low  $J$  to high  $J'$  most likely take place by this second type of mechanism. At low to moderate  $J$ , where a case (a) description is appropriate for NO, we see from Eqs. (29) and (30) that inelastic coupling *within* each spin-orbit manifold ( $\Omega = \frac{1}{2}$  and  $\Omega = \frac{3}{2}$ ) will be governed by the  $V_{l0}(Z)$  terms in the potential while inelastic coupling *between* the two spin-orbit manifolds will be governed by the  $V_{l2}(Z)$  terms.

The scattering experiments both at Stanford<sup>21</sup> and IBM<sup>24</sup> indicate that the  $^2\Pi_{3/2}(F_2)$  rotational manifold of NO is substantially populated after collision, despite the fact that the initial beam contains virtually no  $^2\Pi_{3/2}$  molecules. This indicates that the  $V_{l2}(Z)$  terms are much stronger than in the case of collisions of NO with Ar, where both theoretical calculations<sup>28</sup> and molecular beam experiments<sup>52</sup> indicate that the cross sections for  $\Omega$ -changing ( $F_1 \rightleftharpoons F_2$ ) transitions are roughly an order of magnitude smaller than those for transitions within one or the other spin-orbit manifold. Our inference that the  $V_{l2}(Z)$  terms are large in the case of NO-Ag(111) collisions implies, from the discussion in Sec. III, that the NO-Ag(111) interaction potential depends strongly on the orientation of the NO unfilled  $\pi$  electron with respect to the surface, certainly more strongly than in the case of the interaction of NO( $X^2\Pi$ ) with Ar.

A possible explanation involves the contribution of ionic  $\text{Ag}^+ - \text{NO}^- (X^3\Sigma^-)$  structures to the wave function which arise from transfer of an electron from Ag into the other, unfilled NO  $\pi$  orbital. Since the work function of Ag is  $\sim 4.3$  eV<sup>53</sup> and the electron affinity of NO is 0.02 eV,<sup>54</sup> we expect, based on simple ionic-covalent curve-crossing arguments,<sup>55</sup> that these ionic structures will contribute significantly whenever the NO-Ag distance is less than  $\sim 3$  Å. The coupling between the ionic and covalent [ $\text{Ag} - \text{NO}(X^2\Pi)$ ] structures will be roughly proportional<sup>56</sup> to the overlap between the initially occupied Ag surface state wave function and the NO  $\pi$  orbital occupied by the transferred electron. For geometries where the NO molecule lies in the plane of the surface, this overlap will be substantially larger if the electron transfers into the  $\pi$  orbital which is perpendicular to the surface, which implies that the unfilled  $\pi$  orbital of the original NO lies in the plane of the surface. In other words, the  $\text{Ag}^+ - \text{NO}^-$  ionic structures may contribute more substantially to the  $|\Lambda\eta\rangle$  wave function with  $\eta = +1$  [Eq. (21)] than to the



wave function with  $\eta = -1$ . Since the  $V_{12}(Z)$  terms arise from the expansion of the difference in the effective potentials for the  $\eta = +1$  and  $\eta = -1$  wave functions, it is understandable that these terms may be large for the NO–Ag(111) interaction.

To return to our discussion of the relative strength of the spin-orbit changing and spin-orbit conserving transitions, it is instructive, for transitions terminating in high  $J$  final states, to examine the case (b) potential matrix elements, given in Eqs. (31) and (32). We notice first that the  $F_1 \rightarrow F_2$  coupling vanishes in the case (b) limit, so that the  $F_1:F_2$  population ratio for high  $J$  final states probably becomes “frozen in” at lower  $J$  and probably will not change significantly with  $J$  once the final states enter the case (b) region. Again, we see evidence for this in the experimental results from the IBM group.<sup>24</sup>

