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M dependence in rotationally inelastic collisions in cell experiments: Implications of an irreducible tensor expansion for molecules in $^1\Sigma$ electronic states

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The tensorial coupling of initial and final angular momenta, commonly used in atomic collisions and attributed to Grawert, is here applied to M dependent collisions of molecules in $^1\Sigma$ electronic states under conditions where the relative velocity vectors of the collision partners are uniformly distributed with respect to a laboratory fixed z axis. The integral inelastic cross sections are given by sums over tensor opacities, weighted by squares of vector coupling coefficients. The resulting expressions differ from those obtained within the tensorial treatment usually applied to molecular collisions. One can rigorously show that strict M conservation will not occur and, furthermore, that the complete matrix of $M \rightarrow M'$ cross sections can be related to the smaller set of tensor opacities. In the energy sudden limit the $JM \rightarrow J'M'$ cross sections can be related to the degeneracy-averaged $J'' \rightarrow 0$ cross sections. Accurate close-coupling cross sections for the He–CO system due to Green are used to obtain the relevant tensor opacities and to demonstrate how degeneracy averaged $J'' \rightarrow 0$ cross sections can be extracted from the fully resolved $JM \rightarrow J'M'$ cross sections. Finally, the sudden scaling relation is used to analyze rotational relaxation in the $Na_2(A\ ^1\Sigma_u^+) + He$ system. We show that θ conservation, where $\theta = \cos^{-1}(\mathbf{J} \cdot \hat{z})$, is a more appropriate dynamical model than M conservation.

I. INTRODUCTION

There has been much recent interest in the determination of the extent to which the projection of the rotational angular momentum quantum number M is conserved during inelastic collisions of atoms with small molecules. Several years ago McCaffery, Pritchard, and their coworkers interpreted[1–3] a series of experiments involving fluorescence measurement of inelastic energy transfer in laser excited I_2,[1,4] Li_2,[2] and Na_2[3] to be consistent with rigorous conservation of M in a laboratory fixed coordinate system. Subsequently, these authors have concluded[5–7] that strict M conservation may be only a sufficient rather than necessary condition for agreement with the body of experimental data. This would be consistent with the reanalysis of the Na_2^*–Xe data[3] by De-Pristo and co-workers[8] as well as with the results of a double resonance experiment on rotational energy transfer in the $A\,^1\Sigma^+$ state of BaO by Silvers, Gottscho, and Field,[9] who found, again in a laboratory frame, that M was neither conserved nor totally randomized.

Concurrent with this experimental work have been a number of theoretical papers, aimed both at the determination of fully M-state resolved inelastic cross sections for particular atom–molecule systems,[10–24] and at the development of models[5,25–30] to explain the existence or absence of constraints on changes in M in inelastic collisions. Except for studies of the H_2–CO,[22] He–CO,[27,31] and He–NH_3[24] systems, in all this theoretical work the rotational angular momentum has been quantized in a coordinate frame where the particular z axis has a specifiecd orientation with respect to the initial relative velocity vector.[32] Although this would be appropriate to molecular beam experiments, in cell experiments, such as those of McCaffery,[1,2,4] Pritchard,[3,6,7] Field and co-workers,[9] there exists a distribution of relative velocity vectors with respect to the laboratory fixed z axis. It is as yet unclear to what extent the transformation from the collision to laboratory frame, or vice versa, will affect either predicted or observed M distributions.[9,27,29]

General expressions for M resolved integral cross sections in terms of the basic inelastic T-matrix elements have been given by Reuss and Stolte[33] as well as Alexander and collaborators[32] for the collision frame; by Kinsey, Riehl, and Waugh[34] for conditions where the distribution of relative velocity vectors in the laboratory frame is isotropic; and by Monchick[27] for a cylindrical distribution of relative velocity vectors. In the work of Kinsey *et al.*[34] and Monchick,[27] as well as in the analysis by Rowe and McCaffery[5] and by Brechignac *et al.*[22] of their respective experimental results, rotationally invariant tensors were used to decompose the scattering problem. The formalism draws heavily on methods which have been developed to analyze pressure broadening of spectral lines,[35–39] and is based on the expansion of the initial and final quantum mechanical density matrices in terms of spherical tensor dyadic operators. In this formulation the Dirac kets corresponding to the initial JM states are coupled with their Dirac bras, and similarly for the final $J'M'$ states.

Alternatively, it is possible to form rotationally invariant dyadic operators by coupling the JM kets with the $J'M'$ bras, and vice versa. Although this approach, attributed to Grawert,[40] has been often applied to the analy-

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sis of M dependence in collisions of atoms in electronic states of nonzero spin and orbital angular momenta (^2P, ^3P) with spherical partners,[41,42] it has not been applied, outside of a recent interesting paper by Elbel,[28] to rotationally inelastic molecular collisions. This application is the subject of the present paper. Specifically, we shall use the alternative tensor formalism, discussed at the beginning of this paragraph, and the resulting expressions for M resolved cross sections, to derive a number of interesting and useful relations bearing on M dependence in cell type experiments, where there is an isotropic distribution of relative velocity vectors with respect to the laboratory fixed z axis.

