Polarization and Mdependent effects in rotationally inelastic collisions of openshell diatomic molecules: Ar–NO(X 2Π1 / 2)

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Polarization and M-dependent effects in rotationally inelastic collisions of open-shell diatomic molecules: Ar–NO($X\,^2\Pi_{1/2}$)

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Our earlier quantum study of collisions of NO($X\,^2\Pi$) with Ar [T. Orlikowski and M. H. Alexander, J. Chem. Phys. **79**, 6006 (1983)] is here extended to the calculation of M-dependent cross sections in the case of laboratory-frame quantization, as would be appropriate to collision cell experiments. The calculations confirm the earlier prediction of Alexander and Davis [J. Chem. Phys. **79**, 227 (1983)] that the $JM \rightarrow J, -M$ cross sections will be vanishingly small for transitions which preserve the e or $f\Lambda$-doublet symmetry. This propensity rule is here shown to be rigorous within the coupled-states (CS) limit. The effect of collisions on the initial rotational density matrix can be expressed in terms of multipole transfer efficiencies. The calculated values for Ar–NO collisions indicate that e/f changing collisions are much more strongly depolarizing, in the sense of destroying the multipole moments of the initial density matrix, than those collisions which preserve the $e/f\Lambda$-doublet label. Since the circular or linear polarization of the fluorescence from a laser excited molecule can be written in terms of these multipole transfer efficiencies, we are able to use the Ar–NO($X\,^2\Pi$) cross sections reported here to model qualitatively the depolarization effects one might expect to see in experiments involving excited molecules in $^2\Pi$ electronic states.

I. INTRODUCTION

Over the past several years, there has been considerable theoretical interest[1-14] in rotational energy transfer in collisions involving open-shell diatomic molecules, where the total angular momentum of the molecule has a nonzero projection along the molecular axis. The degeneracy with respect to the sign of the projection quantum number is lifted by small terms in the molecular Hamiltonian, resulting in a slight splitting of the rotational levels.[15] Alexander and Davis have shown how one can develop selection rules for collision induced transitions between these rotational multiplets. One of these selection rules[10,11] applies to M-dependent cross sections, in particular, to the situation of laboratory frame quantization, where there exists a distribution of collision frames with respect to the laboratory fixed z axis. This would be appropriate to the analysis of experimental observations of M-dependent collisions in cell experiments.[16-25]

In the present article, we shall extend our earlier fully quantum study of Ar–NO($X\,^2\Pi$) collisions to the calculation of laboratory frame M-dependent cross sections, specifically within the $\Omega = \frac{1}{2}$ spin-orbit manifold. These cross sections dramatically confirm the earlier prediction of Alexander and Davis[11] that for spin $\frac{1}{2}$ systems the $JM\Omega \rightarrow J, -M, \Omega$ cross sections will be negligibly small for transitions which preserve the e or $f\Lambda$-doublet symmetry.[26] This selection rule was originally derived within both the first-order Born[4,27] and infinite order sudden[7,9,14,28-32] treatments of the collision dynamics. We shall show here that the validity of this selection rule extends to the coupled-states (CS)[7,9,28,29,33,34] limit. We shall use the results of an exact close-coupling[4-7,9,35,36]

study of Ar–NO collisions to demonstrate that collisional transfer of the various tensor multipole moments[16,18-21,23,37-40] of the NO rotational population distribution is significantly different for processes which conserve, on the one hand, or change, on the other hand, the e/f symmetry[26] of the Λ doublets.

The organization of the present paper is as follows: In the next section, we shall review necessary elements of the formal treatment of the collision dynamics. It will be useful to introduce several notational and conceptual elements from the nuclear physics literature.[41] Additionally, we shall make use of a rotationally invariant expansion of the T matrix,[23,40,42-49] introduced originally by Curtiss, Snider, Hunter, and their co-workers,[44-46] by Grawert,[47] and by Fano and Dill.[48] Then in Sec. III we shall discuss how the $JM \rightarrow J, -M$ selection rule, mentioned above, follows from the vanishing of either the even or odd tensor orders in the rotationally invariant expansion of the T matrix. This vanishing will be rigorously demonstrated in the CS limit. This formal work will be confirmed in Sec. IV by the results of our exact close-coupling treatment of Ar–NO($X\,^2\Pi_{1/2}$) collisions. In Sec. V we shall use these numerical results to speculate on possible polarization effects in experimental studies of relaxation of molecules in excited $^2\Pi$ electronic states, where polarized light would be used to populate the excited state in a manner similar to experiments already reported in the literature.[17,18,22,24,25,50,51] A brief conclusion follows.

II. COLLISION DYNAMICS

We shall follow our earlier publications[9,11,13] as closely as possible and reproduce here only those equations which are directly relevant. In a Hund's case (a) basis the definite parity wave functions of an open-shell diatomic molecule are

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written as

$$|JM\Omega\epsilon\rangle = 2^{-1/2}[\,|JM\Omega\rangle|\Lambda\,S\Sigma\rangle$$
$$+ \epsilon|JM, -\Omega\rangle| - \Lambda, S, -\Sigma\rangle\,]. \qquad (1)$$

Here J is the total angular momentum of the molecule with space- and body-frame projections M and Ω; S and Σ denote the spin angular momentum and its body-frame projection; and Λ is the body-frame projection of the electronic orbital angular momentum. The symmetry index ϵ can take on the values ± 1. The total parity of the wave functions is given by[52]

$$i|JM\Omega\epsilon\rangle = \epsilon(-1)^{J-S-s}|JM\Omega\epsilon\rangle, \qquad (2)$$

where $s = 1$ for Σ^- states and zero otherwise. The current spectroscopic practice is to label the Λ doublets e and f,[26] with[11]

$$\epsilon = \pm(-1)^{S-s-q}, \qquad (3)$$

where the plus sign refers to the e levels and where $q = 0$ for integer spins and $q = \frac{1}{2}$ for half-integer spins.

The collision between a molecule in the $|JM\Omega\epsilon\rangle$ state and a structureless target is usually treated[4-9] by expanding the overall wave function in terms of eigenfunctions of the total angular momentum $\mathscr{J}$, namely

$$|JL\Omega\epsilon\mathscr{J}\mathscr{M}\rangle = \sum_{MM_L} \langle JMLM_L|\mathscr{J}\mathscr{M}\rangle|JM\Omega\epsilon\rangle|LM_L\rangle. \qquad (4)$$

Here $\langle\cdots|\cdots\rangle$ is a Clebsch–Gordan coefficient;[39] $\mathscr{M}$ is the space-frame projection of $\mathscr{J}$; and L is the orbital angular momentum of the atom–molecule system with space-fixed projection M_L. The $|LM_L\rangle$ functions are spherical harmonics with parity $(-1)^L$.[39] Taking into account the parity of the molecular wave functions [Eq. (2)], we see that the parity of the total angular momentum wave functions [Eq. (4)] is

$$i|JL\Omega\epsilon\mathscr{J}\mathscr{M}\rangle = \epsilon(-1)^{J+L+S-s}|JL\Omega\epsilon\mathscr{J}\mathscr{M}\rangle. \qquad (5)$$

The coefficients which describe the expansion of the scattering wave function in terms of the $|JL\Omega\epsilon\mathscr{J}\mathscr{M}\rangle$ wave functions satisfy the close-coupled (CC) equations.[4-7,9,35,36] From the asymptotic behavior of the solutions, one can extract the relevant S-matrix elements, indexed in $\mathscr{J}$ and in the $JL\Omega\epsilon$ quantum numbers of the initial and final total angular momentum states. The scattering amplitude is given[11,19,42,53]:

$$f_{JM\Omega\epsilon,J'M'\Omega'\epsilon'}(\hat{R},\hat{R}') = 2\pi \sum_{\mathscr{J}\mathscr{M}LM_LL'M'_L} i^{L-L'}(-1)^{L+L'+J+J'}(2\mathscr{J}+1)$$

$$\begin{pmatrix} J & L & \mathscr{J} \\ M & M_L & -\mathscr{M} \end{pmatrix}\begin{pmatrix} J' & L' & \mathscr{J} \\ M' & M'_L & -\mathscr{M} \end{pmatrix} Y^*_{LM_L}(\hat{R}')Y_{L'M'_L}(\hat{R})T^{\mathscr{J}}_{JL\Omega\epsilon,J'L'\Omega'\epsilon'}. \qquad (6)$$