In a rotationally cold NO beam, only the low  $J, F_1$  levels will be significantly populated. If we look at the sudden limit  $S$ -matrix elements for transitions from a low  $J, F_1$  level into a high  $J'$  level [Eqs. (37) and (38)], we observe that the transition probabilities satisfy the following symmetry relations:

$$P_{JMF_1e/f \rightarrow J'M'F_1e/f} = P_{JMF_1f/e \rightarrow J'M'F_2f/e}, \quad (39)$$

and

$$P_{JMF_1e/f \rightarrow J'M'F_1f/e} = P_{JMF_1f/e \rightarrow J'M'F_2e/f}. \quad (40)$$

Thus, if one sums over the initial and final  $A$  doublets one predicts that transitions to the  $F_1$  and  $F_2$  levels at high  $J$  will be equally probable, again in agreement with the experimental results of Luntz, Kleyn, and Auerbach<sup>24</sup> as well as with those of Kubiak and co-workers<sup>21</sup> at their highest collision energy.

### C. $A$ -doublet propensities

If we take Eqs. (39) and (40) and sum only over the initial state  $A$  doublets, we find

$$P_{JMF_1 \rightarrow J'M'F_1e/f} = P_{JMF_1 \rightarrow J'M'F_2f/e}, \quad (41)$$

which implies that of the four possible final levels, for a given  $J'$ , the  $F_1e$  and  $F_2f$  levels will be produced equally and, similarly, the  $F_1f$  and  $F_2e$  levels. We cannot predict which of these two pairs will be produced preferentially; this will depend on the relative signs and magnitudes of the  $S_{10}$  and  $S_{12}$  coefficients in the expansion of the sudden  $S$  function, which themselves depend on the relative signs and magnitudes of the  $V_{10}(Z)$  and  $V_{12}(Z)$  terms in the expansion of the potential.

For a  $^2\Pi$  molecule at large  $J$ , the wave functions of the  $F_1e$  and  $F_2f$   $A$ -doublet levels are *symmetric* with respect to reflection of the electronic coordinates in the plane of rotation of the molecule,<sup>37</sup> and would be probed by  $P$ - and  $R$ -branch lines of a  $^2\Sigma^+ \rightarrow ^2\Pi$  transition (as, for example, the  $A \leftarrow X$  transition in NO). The wave functions of the  $F_1f$  and  $F_2e$  levels are *antisymmetric* with respect to this operation, and would be probed by  $Q$ -branch lines.<sup>37</sup> Thus within the energy sudden limit, we predict that the final  $A$ -doublet levels will be produced in two unequal pairs, with a propensity toward either the two levels which are symmetric with respect to reflection in the plane of rotation or the two levels which are antisymmetric. This is entirely consistent with the

observations of Luntz, Kleyn, and Auerbach<sup>24</sup> that in the scattering of high energy ( $E = 0.86$  eV) beams of NO by Ag(111), for  $J' > 30.5$  the  $A$ -doublet levels probed by  $P$ - and  $R$ -branch lines ( $F_1e$  and  $F_2f$ ) are produced in greater abundance than the two levels probed by  $Q$ -branch lines ( $F_1f$  and  $F_2e$ ).

## VII. CONCLUSION

In this article, we have extended the quantum theory of collisions of a diatomic molecule with an uncorrugated surface to treat the case of an open-shell  $^2\Pi$  molecule. We have shown how, similarly to the gas-phase collision of a  $^2\Pi$  molecule with an atom, the matrix elements of the interaction potential can be expanded in terms which involve the sum and difference of the two electrostatic potentials corresponding to the two possible orientations of the unfilled  $\pi$  shell. The close-coupled equations were formulated in an intermediate coupling basis, which allowed the treatment of rotational states at both low  $J$ , where a Hund's case (a) description is appropriate, and high  $J$ , where a Hund's case (b) description is appropriate. Expressions for the inelastic  $S$ -matrix elements were derived within the energy sudden limit. We were able to use this general formal work to make the following predictions for the scattering of a rotationally cold beam of  $^2\Pi$  molecules with a flat, rigid surface:

(1) For moderate to high values of the final rotational quantum number, the  $M$ -dependent populations will be strongly peaked at low values of  $M$ , implying that the molecules will be scattered so that  $\mathbf{J}$  lies in the plane of the surface. This propensity applies also to the scattering of a closed-shell molecule, as predicted by other authors.<sup>7–10,17,18,51</sup>

(2) Transitions between the two spin-orbit manifolds ( $F_1$  and  $F_2$ ) are induced by the difference in the two electrostatic potentials. The  $F_1 \rightarrow F_2$  coupling is strongest at low  $J$  and gradually diminishes as the Hund's case (b) limit is attained. In the energy sudden limit, we predict that the  $F_1$  and  $F_2$  manifolds will be populated equally. The strength of the spin-orbit changing transitions observed in NO–Ag(111) scattering experiments<sup>24</sup> might reflect a substantial contribution of  $\text{Ag}^+ \text{--} \text{NO}^-$  ionic structures to the electronic wave function at close approach.

(3) Also in the energy sudden limit, we predict that preferential population will occur of either the two  $A$ -doublet levels which are symmetric with respect to reflection in the plane of rotation of the molecule ( $F_1e$  and  $F_2f$ ) or the two  $A$ -doublet levels which are antisymmetric with respect to this reflection ( $F_1f$  and  $F_2e$ ). Which pair of levels is favored in any given system will depend on the details of the interaction potential.

The reader should observe that all three of the above predictions are completely general in the sense that they are independent of a particular choice of interaction potential, but apply only to single collisions with an uncorrugated, rigid surface. Obviously, surface corrugations could well cause substantial deviations from these predictions. On the other hand, trapping–desorption processes might not scramble the propensity either toward equal  $F_1:F_2$  ratios or toward unequal  $A$ -doublet level populations at high  $J$ . This conclusion



would be justified if trapping-desorption could be treated as two, distinct half-collisions, each one conserving these properties.

It could be argued that the energy sudden limit is not valid for the high  $\Delta J$  transitions ( $\Delta J > 30$ ) at which the marked spin-orbit and  $\Lambda$ -doublet effects have been observed by Luntz, Kleyn, and Auerbach<sup>24</sup> in NO-Ag(111) scattering. Fitz *et al.*<sup>9</sup> found the energy sudden transition probabilities to be highly inaccurate for collisions of H<sub>2</sub> with a model uncorrugated surface. However, in studies of NO( $X^2\Pi$ )-Ag(111) scattering with a basically repulsive potential, Voges and Schinke<sup>14</sup> have shown how energy sudden calculations can accurately predict the overall  $J$  dependence of exact CC transition probabilities. Also, it may well be that qualitative predictions, such as those in Sec. VI, based on a sudden limit analysis are entirely reasonable even for interaction potentials or collision regimes where the sudden transition probabilities would not be of quantitative accuracy.

Obviously, this question could be answered, and our understanding of NO-Ag(111) collisions advanced, by following up the present formal study by actual close-coupling calculations. One of the available potentials<sup>14,17,49</sup> could be used for the  $V_{l0}(Z)$  terms, and a reasonable choice made for the lowest  $V_{l2}(Z)$  terms ( $l = 2, 3$ ). An important question is whether, for a given set of  $V_{l0}(Z)$  terms, treating the molecule as a  $^2\Pi$  rather than  $^1\Sigma$  molecule would result in a significant change in the calculated transition probabilities. As stated in the Introduction, our recent study of Ar-NO( $X^2\Pi$ ) collisions<sup>28</sup> indicated that substantial errors (factors of 2–3) were introduced in the cross sections when the molecule was treated as a  $^1\Sigma$  system, even if the  $\Lambda$  doublets were not resolved. Only by this type of study, and by related high resolution experimental work, will we be able to obtain a clearer understanding of the subtle interactions which characterize collisions of open-shell molecules with surfaces.