The organization of this paper is as follows: In the next section we derive the general expression for integral M resolved cross sections for collisions of molecules in $^1\Sigma^+$ electronic states. We discuss in Sec. III some conclusions for M conservation and show in Sec. IV how within the energy sudden limit cross sections for particular $M \to M'$ transitions can be related to the degeneracy averaged $J \to J'$ cross sections. This is followed in Sec. V by the extraction of the fundamental tensor opacities from Green's[31] M dependent cross sections for the He–CO system, and by the demonstration that a large set of degeneracy averaged cross sections can be extracted from the fully M resolved cross sections for only a few transitions. In Sec. VI we use the $J \to J' = 0$ rate constants for $Na_2(A\,^1\Sigma_u^+) + He$ collisions reported by Pritchard and co-workers[7] to simulate the M dependence for this system. A brief conclusion follows.

II. TENSOR EXPANSION OF INELASTIC CROSS SECTIONS

Curtiss and Adler[43] and, more recently, Rowe and McCaffery[5] have presented the quantum treatment of rotationally inelastic collisions when the incoming plane wave is arbitrarily oriented with respect to an external axis, in our case the laboratory frame. The scattering wave function has the asymptotic form

$$\lim_{R\to\infty} \phi_{JM}(\mathbf{R}, \hat{r}, \hat{R}_{\rm lab}) = \exp(i\mathbf{k}_J \cdot \hat{R}_{\rm lab}) Y_{JM}(\hat{r}) + \frac{i}{R} \sum_{J'M'} (k_J k_{J'})^{-1/2} f_{JM,J'M'}(\hat{R}, \hat{R}_{\rm lab}) \times Y_{J'M'}(\hat{r}) \exp(ik_{J'}R) \ . \quad (1)$$

Here $\hat{R}$ describes the scattering in the collision frame, where the z axis is taken to be the initial relative velocity vector or, equivalently, the initial wave vector $\mathbf{k}_J$[44]; $\hat{r}$ describes the orientation of the molecule in the collision frame; and $\hat{R}_{\rm lab}$ describes the orientation of the collision frame z axis in the laboratory frame. The first term on the right-hand side of Eq. (1) can be expanded, using the known expansion of a plane wave,[45] in the following way:

$$\exp(i\mathbf{k}_J \cdot \hat{R}_{\rm lab}) Y_{JM}(\hat{r}) = \frac{1}{k_J R} \sum_{LM_L} \sum_{\mathcal{J}\mathfrak{M}} i^{L+1} 2\pi (JMLM_L|\mathcal{J}\mathfrak{M}) \times \{\exp[-i(k_J R - L\pi/2)] - \exp[i(k_J R - L\pi/2)]\} \times \mathcal{Y}_{JL}^{\mathcal{J}\mathfrak{M}}(\hat{r}, \hat{R}) Y_{LM_L}^*(\hat{R}_{\rm lab}) \ , \quad (2)$$

where $(\cdots\,|\cdots)$ is a Clebsch–Gordan coefficient,[45] and

$$\mathcal{Y}_{JL}(\hat{r}, \hat{R}) = \sum_{MM_L} (JMLM_L|\mathcal{J}\mathfrak{M}) Y_{JM}(\hat{r}) Y_{LM_L}(\hat{R}) \ . \quad (3)$$

Here L and $\mathcal{J}$ denote the orbital and total angular momenta, respectively.

In the total angular momentum representation the scattering can be described by solution of a set of coupled differential equations,[46] the close-coupled equations. The scattering wave function can also be expressed as a linear combination of the solutions to these equations, so that

$$\lim_{R\to\infty} \phi_{JM}(\hat{R}, \hat{r}, \hat{R}_{\rm lab}) = \sum_{\substack{\mathcal{J}\mathfrak{M}J' \\ LL'}} \frac{1}{R} U_{JL}^{\mathcal{J}\mathfrak{M}}(\hat{R}_{\rm lab}) \{\delta_{LL'}\delta_{JJ'} \times \exp[-i(k_J R - L\pi/2)] - (k_J/k_{J'})^{1/2} S_{JL,J'L'}^{\mathcal{J}} \times \exp[i(k_{J'}R - L'\pi/2)]\} \mathcal{Y}_{J'L'}^{\mathcal{J}\mathfrak{M}}(\hat{r}, \hat{R}) \ , \quad (4)$$