Here $\begin{pmatrix}\cdots\end{pmatrix}$ is a $3j$ symbol;[39] Y_{LM_L} is a spherical harmonic; the T-matrix element is

$$T^{\mathscr{J}}_{JL\Omega\epsilon,J'L'\Omega'\epsilon'} \equiv \delta_{JJ'}\cdot\delta_{LL'}\cdot\delta_{\Omega\Omega'}\cdot\delta_{\epsilon\epsilon'} - S^{\mathscr{J}}_{JL\Omega\epsilon,J'L'\Omega'\epsilon'};$$

$\hat{R}$ describes the scattering in the collision frame, with z axis along the initial relative velocity vector $\mathbf{v}_{rel}$; and $\hat{R}'$ describes the orientation of the collision frame with respect to an external (laboratory) frame z axis to which the M and M' quantum numbers refer.

Since the T matrix is rotationally invariant, it is possible to expand the T-matrix elements in Eq. (6) in terms of irreducible tensor components.[11,23,40,42-49] The resulting reduced T-matrix elements are defined by[11,42,43]

$$\langle J'L'\Omega'\epsilon'\|T_K\|JL\Omega\epsilon\rangle = (-1)^{-J-L'}(2K+1)$$

$$\times\sum_{\mathscr{J}}(-1)^{-\mathscr{J}}(2\mathscr{J}+1)$$

$$\times\begin{Bmatrix} L' & J' & \mathscr{J} \\ J & L & K \end{Bmatrix}T^{\mathscr{J}}_{JL\Omega\epsilon,J'L'\Omega'\epsilon'}, \qquad (7)$$

where $\begin{Bmatrix}\cdots\end{Bmatrix}$ is a $6j$ symbol.[39] This decomposition was first introduced in the field of molecular collisions by Curtiss, Hunter, Snider, and co-workers[44-46] and was designated by them as the "translational-internal" coupling scheme. They, as well as Bréchignac and co-workers[23] and Derouard,[49] have identified the tensor order K in Eq. (7) with the amount of angular momentum transferred during the collision, since in a vector coupling argument we would have

$$K = |\mathbf{J} - \mathbf{J}'| = |\mathbf{L} - \mathbf{L}'|.$$

A *necessary* condition for the validity of Eq. (7) is the rotational invariance of the T matrix; a *sufficient*, but not *necessary* condition, is that the scalar collision (or T) operator be factorable as a double sum of products of spherical tensor operators, namely[43,54]

$$T = \sum_{KQ}(-1)^Q A(KQ)B(K-Q), \qquad (8)$$

where A denotes an operator in the $\hat{R}$ space, which describes the relative orientation of the collision partners; and B denotes an operator in the so-called $\hat{r}$ space,[43] which describes the internal degrees of freedom of the molecule and its orientation in the collision frame.

It will be important in the discussion in Sec. IV to observe that the triangular relations contained in the $6j$ symbol in Eq. (7) imply that for $K = 0$, J must equal J' and L must equal L'. Since the T-matrix elements vanish unless the parity of the initial and final states is the same, it follows from Eqs. (5) and (7) that the $K = 0$ reduced T-matrix element will vanish unless $\epsilon' = \epsilon$.

As discussed originally by Grawert[47] in the field of atomic collisions, and by Hunter and Curtiss[44] in the field of molecular collisions, the scattering amplitude itself can be expanded in irreducible tensor components, namely[11,42]

$$f_{JM\Omega\epsilon,J'M'\Omega'\epsilon'} = (-1)^{-J-M}\sum_{KQ}(2K+1)^{1/2}(-1)^{K-Q}$$

$$\times\begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix}f^{KQ}_{J\Omega\epsilon,J'\Omega'\epsilon'}, \qquad (9)$$

where

$$f^{KQ}_{J\Omega\epsilon,J'\Omega'\epsilon'} = 2\pi(2K+1)^{1/2}\sum_{LM_LL'M'_L} i^{L-L'}(-1)^{M_L}Y^*_{LM_L}(\hat{R}')$$

$$\times Y_{L'M'_L}(\hat{R})\begin{pmatrix} L & L' & K \\ M_L & -M'_L & -Q \end{pmatrix}$$

$$\times (J'L'\Omega'\epsilon'\|T_K\|JL\Omega\epsilon). \tag{10}$$

Equation (10) can be derived from Eqs. (6), (7), and (9).

If one squares Eq. (9), integrates over $\hat{R}$, and averages over all possible values of $\hat{R}$, then one obtains the following expression for the integral M-state resolved cross sections:

$$\sigma_{JM\Omega\epsilon\rightarrow J'M'\Omega'\epsilon'} = \frac{\pi}{k^2_{J\Omega\epsilon}}\sum_{KQ}\begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix}^2$$

$$\times P^K_{J\Omega\epsilon,J'\Omega'\epsilon'}, \tag{11}$$

where the *tensor opacity* $P^K_{J\Omega\epsilon,J'\Omega'\epsilon'}$ is defined in terms of the reduced T-matrix elements as[11,42]

$$P^K_{J\Omega\epsilon,J'\Omega'\epsilon'} = \frac{1}{2K+1}\sum_{LL'}|(J'L'\Omega'\epsilon'\|T_K\|JL\Omega\epsilon)|^2. \tag{12}$$

Equation (11) is the appropriate expression for collision cell

$$\rho^K_Q(J\Omega\epsilon) = (2K+1)^{1/2}(-1)^{K-Q-J}\sum_M(-1)^{-M}\begin{pmatrix} J & J & K \\ -M & M'' & -Q \end{pmatrix}\rho_{JM\Omega\epsilon,JM''\Omega\epsilon}, \tag{14}$$

and similarly for $\rho^K_Q(J'\Omega'\epsilon')$. The $K=1$ components describe the *orientation* vector of the rotational state, and the $K=2$ components describe the *alignment* tensor of the rotational state.[41] If any of the $K=1$ or $K=2$ components is nonvanishing, the rotational state is said to be *polarized*.

In Eq. (14), as well as hereafter, it is important to distinguish between the tensor orders which appear in the irreducible expansion of both the T matrix [Eq. (7)] and, subsequently, the scattering amplitude [Eqs. (9) and (10)] and tensor opacities [Eq. (12)]; and the tensor orders which appear in the irreducible expansion of the density matrices of the initial and final rotational states [Eq. (14)]. In the former case, we have formed *statistical tensors*[39] by coupling the $\langle JM|$ states with the $|J'M'\rangle$ states, with the allowed values of

experiments, where the individual collision frames are isotropically distributed with respect to the laboratory frame quantization axis. A consequence of the discussion in the paragraph preceding Eq. (9) is that the $K=0$ tensor opacities will vanish unless $\epsilon'=\epsilon$.