## ACKNOWLEDGMENTS

The research reported here was supported in part by the National Science Foundation, Grant CHE81-08462. The author would like to thank David King, Alan Luntz, and John Tully for helpful comments and suggestions. He is also particularly grateful to Andrew DePristo for his encouragement, for a critical reading of the manuscript, and for pointing out the importance of charge-transfer structures in the electronic wave function.

## APPENDIX: RELATIVE SIGNS OF $V_{\mu}(Z)$ TERMS

To determine the dependence of the  $V_{\mu}(Z)$  terms [Eq. (19)] on the sign of  $\mu$  it is sufficient to consider only those electrons in unfilled  $\pi$  orbitals. These  $\pi$  orbitals can be expanded as LCAO's, namely (in R eggen's notation<sup>57</sup>)

$$|\pi_{\lambda}\rangle = \sum_{jkl} |jkl\lambda\rangle \langle jkl\lambda | \pi_{\lambda} \rangle, \quad (\text{A1})$$

where  $j$  denotes the atomic center, and  $k$  and  $l$  index the atomic orbitals of azimuthal symmetry  $\lambda = \pm 1$ . We also have<sup>57</sup>  $\langle jkl - \lambda | \pi_{-\lambda} \rangle = \langle jkl\lambda | \pi_{\lambda} \rangle$ . From Eq. (19) the dependence on  $\mu$  of the  $V_{\mu}(Z)$  terms is given by the integral

$$\sum_i \int d\phi_{m_i} \langle \Lambda' | C_{i\mu}(\hat{\rho}_{m_i}) | \Lambda \rangle, \quad (\text{A2})$$

where  $\phi_{m_i}$  is the molecule-frame azimuthal angle of the  $i$ th electron. Since the angular dependence of the atomic orbitals in Eq. (A1) is governed by the spherical harmonics  $Y_{\lambda\lambda}$ , it can be shown that for a singly occupied  $\pi$  orbital [as in NO( $X^2\Pi$ )] this integral vanishes except for  $\mu = 0, \pm 2$  and, furthermore, for  $\mu = \pm 2$  the sign of the integral is independent of the sign of  $\mu$ .

For a  $\pi^3$  electron occupancy [as in OH( $X^2\Pi$ )] the three electrons in the unfilled  $\pi$  orbital can be described by Slater determinants, namely<sup>58</sup>

$$|\Lambda = 1\rangle = |\pi_1 \bar{\pi}_1 \pi_{-1}\rangle \quad (\text{A3})$$

and

$$|\Lambda = -1\rangle = |\pi_{-1} \bar{\pi}_{-1} \pi_1\rangle. \quad (\text{A4})$$

It follows that<sup>58</sup>

$$\begin{aligned} \sum_i \int d\phi_{m_i} \langle \Lambda' = \mp 1 | C_{i\mu}(\hat{\rho}_{m_i}) | \Lambda = \pm 1 \rangle \\ = - \int d\phi_m \langle \pi_{\lambda = \mp 1} | C_{\mu}(\hat{\rho}_m) | \pi_{\lambda = \pm 1} \rangle. \end{aligned} \quad (\text{A5})$$

Thus, exactly as in the case of a singly filled  $\pi$  orbital, the  $V_{\mu}(Z)$  terms for  $\mu = \pm 2$  are independent of the sign of  $\mu$ .

<sup>1</sup>G. Wolken, Jr., J. Chem. Phys. **59**, 1159 (1973).

<sup>2</sup>F. O. Goodman and W. S. Liu, Surf. Sci. **49**, 417 (1975).

<sup>3</sup>U. Garibaldi, A. C. Levi, R. Spacini, and G. E. Tommei, Surf. Sci. **55**, 40 (1976).

<sup>4</sup>J. C. Tully, Annu. Rev. Phys. Chem. **31**, 319 (1980).

<sup>5</sup>J. C. Tully, C. W. Muhlhausen, and L. R. Ruby, Ber. Bunsenges. Phys. Chem. **86**, 433 (1982); C. W. Muhlhausen, J. A. Serri, J. C. Tully, G. E. Becker, and M. J. Cardillo, Isr. J. Chem. **22**, 315 (1982).