where $S_{JL,J'L'}^{\mathcal{J}}$ designates an S-matrix element, and the $U_{JL}^{\mathcal{J}\mathfrak{M}}$ are expansion coefficients. By setting Eqs. (1) and (4) equal we obtain the following expression for the scattering amplitude[47]:

$$f_{JM,J'M'}(\hat{R}, \hat{R}_{\rm lab}) = 2\pi \sum_{\substack{\mathcal{J}\mathfrak{M}LM_L \\ L'M_L'}} i^{L-L'}(-1)^{L+L'+J+J'}(2\mathcal{J}+1) \times \begin{pmatrix} J & L & \mathcal{J} \\ M & M_L & -\mathfrak{M} \end{pmatrix} \begin{pmatrix} J' & L' & \mathcal{J} \\ M' & M_L' & -\mathfrak{M} \end{pmatrix} \times Y_{LM_L}^*(\hat{R}_{\rm lab}) Y_{L'M_L'}(\hat{R}) T_{JL,J'L'}^{\mathcal{J}} \ . \quad (5)$$

Here $(:::)$ is a $3j$ symbol[45] and $T_{JL,J'L'}^{\mathcal{J}} \equiv \delta_{JJ'}\delta_{LL'} - S_{JL,J'L'}^{\mathcal{J}}$ is a T-matrix element.[46]

The $\langle JM|$ states can be coupled with the $|J'M'\rangle$ states to form *statistical tensors*,[48] which are vectors of tensorial character in the dual (or Liouville)[36] space. These are defined as[48]

$$\rho_{KQ}(J, J') = (2K+1)^{1/2}(-1)^{K-J-Q} \sum_{MM'} (-1)^{-M} \times \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix} |J'M'\rangle\langle JM| \ . \quad (6)$$

Similarly, the scattering amplitude itself may be expanded in terms of irreducible tensor components $f_{JJ'}^{KQ}$, where, by analogy with Eq. (6),

$$f_{JJ'}^{KQ} = (2K+1)^{1/2}(-1)^{K-J-Q} \sum_{MM'} (-1)^{-M} \times \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix} f_{JM,J'M'} \ , \quad (7)$$

or, inversely

$$f_{JM-J'M'} = (-1)^{-J-M} \sum_{KQ} (2K+1)^{1/2}(-1)^{K-Q} \times \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix} f_{JJ'}^{KQ} \ . \quad (8)$$

Inserting Eq. (5) into Eq. (7), we find, after some angular momentum algebra,

$$f^{KQ}_{JJ'} = 2\pi(2K+1)^{1/2} \sum_{LL'M_LM'_L} i^{L-L'}(-1)^{M_L} Y^*_{LM_L}(\hat{R}_{\rm lab}) Y_{L'M'_L}(\hat{R}) \begin{pmatrix} L & L' & K \\ M_L & -M'_L & -Q \end{pmatrix} \times \sum_{\mathcal{J}} (2\mathcal{J}+1)(-1)^{\mathcal{J}+J'} T^{\mathcal{J}}_{JL,J'L'} \begin{Bmatrix} J & J' & K \\ L' & L & \mathcal{J} \end{Bmatrix} , \tag{9}$$

where $\{:::\}$ is a $6j$ symbol.[45,48]

The integral cross section for the $JM \to J'M'$ transition can be obtained by squaring the scattering amplitude, integrating over all scattering angles $\hat{R}$, and dividing by the square of the initial wave vector. Then, to average over all orientations of $v_{\rm rel}$, it is necessary to integrate over $\hat{R}_{\rm lab}$ and divide by 4π. The orthogonality of the spherical harmonics and $3j$ symbols in Eqs. (5) and (9) gives rise, again after some algebra, to the following expression for the integral cross section:

$$\sigma_{JM\to J'M'} = \sum_{KQ} (2K+1) \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix}^2 B(JJ',K) , \tag{10}$$

where

$$B(JJ',K) = \frac{\pi}{k_J^2} \sum_{LL'} \left| \sum_{\mathcal{J}} (2\mathcal{J}+1)(-1)^{\mathcal{J}+J'} T^{\mathcal{J}}_{JL,J'L'} \times \begin{Bmatrix} J & J' & K \\ L' & L & \mathcal{J} \end{Bmatrix} \right|^2 . \tag{11}$$

As discussed in the Introduction, this expression is well known in the theory of atomic collisions[40-42]; the $B(JJ',K)$ factors are called Grawert coefficients.