As discussed 30 years ago in the nuclear physics literature,[37,38] the density matrix[37–40,55] which characterizes the distribution of final M' states can be written in terms of the density matrix of the initial rotational state as[56]

$$\rho_{J'M'\Omega'\epsilon',J'M''\Omega'\epsilon'} = \sum_{MM''}\rho_{JM\Omega\epsilon,JM''\Omega\epsilon}$$

$$f_{JM\Omega\epsilon,J'M'\Omega'\epsilon'}f^*_{JM''\Omega\epsilon,J'M''\Omega'\epsilon'}. \tag{13}$$

Thus, the M-dependent scattering amplitudes can be seen to form, for the scattering event described by the angles $\hat{R}$ and $\hat{R}'$, the transformation matrix from the density matrix of initial rotational states (J) in the incoming beam to the density matrix of final rotational states (J'). It is often convenient to work with *state multipoles*, which are the rotationally invariant components of the initial and final density matrices, and which we define, following Brink and Satchler,[39] as

the tensor order being given by

$$|J-J'|\leqslant K\leqslant J+J'.$$

In the latter case (initial and final density matrices), we are coupling the $\langle JM|$ states with the $|JM''\rangle$ states, or, for the final state, the $\langle J'M'|$ states with the $|J'M'''\rangle$ states, with the allowed values of the tensor order being given by $0\leqslant K\leqslant 2J$ (or $0\leqslant K\leqslant 2J'$). Whenever confusion could arise the tensor orders for the T-matrix multipoles will be designated by K_1 and, if needed, K_2.

If we insert Eqs. (9), (10), and (14) into Eq. (13), we find that the final state multipoles, for a scattering event described by the angles $\hat{R}$ and $\hat{R}'$, can be written in terms of the initial state multipoles and reduced T-matrix elements as

$$\rho^{K'}_{Q'}(J'\Omega'\epsilon') = (-1)^{K'-Q'-J'}(2\pi)^2(2K'+1)^{1/2}\sum(-1)^\phi i^{L-L'-L''+L'''}(2K+1)^{1/2}$$

$$\times\begin{pmatrix} J' & J' & K' \\ -M' & M''' & -Q' \end{pmatrix}\begin{pmatrix} J & J & K \\ -M & M'' & -Q \end{pmatrix}\begin{pmatrix} J & J' & K_1 \\ -M & M' & -Q_1 \end{pmatrix}$$

$$\times\begin{pmatrix} J & J' & K_2 \\ -M'' & M''' & -Q_2 \end{pmatrix}\begin{pmatrix} L & L' & K_1 \\ M_L & -M'_L & -Q_1 \end{pmatrix}\begin{pmatrix} L'' & L''' & K_2 \\ M''_L & -M'''_L & -Q_2 \end{pmatrix}$$

$$\times\rho^K_Q(J\Omega\epsilon)(J'L'\Omega'\epsilon'\|T_{K_1}\|JL\Omega\epsilon)(J'L'''\Omega'\epsilon'\|T_{K_2}\|JL''\Omega\epsilon)^*$$

$$\times Y^*_{LM_L}(\hat{R}')Y_{L'M'_L}(\hat{R}')Y_{L''M''_L}(\hat{R})Y^*_{L'''M'''_L}(\hat{R}). \tag{15}$$

Here the summation extends over the indices $M, M', M'', M''', K_1, Q_1, K_2, Q_2, K, Q, L, M_L, L', M'_L, L'', M''_L, L''', M'''_L$, and the phase factor is given by

$$\phi = K_1 - Q_1 + K_2 - Q_2 + K - Q - J - M'' - M' - L' - L''' + M_L + M''_L. \tag{16}$$

By integrating over $\hat{R}$ and averaging over $\hat{R}'$, we obtain an expression for the relation between the multipole moments of the initial and final density matrices, appropriate to a collision cell experiment. The orthogonality relation of the spherical harmonics reduces the number of indices in the summation in Eq. (15). This summation can then be evaluated most easily by graphical techniques[39], to yield

$$\rho_Q^{K'}(J'\Omega'\epsilon') = \delta_{KK'}\delta_{QQ'}(-1)^{K-J-J'}\pi\rho_Q^K(J\Omega\epsilon)$$

$$\times \sum_{K_1}(-1)^{-K_1}\begin{Bmatrix} J & J & K \\ J' & J' & K_1 \end{Bmatrix} P^{K_1}_{J\Omega\epsilon,J'\Omega'\epsilon'}. \quad (17)$$

As has been discussed by several authors,[19,23,40] under isotropic conditions the individual state multipoles evolve independently of each other. An expression equivalent to Eq. (17), but involving dimensioned quantities, has been derived separately by Derouard.[49]

From Eq. (17) one can derive the following relation between the ratios of the KQ and $K = 0$, $Q = 0$ multipoles of the initial and final density matrices:

$$\rho_Q^K(J'\Omega'\epsilon')/\rho_0^0(J'\Omega'\epsilon')$$
$$= E_K(J\Omega\epsilon,J'\Omega'\epsilon')[\,\rho_Q^K(J\Omega\epsilon)/\rho_0^0(J\Omega\epsilon)], \quad (18)$$

where we have defined, in analogy with the practice in nuclear physics,[41,57] a *multipole transfer efficiency* E_K, given by

$$E_K(J\Omega\epsilon,J'\Omega'\epsilon') = (-1)^{K-J-J'}[(2J+1)(2J'+1)]^{1/2}$$

$$\times \frac{\sum_{K_1}(-1)^{-K_1}\begin{Bmatrix} J & J & K \\ J' & J' & K_1 \end{Bmatrix} P^{K_1}_{J\Omega\epsilon,J'\Omega'\epsilon'}}{\sum_{K_1}P^{K_1}_{J\Omega\epsilon,J'\Omega'\epsilon'}}.$$
$$(19)$$

Obviously, these transfer efficiencies indicate the degree to which the Kth multipole of the initial density matrix, normalized to the zeroth moment, is preserved by the collision. Analogous multipolar transfer cross sections have been defined and used by various authors.[19–21,23,40,45,49]

To continue this analysis let us assume that the initial density matrix contains no off-diagonal terms (coherences), so that only the $Q = 0$ multipoles are nonvanishing. The relative populations in the individual $J'M'\Omega'\epsilon'$ levels are just the diagonal elements of the density matrix, which we will designate $n_{J'M'\Omega'\epsilon'}$, with an assumed normalization

$$\sum_{M'} n_{J'M'\Omega'\epsilon} = 1. \quad (20)$$

From Eqs. (14) and (18) it is easy to show that these relative populations will be given by

$$n_{J'M'\Omega'\epsilon'} = (2J'+1)^{-1}$$

$$\times \left[1 + \sum_K t_{K0}(J'M')E_K(J\Omega\epsilon,J'\Omega'\epsilon')\frac{\rho_0^K(J\Omega\epsilon)}{\rho_0^0(J\Omega\epsilon)}\right], \quad (21)$$

where the multipole operators t_{K0} are defined, following the Madison convention,[41] as

$$t_{K0}(J'M') = [(2K+1)(2J'+1)]^{1/2}(-1)^{K-J'-M'}$$

$$\times \begin{pmatrix} J' & J' & K \\ -M' & M' & 0 \end{pmatrix}. \quad (22)$$

In the large J limit these multipole operators are given by

$$\lim_{J'\gg1} t_{K0}(J'M') = (2J'+1)^{1/2}\langle P_K(\hat{J}'\cdot\hat{z})\rangle, \quad (23)$$

where $P_K(x)$ is a Legendre polynomial and the averaging denoted by the angle brackets is defined by

$$\langle P_K(\hat{J}'\cdot\hat{z})\rangle = \sum_{M'} n_{J'M'\Omega'\epsilon'}P_K[M'/(J'+\tfrac{1}{2})]. \quad (24)$$

Various authors[58–60] have found it useful to characterize final state rotational distributions in terms of Legendre moments of $\hat{J}'\cdot\hat{z}$, so that

$$n_{J'M'\Omega'\epsilon'} = (2J'+1)^{-1}$$

$$\times \left[1 + \sum_{K>1}A_K(J\Omega\epsilon,J'\Omega'\epsilon')\langle P_K(\hat{J}'\cdot\hat{z})\rangle\right]. \quad (25)$$

It is clear from the comparison of Eqs. (21) and (25) that in the large J (classical) limit the A_K expansion terms in Eq. (25) are given by

$$A_K(J\Omega\epsilon,J'\Omega'\epsilon')$$

$$= (2J'+1)^{1/2}E_K(J\Omega\epsilon,J'\Omega'\epsilon')\rho_0^K(J\Omega\epsilon)/\rho_0^0(J\Omega\epsilon). \quad (26)$$

We wish to point out that Derouard[49] has carried out a classical limit analysis similar to that presented here, but with different notation and expressions.