<sup>6</sup>J. E. Adams, Surf. Sci. **97**, 43 (1980).

<sup>7</sup>R. B. Gerber, A. T. Yinnon, Y. Shimoni, and D. J. Kouri, J. Chem. Phys. **73**, 4397 (1980).

<sup>8</sup>R. B. Gerber, L. H. Beard, and D. J. Kouri, J. Chem. Phys. **74**, 4709 (1981).

<sup>9</sup>D. E. Fitz, A. O. Bawagan, L. H. Beard, D. J. Kouri, and R. B. Gerber, Chem. Phys. Lett. **80**, 537 (1981); D. E. Fitz, L. H. Beard, and D. J. Kouri, Chem. Phys. **59**, 257 (1981).

<sup>10</sup>D. J. Kouri and R. B. Gerber, Isr. J. Chem. **22**, 321 (1982).

<sup>11</sup>H. Asada, Surf. Sci. **110**, 270 (1981).

<sup>12</sup>R. Schinke, J. Chem. Phys. **76**, 2352 (1982).

<sup>13</sup>H. Voges and R. Schinke, Chem. Phys. Lett. **95**, 221 (1983).

<sup>14</sup>H. Voges and R. Schinke, Chem. Phys. Lett. **100**, 245 (1983).

<sup>15</sup>L. M. Hubbard and W. H. Miller, J. Chem. Phys. **78**, 1801 (1983).

<sup>16</sup>C. J. Ray and J. M. Bowman, J. Chem. Phys. **66**, 1122 (1977); J. M. Bowman and S. C. Park, *ibid.* **76**, 1168 (1982); **77**, 5441 (1982); **79**, 3172(E) (1983).

<sup>17</sup>J. A. Barker, A. W. Kleyn, and D. J. Auerbach, Chem. Phys. **97**, 9 (1983).

<sup>18</sup>J. E. Hurst, Jr., G. D. Kubiak, and R. N. Zare, Chem. Phys. Lett. **93**, 235 (1982).

<sup>19</sup>F. Frenkel, J. H ager, W. Krieger, H. Walther, C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, Phys. Rev. Lett. **46**, 152 (1981); F. Frenkel, J. H ager, W. Krieger, H. Walther, G. Ertl, J. Segner, and W. Vielhaber, Chem. Phys. Lett. **90**, 225 (1982).

<sup>20</sup>G. M. McClelland, G. D. Kubiak, H. G. Rennagel, and R. N. Zare, Phys. Rev. Lett. **46**, 831 (1981).

<sup>21</sup>G. D. Kubiak, J. E. Hurst, Jr., H. G. Rennagel, G. M. McClelland, and R. N. Zare, J. Chem. Phys. **79**, 5163 (1983).

<sup>22</sup>A. W. Kleyn, A. C. Luntz, and D. J. Auerbach, Phys. Rev. Lett. **47**, 1169 (1981); Surf. Sci. **117**, 33 (1982).

<sup>23</sup>A. C. Luntz, A. W. Kleyn, and D. J. Auerbach, Phys. Rev. B **25**, 4273 (1982).

- <sup>24</sup>A. C. Luntz, A. W. Kleyn, and D. J. Auerbach, *J. Chem. Phys.* **76**, 737 (1982).
- <sup>25</sup>M. Asscher, W. L. Guthrie, T.-H. Lin, and G. A. Somorjai, *Phys. Rev. Lett.* **49**, 76 (1982); *J. Chem. Phys.* **78**, 6992 (1983).
- <sup>26</sup>J. S. Hayden and G. J. Diebold, *J. Chem. Phys.* **77**, 4767 (1982).
- <sup>27</sup>R. R. Cavanaugh and D. S. King, *Phys. Rev. Lett.* **47**, 1829 (1981).
- <sup>28</sup>T. Orlikowski and M. H. Alexander, *J. Chem. Phys.* **79**, 6006 (1983).
- <sup>29</sup>H. Klar, *J. Phys. B* **6**, 2139 (1973).
- <sup>30</sup>S. Green and R. N. Zare, *Chem. Phys.* **7**, 62 (1975).
- <sup>31</sup>R. N. Dixon and D. Field, *Proc. R. Soc. London Ser. A* **368**, 99 (1979).
- <sup>32</sup>M. Shapiro and H. Kaplan, *J. Chem. Phys.* **71**, 2182 (1979).
- <sup>33</sup>M. H. Alexander, *J. Chem. Phys.* **76**, 5974 (1982).
- <sup>34</sup>D. Secrest, *J. Chem. Phys.* **62**, 710 (1975).
- <sup>35</sup>L. W. Hunter, *J. Chem. Phys.* **62**, 2855 (1975).
- <sup>36</sup>G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, Princeton, 1950).
- <sup>37</sup>M. H. Alexander and P. J. Dagdigian, *J. Chem. Phys.* (in press).
- <sup>38</sup>J. T. Hougen, *Natl. Bur. Stand. (U.S.) Monogr.* **115** (1970).
- <sup>39</sup>M. H. Alexander and P. J. Dagdigian, *J. Chem. Phys.* **79**, 302 (1983).
- <sup>40</sup>R. N. Zare, A. L. Schmeltekopf, W. J. Harrop, and D. L. Albritton, *J. Mol. Spectrosc.* **46**, 37 (1973).
- <sup>41</sup>J. M. Brown, J. T. Hougen, K. P. Huber, J. W. C. Johns, I. Kopp, H. Lefebvre-Brion, A. R. Merer, D. A. Ramsay, J. Rostas, and R. N. Zare, *J. Mol. Spectrosc.* **55**, 500 (1975).
- <sup>42</sup>M. Larsson, *Phys. Scr.* **23**, 835 (1981).
- <sup>43</sup>D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd ed. (Oxford University, Oxford, 1975).
- <sup>44</sup>C. G. Gray, *Can. J. Phys.* **54**, 505 (1976).
- <sup>45</sup>G. C. Nielson, G. A. Parker, and R. T. Pack, *J. Chem. Phys.* **66**, 1396 (1977).
- <sup>46</sup>The proof of Eq. (33) is analogous to that given on pp. 157–158 of A. Messiah, *Mécanique Quantique* (Dunod, Paris, 1965), Vol. 1.
- <sup>47</sup>See, for example, V. Khare, *J. Chem. Phys.* **68**, 4631 (1978).
- <sup>48</sup>R. T. Pack, *J. Chem. Phys.* **60**, 633 (1974); G. A. Parker and R. T. Pack, *ibid.* **66**, 2850 (1977).
- <sup>49</sup>J. C. Tully (unpublished).
- <sup>50</sup>See, for example, G. G. Balint-Kurti, in *Theoretical Chemistry*, MTP International Review of science, Physical Chemistry, Ser. 2 (Butterworths, London, 1975), Vol. 1.
- <sup>51</sup>J. G. Lauderdale, J. F. McNutt, and C. W. McCurdy, *Chem. Phys. Lett.* (to be published).
- <sup>52</sup>H. Joswig and P. Andresen (to be published).
- <sup>53</sup>American Institute of Physics Handbook, 3rd ed. (McGraw-Hill, New York, 1972).
- <sup>54</sup>M. W. Siegel, R. J. Celotta, J. L. Hall, J. Levine, and R. A. Bennett, *Phys. Rev. A* **6**, 607 (1972).
- <sup>55</sup>E. A. Gislason and J. G. Sachs, *J. Chem. Phys.* **62**, 2678 (1975).
- <sup>56</sup>See, for example, M. H. Alexander, *J. Chem. Phys.*, **69**, 3502 (1978).
- <sup>57</sup>I. Röeggen, *Theor. Chim. Acta* **21**, 398 (1971).
- <sup>58</sup>E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, 1963) Chap. VI.