III. SELECTION RULES

Alexander and Davis have shown that within both the first-order Born[4,27] and IOS[7,9,14,28–32] approximations the reduced T-matrix elements and, consequently, the tensor opacities will vanish *unless* the tensor order in Eqs. (7) and (12) is given by

$$(-1)^K = \epsilon\epsilon'(-1)^{J+J'+2\Omega}. \quad (27)$$

In this section we shall demonstrate that an equivalent selection rule is also valid within the coupled-state (CS) approximation.[28,29,33,34]

In this approximation the operator for the orbital angular momentum of the atom–molecule pair is replaced by a constant $\bar{L}$. The CC equations can then be block diagonalized in a new index ν by transformation to a new basis defined by[7,9,61]

$$|J\nu\Omega\epsilon\mathscr{J}\mathscr{M}\rangle = \sum_L(-1)^\nu(2L+1)^{1/2}\begin{pmatrix} L & J & \mathscr{J} \\ 0 & \nu & -\nu \end{pmatrix}$$

$$\times |JL\Omega\epsilon\mathscr{J}\mathscr{M}\rangle, \quad (28)$$

where $-J\leqslant\nu\leqslant J$. The potential matrix elements are given by[13]

$$\langle J'\nu'\Omega'\epsilon'\mathscr{J}\mathscr{M}|V|J\nu\Omega\epsilon\mathscr{J}\mathscr{M}\rangle = \delta_{\nu\nu'}(-1)^{\nu-\Omega}$$

$$\times [(2J+1)(2J'+1)]^{1/2}\sum_l \begin{pmatrix} J' & l & J \\ -\nu & 0 & \nu \end{pmatrix}$$

$$\times F_l(J\epsilon,J'\epsilon')G_l(J\Omega\epsilon,J'\Omega'\epsilon'), \quad (29)$$

where

$$F_l(J\epsilon,J'\epsilon') = \tfrac{1}{2}[1 + \epsilon\epsilon'(-1)^{J+J'+l+2\Omega}] \quad (30)$$

and

$$G_l(J\Omega\epsilon,J'\Omega'\epsilon') = \delta_{\Omega\Omega'}v_1(R)\begin{pmatrix} J' & l & J \\ -\Omega & 0 & \Omega \end{pmatrix}$$

$$- \epsilon(1-\delta_{\Omega\Omega'})v_2(R)\begin{pmatrix} J' & l & J \\ -\Omega' & 2 & -\Omega \end{pmatrix}. \quad (31)$$

Here $v_1(R)$ and $v_2(R)$ are terms arising from the expansion of the atom–molecule potential. The exact form of these two terms will be irrelevant to the discussion here.

We observe from the symmetry of the $3j$ symbol in Eq.

(29) that the CS potential matrix elements have the symmetry

$$\langle J'v\Omega'\epsilon'\mathscr{J}\mathscr{M}|V|Jv\Omega\epsilon\mathscr{J}\mathscr{M}\rangle = (-1)^{2v+J+J'+l}$$

$$\times \langle J', -v,\Omega'\epsilon'\mathscr{J}\mathscr{M}|V|J, -v,\Omega\epsilon\mathscr{J}\mathscr{M}\rangle. \qquad (32)$$

Recognizing that

$$(-1)^{2v} = (-1)^{2\Omega}, \qquad (33)$$

we see that the phase factor in Eq. (32), taken together with Eq. (30), implies that when v is replaced by $-v$ the potential matrix elements for coupling between channels with $\epsilon' = \epsilon$ are unchanged and are multiplied by -1 for coupling between channels with $\epsilon' = \epsilon$. From a quantum mechanical

viewpoint this implies that the $-v$ CS equations could be obtained from the $+v$ equations if all the $\epsilon = -1$ basis states were multiplied by -1. Since the S-matrix elements relate the incoming amplitude in a particular state to the outgoing amplitude in another state, it is clear that if all the $\epsilon = -1$ states are multiplied by -1, then the $\epsilon = 1 \rightarrow \epsilon = -1$ S-matrix elements will be all multiplied by -1, but otherwise unchanged. Thus the CS S-matrix elements for $\pm v$ must satisfy the simple symmetry relation

$$S^{\bar{L},-v}_{J\Omega\epsilon,J'\Omega'\epsilon'} = \epsilon\epsilon'S^{\bar{L}v}_{J\Omega\epsilon,J'\Omega'\epsilon'}. \qquad (34)$$

The T-matrix elements which appear in the expression for the scattering amplitude [Eq. (6)] are given by

$$T^{\mathscr{J}}_{JL\Omega\epsilon,J'L'\Omega'\epsilon'} = i^{L+L'-2\bar{L}}\sum_v [(2L+1)(2L'+1)]^{1/2}\begin{pmatrix} L & J & \mathscr{J} \\ 0 & v & -v \end{pmatrix}\begin{pmatrix} L' & J' & \mathscr{J} \\ 0 & v & -v \end{pmatrix}T^{\bar{L}v}_{J\Omega\epsilon,J'\Omega'\epsilon'}, \qquad (35)$$

where

$$T^{\bar{L}v}_{J\Omega\epsilon,J'\Omega'\epsilon'} = \delta_{JJ'}\delta_{\Omega\Omega'}\delta_{\epsilon\epsilon'} - S^{\bar{L}v}_{J\Omega\epsilon,J'\Omega'\epsilon'}.$$

The phase factor in front of the summation corresponds to the "correct phase" choice of Khare et al.[62] Taking into account Eq. (34) one can show with a little angular momentum algebra that the reduced T-matrix elements of Eq. (7) will, for half-integer values of J, be given by

$$(J'L'\Omega'\epsilon'\|T_K\|JL\Omega\epsilon) = (-1)^{-J-L'+K}i^{L+L'-2\bar{L}}(2K+1)\left[[(2L+1)(2L'+1)]^{1/2}\begin{pmatrix} L & L' & K \\ 0 & 0 & 0 \end{pmatrix}\right]\sum_{v>0}$$

$$(-1)^{-v}\begin{pmatrix} J & J' & K \\ -v & v & 0 \end{pmatrix}\left]\{\Delta^{Kv}_{JL\Omega\epsilon,J'L'\Omega'\epsilon'} - [1+\epsilon\epsilon'(-1)^{J+J'+K+2v}]S^{\bar{L}}_{J\Omega\epsilon,J'\Omega'\epsilon'}\}, \qquad (36)$$

where

$$\Delta^{Kv}_{JL\Omega\epsilon,J'L'\Omega'\epsilon'} = [1+(-1)^{J+J'+K+2v}]\delta_{JJ'}\delta_{LL'}\delta_{\Omega\Omega'}\delta_{\epsilon\epsilon'}. \qquad (37)$$

The $\delta_{JJ'}$ restriction and the fact that $(-1)^{2J+2v} = 1$, implies that the Δ^{Kv} factor will vanish unless K is even, and unless the primed and unprimed J, L, Ω, and ϵ indices are identical. The symmetry factor in square brackets inside the summation in Eq. (36) will vanish unless

$$(-1)^K = \epsilon\epsilon'(-1)^{J+J'+2v}. \qquad (38)$$

These considerations, and Eq. (33), taken together, imply that the reduced T matrix elements in the CS limit will vanish unless Eq. (27) is satisfied.

The above discussion pertains to molecules with half-integer angular momentum. For integer values of J, Eq. (36) will contain inside the summation the additional term

$$\begin{pmatrix} J & J' & K \\ 0 & 0 & 0 \end{pmatrix}T^{\bar{L},v=0}_{J\Omega\epsilon,J'\Omega'\epsilon'}. \qquad (39)$$

From Eqs. (29) and (30), and the evenness restriction on the $3j$ symbol with zero denominators, we see that there will be no coupling between the $\epsilon = +1$ and $\epsilon = -1$ levels in the $v = 0$ block of the CS equations. Thus the term (39) will contribute only when $\epsilon = \epsilon'$ and when $(-1)^{J+J'+K} = 1$. This is entirely consistent with Eq. (27), although more restrictive. Hence we see that Eq. (27) applies in the CS limit for both integer and half-integer values of the molecular angular momentum.

A simple physical interpretation of this selection rule is possible. As we have seen, a sufficient condition for the validity of the expansion of the T matrix in irreducible tensor components [Eq. (7)] is the factorization of the T operator

into a sum of scalar products of two tensor operators in, respectively, the orbital and molecular space [Eq. (8)]. These spherical tensor operators behave under rotations as spherical harmonics with parity equal to $(-1)^K$.[39] The parity of the molecular wave functions is given by Eq. (2); the even K terms in Eq. (8) will result in transitions only between molecular states of the same parity, and the odd K terms in transitions only between molecular states of opposite parity. Mathematically, this implies

$$(-1)^K = \epsilon\epsilon'(-1)^{J+J'-2S}. \qquad (40)$$

Since

$$(-1)^{-2S} = (-1)^{2\Omega},$$

we see that this condition is equivalent to Eq. (27).

Thus the validity of Eq. (27), which was demonstrated here in the CS limit, and by Alexander and Davis[11] in the IOS and first-order Born limits, is a sufficient condition for the tensor factorization of the T matrix [Eq. (8)] to be valid in each of these limits. This is clearly the case for the Born limit,[27] where the T-matrix elements are formally equivalent to the matrix elements of the interaction potential, which itself can be written as a tensor expansion.[63] An additional justification of this factorization in the CS and IOS limits, as well as in the pure energy sudden (ES) limit,[64] has been given by Coombe and Snider.[46]

As discussed by Alexander and Davis,[11] the $3j$ symbol

$$\begin{pmatrix} J & J & K \\ -M & -M & 2M \end{pmatrix}$$

vanishes unless $(2J+K)$ is even.[65] This, together with Eqs. (11) and (40) implies that in a cell experiment the cross sec-

tion for the $JM\Omega \to J$, $-M$, Ω transition will vanish unless $\epsilon\epsilon' = (-1)^{25}$. For the specific case of collisions of molecules of even multiplicity, we see that $JM \to J$, $-M$ transitions will be forbidden for transitions in which the value of the e/f symmetry label is conserved.

IV. SCATTERING CALCULATIONS

As discussed in the Introduction, we have carried out full CC calculations for collisions of Ar with NO in the $\Omega = \frac{1}{2}$ manifold of the ground $X^2\Pi$ state. The rotational wave functions were described in the pure Hund's case (a) limit,[66] which we have previously shown[13] to be entirely justified for low J transitions in this system. The electron gas interaction potential of Nielson, Parker, and Pack[67] was used without alteration and, specifically, without the modifications suggested by these authors in the concluding section of their paper. The CC potential matrix elements for collisions of a molecule in a $^2\Pi$ electronic states have been given previously.[9,13] Cross section calculations were carried out using the recent VIVAS algorithm[68] at a total energy of 0.035 eV. The rotational levels $J = \frac{1}{2}$ to $J = \frac{9}{2}$, inclusive, were used in the channel basis, which resulted in two sets of 30 CC equations for each value of $\mathscr{J}$, corresponding to both parities. The CC equations were solved for all contributing values of $\mathscr{J}$. Although our prior experience[13] indicates that the calculated cross sections for transitions between the lowest levels ($J = \frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$) will probably not be fully converged with respect to the size of the channel basis, nevertheless we feel that the basis is sufficiently large to provide a qualitatively meaningful investigation of the symmetry selection rules discussed in the preceding section and of M-dependent effects.

Table I displays the contributing tensor opacities [Eq. (12)] for both elastic and inelastic transitions involving the $J = \frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$ levels. We see that the selection rule contained in Eq. (27) is remarkably well satisfied; for all the transitions considered, either the even or odd tensor orders make the dominant contribution. This alternation is true even at the

level of the reduced T-matrix elements, as is demonstrated by Fig. 1, which displays the square magnitude of the reduced T-matrix elements

$$\langle JL\Omega\epsilon \| T_1 \| J,L + 1,\Omega\epsilon' \rangle$$

as a function of L with $J = \Omega = \frac{1}{2}$ and $\epsilon' = \pm\epsilon$. The prediction from Eq. (27) is that this reduced T-matrix element will vanish in the case where $\epsilon' = \epsilon$. In fact, for all L, the CC reduced T-matrix element with $\epsilon' = \epsilon$ is more than two orders of magnitude smaller than the one with $\epsilon' = -\epsilon$.

In the CS limit the alternation in the magnitude of the tensor opacities for even and odd K would be total, as discussed in the preceding section. Thus the marked alternation in the tensor opacities in Table I could be seen as an indication of the accuracy of the CS approximation for Ar–NO collisions, at least at $E = 0.035$ eV. This is an additional confirmation of the similar conclusion arrived at in our earlier article,[13] based on a comparison of CC and CS degeneracy averaged integral cross sections.

As discussed in the preceding section, a direct consequence of the large alternation in the relative magnitude of the even and odd reduced T-matrix elements is the prediction of small cross sections for the laboratory-frame $JM\epsilon \to J$, $-M$, ϵ transitions in a molecule of even multiplicity, e.g., a $^2\Pi$ state. In Table II we list M-dependent cross sections for Ar–NO $(X^2\Pi_{1/2})$ collisions for all transitions involving the $J = \frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$ levels. We observe that for the $JM \to J$, $-M$ transitions, the propensity toward change in the e/f label is extremely strong, and is increasingly pronounced as M increases. The explanation for this latter observation is as follows: The angular momentum constraints contained in the $3j$ symbol in Eq. (11) imply that only tensor orders with $K \geqslant 2M$ will contribute to the cross sections. Furthermore, as discussed in the preceding section, the $3j$ symbol will vanish unless K is odd (for $J' = J$). We see in Table I that the ratio of the odd tensor opacities for e/f conserving as opposed to e/f changing $J \to J$ transitions becomes increasingly small as K increases. Thus the tendency against conservation of the symmetry label is largest for large M, where only the high tensor orders contribute.

TABLE I. Tensor opacities, Ar–NO($X^2\Pi_{1/2}$) collisions at $E = 0.035$ eV.

J	J'	$P^K_{J\epsilon,J'\epsilon'}$ [a]					
		$K = 0$	1	2	3	4	5
1/2	1/2	17 285	0.23				
		0	96.70				
3/2	3/2	34 180	4.07	477.40	0.34		
		0	28.59	0.37	152.49		
5/2	5/2	50 400	15.46	991.10	1.75	227.81	0.11
		0	33.77	0.94	58.72	0.58	133.20
1/2	3/2		129.00	0.11			
			0.12	438.91			
3/2	5/2		276.61	0.78	75.17	0.11	
			0.52	238.38	0.57	471.55	
1/2	5/2			785.2	0.05		
				0.10	96.33		

[a] The first entry refers to the e/f conserving transitions ($\epsilon' = \epsilon$); the second, to the e/f changing transitions ($\epsilon' = -\epsilon$). The tensor opacities are defined in Eq. (12). As discussed in Ref. 13, to within the numerical accuracy of the calculations, the tensor opacities are independent of the sign of ϵ.
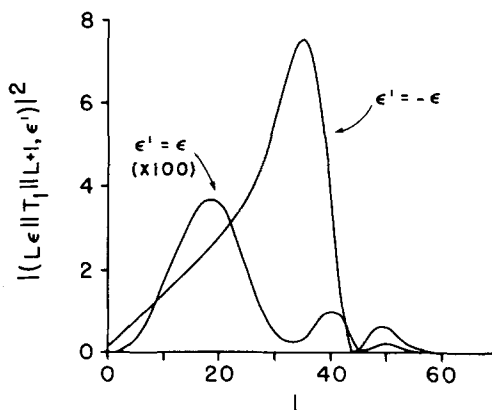

FIG. 1. Square magnitude of the reduced T-matrix elements $\langle JL\Omega\epsilon \| T_1 \| J,L + 1,\Omega\epsilon' \rangle$ as a function of L with $J = \Omega = \frac{1}{2}$; Ar–NO($X^2\Pi$) collisions at $E = 0.035$ eV. Note that the curves for $\epsilon' = \epsilon$ have been multiplied by 100.

TABLE II. Laboratory frame $JM \rightarrow J'M'$ cross sections (Å^2):Ar-NO($X\,^2\Pi_{1/2}$) collisions at $E = 0.035$ eV[a]

J	M	$J' = \frac{1}{2}$ $M' = -\frac{1}{2}$	$\frac{1}{2}$
1/2	1/2	0.002	257.7
		0.961	0.481

J	M	$J' = 3/2$ $M' = -3/2$	$-1/2$	$1/2$	$3/2$
1/2	1/2	0.0006	0.321	0.641	0.962
		2.617	1.963	1.309	0.655
3/2	1/2	b	0.017	260.1	b
		b	0.512	0.313	b
	3/2	0.001	1.450	1.462	260.1
		0.661	0.332	0.220	0.164

J	M	$J' = 5/2$ $M' = -5/2$	$-3/2$	$-1/2$	$1/2$	$3/2$	$5/2$
1/2	1/2	0.0002	0.781	1.561	2.341	3.122	3.902
		0.410	0.342	0.273	0.205	0.137	0.069
3/2	1/2	0.204	0.029	0.427	0.905	0.973	0.138
		0.598	1.404	1.284	0.787	0.463	0.861
	3/2	0.0004	0.122	0.164	0.288	0.659	1.442
		1.591	0.995	0.776	0.751	0.736	0.548
5/2	1/2	b	b	0.044	264.2	b	b
		b	b	0.341	0.181	b	b
	3/2	b	0.004	2.136	1.207	263.3	b
		b	0.327	0.182	0.181	0.155	b
	5/2	0.0003	0.396	0.398	1.366	2.355	264.9
		0.379	0.191	0.158	0.143	0.149	0.166

[a] The first entry refers to the e/f conserving ($\epsilon' = \epsilon$) transitions; the second to the e/f changing ($\epsilon' = -\epsilon$) transitions. Cross sections for M negative can be obtained by the symmetry relation $\sigma_{J-M \rightarrow J'M'} = \sigma_{JM \rightarrow J', -M'}$. Cross sections for $J \rightarrow J'$ transitions with $J' < J$ can be obtained by detailed balance: $\sigma_{JM \rightarrow J'M'} = (k_{J'}^2/k_J^2)\sigma_{J'M' \rightarrow JM}$, where k_J and $k_{J'}$ are the wave vectors of the initial (J) and final (J') channels.

[b] For transitions elastic in J, the $M \rightarrow M'$ cross sections with $|M'| > |M|$ are identically equal to the $M' \rightarrow M$ cross sections, which follows from Eq. (11).

If we look at a particular e or $f\,J = \frac{1}{2}$ state, where there are only two M levels, we see that collisions will be almost completely ineffective in transferring population from one M level to another. Thus if either the e or the $f\,J = \frac{1}{2}$ state is prepared completely polarized,[55] with population entirely in one or the other M level, then no collisional depolarization will occur.

For other $JM \rightarrow J'M'$ transitions, the numbers in Table II give evidence for two additional propensity rules. First, we observe that the purely elastic $JM\epsilon \rightarrow JM\epsilon$ cross sections are very large, and dominate the $JM \rightarrow JM$ cross sections which involve a change in ϵ. This is because, as discussed in Sec. II, the large $K = 0$ tensor opacities (Table I) which contribute only to the $JM \rightarrow JM$ cross sections [Eq. (11)] are rigorously zero for e/f changing transitions. Secondly, we see that the J, $M = J \rightarrow J', M' = -J'$ transitions strongly favor a change in the symmetry index. In this case the angular momentum constraints contained in the $3j$ symbol in Eq. (11) imply that only the $K = J + J'$ tensor order will contribute to this transition. However, for this value of K, the tensor opacities are very small for e/f conserving transitions, as a result of the selection rule contained in Eq. (27).

Finally, we see from the relative magnitudes of the cross sections in Table II that, roughly speaking, the laboratory frame orientation of $\mathbf{J}$ will have a greater tendency to be conserved for transitions where ϵ is also conserved. This obviously will imply that the e/f conserving and e/f changing processes will affect differently the anisotropic components

of the density matrix of the NO rotational states. To investigate this, we have computed the pertinent multipole transfer efficiencies, defined in Sec. II, which indicate the degree to which the K th multipole of the initial density matrix, normalized to the zeroth moment, is preserved by the collision. These transfer efficiencies are listed in Table III.

We observe that for the transitions which are elastic in

TABLE III. Multipole transfer efficiencies: Ar-NO($X\,^2\Pi_{1/2}$) collisions at $E = 0.035$ eV.

J	J'	$E_{J\epsilon \rightarrow J'\epsilon'}^{K}$[a]	
		$K = 1$	$K = 2$
1/2	1/2	1.0000	...[b]
		-0.3333	...[b]
3/2	3/2	0.9889	0.9779
		-0.3883	0.1984
5/2	5/2	0.9883	0.9760
		-0.2035	0.1991
1/2	3/2	0.7444	...[b]
		-0.4469	...[b]
3/2	5/2	0.7292	0.4615
		-0.2433	0.1415
1/2	5/2	0.6831	...[b]
		-0.4868	...[b]

[a] The first entry refers to the e/f conserving transitions ($\epsilon' = \epsilon$); the second, to the e/f changing transitions ($\epsilon' = -\epsilon$). The multipole transfer efficiencies are defined in Eq. (19).

[b] Only $K = 0$ and 1 state multipoles can exist for $J = 1/2$.

$J(J' = J)$, both the $K = 1$ and $K = 2$ transfer efficiencies are nearly unity for the e/f conserving transitions. This indicates that collisions which are elastic in both J and ϵ will tend strongly to conserve both the orientation ($K = 1$) and alignment ($K = 2$) of the original rotational population. The tendency is total in the case of the $J = \frac{1}{2}$ level, where the transfer efficiency has a value of unity (at least to five significant figures). As discussed above, virtually no collisional depolarization of this level will occur.

For the processes which are elastic in J but *inelastic* in ϵ the transfer efficiencies are much smaller, indicating that any overall polarization of the initial rotational population will be destroyed by the collision. In particular, the $K = 1$ transfer efficiency is negative for the e/f changing transitions, which indicates that any net orientation of the original J vectors, in a laboratory frame, will actually be reversed. This is apparent in the $JM\rightarrow J'M'$ cross sections listed in Table II, where we see that for the $J\epsilon\rightarrow J, -\epsilon$ process the largest cross sections are associated with the transitions which involve a change in sign in the laboratory frame projection quantum number.

For transitions which are *inelastic* in J we observe that the multipole transfer efficiencies display qualitatively similar behavior. For the e/f conserving processes the transfer efficiencies are positive and fairly large, particularly for $K = 1$, indicating again that any polarization of the initial rotational population will be roughly preserved by the collision. For the e/f changing processes, the transfer efficiencies are much smaller and, as in the case of the processes elastic in J, the $K = 1$ transfer efficiency is negative. This again indicates that the e/f changing collisions will tend to reverse any net orientation of the original J vector.

It is tempting to develop a simple physical model for the dramatic difference in the tensor transfer efficiencies for e/f conserving and e/f changing processes. This might involve consideration of the relative orientation in the e and $f\ \Lambda$ doublets of the J vector with respect to the singly filled NO π-orbital. Similar models have been used before[22,69] to explain variations with Λ doublet of collisional energy transfer in the $B\ ^1\Pi_u$ state of Li_2[69] and in the $C\ ^1\Pi$ state of NaK.[22] These arguments involve[70,71] consideration of the cylindrical asymmetry of the electronic wave function for a $^1\Pi$ electronic state. However, one can show[71] that the electronic wave function of a $^2\Pi$ molecule in a case (a) limit is cylindrically symmetric, so that similar arguments can not be applied to the Ar–NO collisions studied here.

V. MODEL STUDIES OF DEPOLARIZATION IN ELECTRONICALLY EXCITED $^2\Pi$ STATES

We have seen in the preceding section how collisional depolarization of an initially polarized distribution of $^2\Pi$ rotational levels will depend strongly on whether the e/f symmetry label of the initial rotational state is conserved or changed during the collision. In this section we will use our calculated tensor transfer efficiencies, which apply to NO in its ground $X\ ^2\Pi$ state, to investigate what types of effects one might expect in experiments in which a polarized rotational distribution in an electronically excited $^2\Pi$ state is produced by pumping with a linearly or circularly polarized laser, and the subsequent collisional depolarization inferred by looking at the polarization of the fluorescence, either from the initially pumped level or from a collisionally populated level. The idea is similar to the experiments of McCaffery, Nédélec, Steinfeld, and their co-workers.[17–21,25,50] This type of simulation study is particularly appropriate in view of the recent experimental studies of rotational energy transfer in the $A\ ^2\Pi$ state of CdH by Dufayard and Nédélec[50] and in the $A\ ^2\Pi$ state of CaF by Dufour, Pinchemel, and co-workers.[51]

Let us assume than an excited $^2\Pi_{1/2}$ state is pumped from a ground $X\ ^2\Sigma$ state, and that the $X\ ^2\Sigma\leftarrow^2\Pi$ fluorescence is detected and spectrally resolved. From known expressions[72] the relevant dipole matrix elements are given by

$$\langle ^2\Sigma M''\epsilon''|Q_{1m}|^2\Pi M'\epsilon'\rangle \sim \begin{pmatrix} J'' & 1 & J' \\ -\tfrac{1}{2} & 1 & -\tfrac{1}{2} \end{pmatrix}\begin{pmatrix} J'' & 1 & J' \\ -M'' & m & M' \end{pmatrix}, \tag{41}$$

where $m = 0, \pm 1$ is the component of the total angular momentum of the photon along its direction of propagation. The intensity of absorption or emission is proportional to the square of this expression. For circular polarized detection the total emission intensity from a particular $J'\epsilon'$ rotational level of the excited $\Pi_{1/2}$ state, summed over projection quantum numbers, is given by

$$I_\pm \sim \sum_{M'M''} \rho_{J'M'\Omega'\epsilon',J'M'\Omega'\epsilon'}\begin{pmatrix} J'' & 1 & J' \\ -M'' & \mp 1 & M' \end{pmatrix}^2, \tag{42}$$

where we have introduced the density matrix in the excited state. As before, we shall assume that no coherences are present. The circular polarization ratio is defined by[18,19,40]

$$C = (I_+ - I_-)/(I_+ + I_-). \tag{43}$$

Introducing Eq. (14) and carrying out a little angular momentum algebra, we find

$$C = \cfrac{-3^{1/2}\begin{Bmatrix} 1 & 1 & 1 \\ J' & J' & J'' \end{Bmatrix}\rho_0^1(J'\Omega'\epsilon')}{2^{1/2}\begin{Bmatrix} 1 & 1 & 0 \\ J' & J' & J'' \end{Bmatrix}\rho_0^0(J'\Omega'\epsilon') + \begin{Bmatrix} 1 & 1 & 2 \\ J' & J' & J'' \end{Bmatrix}\rho_0^2(J'\Omega'\epsilon')}, \tag{44}$$

which can be written in terms of the multipole transfer efficiencies [Eq. (19)] as

$$C = \frac{-3^{1/2}E_1(J\Omega\epsilon,J'\Omega'\epsilon')\begin{Bmatrix} 1 & 1 & 1 \\ J' & J' & J'' \end{Bmatrix} \rho_0^1(J\Omega\epsilon)}{2^{1/2}\begin{Bmatrix} 1 & 1 & 0 \\ J' & J' & J'' \end{Bmatrix}\rho_0^0(J\Omega\epsilon) + E_2(J\Omega\epsilon,J'\Omega'\epsilon')\begin{Bmatrix} 1 & 1 & 2 \\ J' & J' & J'' \end{Bmatrix}\rho_0^2(J\Omega\epsilon)}, \tag{45}$$

where $J\Omega\epsilon$ designates the level initially populated by the pump laser. If this laser is circularly polarized, then it can be shown from Eq. (41) that the multipole components of the initial density matrix are given by

$$\rho_0^K(J\Omega\epsilon) \sim (2K+1)^{1/2}(-1)^{K-J-J''}\begin{pmatrix} 1 & 1 & K \\ 1 & -1 & 0 \end{pmatrix}\begin{Bmatrix} 1 & 1 & K \\ J & J & J''' \end{Bmatrix}, \tag{46}$$

where J''' designates the initial level of the ground state which is pumped by the laser. In deriving Eq. (46) we have assumed an unpolarized distribution of M''' projection quantum numbers. Substitution of Eq. (46) into Eq. (45) yields

$$C = \frac{3E_1(J\Omega\epsilon,J'\Omega'\epsilon')\begin{Bmatrix} 1 & 1 & 1 \\ J' & J' & J'' \end{Bmatrix}\begin{Bmatrix} 1 & 1 & 1 \\ J & J & J''' \end{Bmatrix}}{2\begin{Bmatrix} 1 & 1 & 0 \\ J' & J' & J'' \end{Bmatrix}\begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix} + E_2(J\Omega\epsilon,J'\Omega'\epsilon')\begin{Bmatrix} 1 & 1 & 2 \\ J' & J' & J'' \end{Bmatrix}\begin{Bmatrix} 1 & 1 & 2 \\ J & J & J''' \end{Bmatrix}}. \tag{47}$$

For the case of resonance fluorescence in the absence of collisions, we have $J' = J, J''' = J''$, and $E_1 = E_2 = 1$, so that Eq. (47) reduces to the expression given earlier by Rowe and McCaffery[19] and Omont.[40,73]

In the case of linearly polarized light, the polarization is defined by[40,55]

$$P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp), \tag{48}$$

where

$$I_\parallel \sim \sum_{M'} \rho_{J'M'\Omega'\epsilon',J'M'\Omega'\epsilon'}\begin{pmatrix} J'' & 1 & J' \\ -M' & 0 & M' \end{pmatrix}^2 \tag{49}$$

and

$$I_\perp \sim \tfrac{1}{2}\sum_{M''M'}\rho_{J'M'\Omega'\epsilon',J'M'\Omega'\epsilon'}\left|\begin{pmatrix} J'' & 1 & J' \\ -M'' & 1 & M' \end{pmatrix} + \begin{pmatrix} J'' & 1 & J' \\ -M'' & -1 & M' \end{pmatrix}\right|^2. \tag{50}$$

Introducing Eq. (14) and carrying out a little angular momentum algebra we find, similarly to Eq. (45),

$$P = \frac{-3E_2(J\Omega\epsilon,J'\Omega'\epsilon')\begin{Bmatrix} 1 & 1 & 2 \\ J' & J' & J'' \end{Bmatrix}\rho_0^2(J\Omega\epsilon)}{2^{3/2}\begin{Bmatrix} 1 & 1 & 0 \\ J' & J' & J'' \end{Bmatrix}\rho_0^0(J\Omega\epsilon) - E_2(J\Omega\epsilon,J'\Omega'\epsilon')\begin{Bmatrix} 1 & 1 & 2 \\ J' & J' & J'' \end{Bmatrix}\rho_0^2(J\Omega\epsilon)}. \tag{51}$$

As before, if the ground state is unpolarized, and the polarization of the pump laser is taken to define the laboratory frame z axis, then the multipole components of the initial density matrix are given by

$$\rho_0^K(J\Omega\epsilon) \sim (2K+1)^{1/2}(-1)^{-J-J''}\begin{pmatrix} 1 & 1 & K \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} 1 & 1 & K \\ J & J & J''' \end{Bmatrix}. \tag{52}$$

Substitution of Eq. (52) into Eq. (51) yields

$$P = \frac{3E_2(J\Omega\epsilon,J'\Omega'\epsilon')\begin{Bmatrix} 1 & 1 & 2 \\ J' & J' & J'' \end{Bmatrix}\begin{Bmatrix} 1 & 1 & 2 \\ J & J & J''' \end{Bmatrix}}{2\begin{Bmatrix} 1 & 1 & 0 \\ J' & J' & J'' \end{Bmatrix}\begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix} + E_2(J\Omega\epsilon,J'\Omega'\epsilon')\begin{Bmatrix} 1 & 1 & 2 \\ J' & J' & J'' \end{Bmatrix}\begin{Bmatrix} 1 & 1 & 2 \\ J & J & J''' \end{Bmatrix}}. \tag{53}$$

Again, for the case of resonance fluorescence, Eq. (53) reduces to the expression given earlier by Omont[40] and by Proctor and McCaffery.[21]

Thus we see from Eqs. (47) and (53) that measurement of the fluorescence polarization yields direct information on the multipole transfer efficiencies, for $K = 1$ (in the case of circular polarization) and for $K = 2$ (for both linear and circular polarization). Alternatively, we can use the multipole transfer efficiencies which we have calculated for Ar–NO(X ²Π₁/₂) (Table III) to speculate on the kind of effects one might observe in an experimental study of rotational relaxation in a ²Π₁/₂ excited state. Since for a given $J\rightarrow J'$ transition the Ar–NO transfer efficiencies are substantially

larger in magnitude for the e/f conserving process, we infer from Eqs. (47) and (53) that the final state polarization, either linear or circular, will be substantially larger for transitions which conserve e/f symmetry, provided, of course, that the initial (J''') and final (J'') quantum numbers are held constant. Also, since the $K = 1$ transfer efficiencies for e/f changing transitions differ in sign from those for e/f conserving transitions, we see from Eq. (47) that the final state circular polarization will differ in sign for these two types of transitions, again provided that J, J', J'', and J''' are held constant.

One final point: We observe in Table III that for the $Je\rightarrow Je$ transitions the multipole transfer efficiencies are both nearly unity for $K = 1$ and $K = 2$. This implies that

both the circular and linear polarization of the resonance fluorescence from the initially excited level will be virtually unchanged from the zero-collision limit. As discussed above, this value is obtained from Eqs. (47) and (53) by setting the multipole transfer efficiencies equal to unity. Thus, experimentally, the polarization of the resonance fluorescence should be expected to show little or no variation with the pressure of the buffer gas. Just this type of behavior has been observed by Dufayard and Nédélec[50] in the $J = \frac{7}{2}$ and $J = \frac{15}{2}$ levels of CdH($A\ ^2\Pi$) in collision with He and Ar, particularly for $J = \frac{7}{2}$ with He as the partner.

V. CONCLUSION

In this article we have presented the formalism for the quantum study of laboratory frame M-dependent transitions in collisions of open-shell diatomics. The treatment of the dynamics involves the use of reduced T-matrix elements and tensor opacities. We have shown how the evolution of the various irreducible components of the rotational state density matrix can be described by multipolar transfer efficiencies, which are ratios of sums of the tensor opacities. The central formal result of this paper was the demonstration that in the coupled-states (CS) limit, the reduced T-matrix elements and tensor opacities vanish for either even or odd values of the tensor order, depending on the particular transition in question. This extends the range of validity of this selection rule, which was previously derived within the first-order Born and IOS limits. One major consequence of this selection rule is that cross sections for the $JM{\rightarrow}J$, $-M$ and $J,M = J{\rightarrow}J',M' = -J'$ transitions will be negligibly small unless the e/f symmetry label is changed during the collision.

Actual close-coupling calculations of cross sections for Ar–NO($X\ ^2\Pi_{1/2}$) collisions of $E = 0.035$ eV indicated that these selection rules are well obeyed for this system. The calculated multipolar transfer efficiencies imply that both the orientation and the alignment of the initial M-level population will be far better preserved in collisions which conserve the e/f symmetry of the initial rotational level. In fact, for e/f changing collisions our calculations suggest that any net orientation of the initial $\mathbf{J}$ vector will be reversed after the collision. Also, the depolarization of an initial level through elastic collisions can be expected to be very inefficient.

Since the numerical results presented here apply just to Ar–NO($X\ ^2\Pi_{1/2}$) collisions, it would be worthwhile to carry out comparable CC calculations of M dependent cross sections for collisions of other open-shell diatomics, to see if the selection rules on the vanishing of the tensor opacities are as pronounced in other systems. An obvious candidate would be OH($X\ ^2\Pi$) for which CC calculations have already been reported.[6] Also, it would be most worthwhile to investigate experimentally the Λ-doublet dependence of the polarization, either circular or linear, of emission from collision induced satellite lines in an excited $^2\Pi$ state. This would provide direct information on the extent to which e/f changing and e/f conserving inelastic collisions preserve the polarization of the initially excited level.[81]

On a more basic level, two fundamental questions remain: First, we have seen that the CC tensor opacities which

are predicted to vanish in the CS limit are small, but non-zero. Does it follow that the factorization of the T matrix contained in Eq. (8) is not entirely general, contrary to what was originally suggested by Alexander[43] and Pickett,[54] but in fact applies only to certain dynamical limits? Alternatively, it may be that this factorization is indeed perfectly general, but in the general case, the A and B operators in Eq. (8) are nonlocal so that the discussion immediately prior to Eq. (40) will not apply. This issue could possibly be resolved by an analysis similar to that described recently by Chan, Evans, and Hoffman[47] or Eno, Chang, and Rabitz.[75]

The second related question is: What becomes of the selection rules for the tensor opacities and the M-dependent cross sections in collisions which cannot be described well in the CS, IOS, or first-order Born limits? As an example, it is well known that in collisions of ^2P atoms with structureless targets $JM{\rightarrow}J$, $-M$ transitions do occur,[76,77] despite the fact that they are forbidden for this type of collision within the CS and first-order Born limits.[78] Since these dynamical approximations do not always apply well to intramultiplet processes,[76,79,80] the breakdown of the $JM{\rightarrow}J$, $-M$ selection rule may not be surprising.

Obviously, these questions provide considerable motivation for further study of M-dependent effects in collisions of open-shell diatomics.

ACKNOWLEDGMENTS

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