We[49] as well as Launay and Brechignac[22,50] have shown explicitly how the T-matrix element in Eq. (5) can be expressed as a sum over reduced matrix elements, namely,[51]

$$T^{\mathcal{J}}_{JL,J'L'} = \sum_K (-1)^{J+L'+\mathcal{J}} \begin{Bmatrix} \mathcal{J} & L' & J' \\ K & J & L \end{Bmatrix} (J'L' \| T_K \| JL) . \tag{12}$$

The orthogonality relation of the $6j$ symbols[45,48] can be used to invert this equation, which gives

$$(J'L' \| T_K \| JL) = (-1)^{-J-L'}(2K+1) \sum_{\mathcal{J}} (-1)^{\mathcal{J}} \times (2\mathcal{J}+1) \begin{Bmatrix} L' & J' & \mathcal{J} \\ J & L & K \end{Bmatrix} T^{\mathcal{J}}_{JL,J'L'} . \tag{13}$$

Equation (12) may be substituted into Eqs. (10) and (11) to obtain an equivalent expression for the integral cross section, namely,

$$\sigma_{JM\to J'M'} = \frac{\pi}{k_J^2} \sum_{KQ} \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix}^2 P^K_{JJ'} . \tag{14}$$

Here we have introduced a *tensor opacity* defined by

$$P^K_{JJ'} = P^K_{J'J} = \frac{1}{2K+1} \sum_{LL'} |(J'L' \| T_K \| JL)|^2 . \tag{15}$$

The unpolarized cross section, obtained by summing over M' and averaging over M, is given by

$$\sigma_{J\to J'} = \frac{\pi}{(2J+1)k_J^2} \sum_K P^K_{JJ'} . \tag{16}$$

This can be shown to reduce to the more familiar expression[46]

$$\sigma_{J\to J'} = \frac{\pi}{(2J+1)k_J^2} \sum_{\mathcal{J}} (2\mathcal{J}+1) \sum_{LL'} |T^{\mathcal{J}}_{JL,J'L'}|^2 . \tag{17}$$

We emphasize that Eqs. (5), (9), (10), and (14) all apply to a situation in which the M projection quantum numbers refer to a laboratory fixed axis system, about which the relative velocity vectors, which define the collision frame, are randomly oriented. By contrast, in a molecular beam experiment where quantization refers to the collision frame, the scattering amplitude is given by the expression[32,33]

$$f_{J\bar{M},J'\bar{M}'}(\hat{R}) = \pi^{1/2} \sum_{\substack{\mathcal{J}\mathfrak{M}L \\ L'M'_L}} i^{L-L'}(2L+1)^{1/2}(-1)^{J+J'-L-L'}(2\mathcal{J}+1) \times \begin{pmatrix} J & L & \mathcal{J} \\ \bar{M} & 0 & -\mathfrak{M} \end{pmatrix} \begin{pmatrix} J' & L' & \mathcal{J} \\ \bar{M}' & M'_L & -\mathfrak{M} \end{pmatrix} T^{\mathcal{J}}_{JL,J'L'} Y_{L'M'_L}(\hat{R}) . \tag{18}$$

The angles $\hat{R}_{\rm lab}$ are missing from Eq. (18), since the incoming plane wave is assumed to be along the z axis. The bars on the M projection quantum numbers are to remind the reader that quantization refers now to the collision frame.

It is possible to define the tensor components of this collision frame scattering amplitude analogously to Eqs. (7) and (9). We find

$$f^{KQ}_{JJ'} = \pi^{1/2}(2K+1)^{1/2} \sum_{LL'M'_L} i^{L-L'}(2L+1)^{1/2} Y_{L'M'_L}(\hat{R}) \times \begin{pmatrix} L & L' & K \\ 0 & M'_L & -Q \end{pmatrix} \times \sum_{J} (2\mathcal{J}+1)(-1)^{\mathcal{J}+J'} T^{\mathcal{J}}_{JL,J'L'} \begin{Bmatrix} J & J' & K \\ L' & L & \mathcal{J} \end{Bmatrix} . \tag{19}$$

Taking the square, then integrating over $\hat{R}$, we can derive an expression similar to Eqs. (14) and (15), namely,

$$\sigma_{J\bar{M}\to J'\bar{M}'} = \frac{\pi}{k_J^2} \sum_{L'} (2L'+1) |C^{L'}_{J\bar{M},J'\bar{M}'}|^2 , \tag{20}$$

where

$$C^{L'}_{J\bar{M},J'\bar{M}'} = \sum_{KQ} \begin{pmatrix} J & J' & K \\ -\bar{M} & \bar{M}' & -Q \end{pmatrix} \sum_L i^L (-1)^{J+J'+L'} \times [(2L+1)/(2L'+1)]^{1/2} \begin{pmatrix} L & L' & K \\ 0 & Q & -Q \end{pmatrix} (J'L' \| T_K \| JL) . \tag{21}$$

Examining Eqs. (20) and (21), we see that here there

will be coupling, and hence interference, between the various tensor orders K in the expression for the integral cross sections. No interference terms between different tensor orders are present in the expression for the cross section appropriate to collision cell experiments [Eqs. (14) and (15)], which suggests that these interference terms are quenched by the increased degree of averaging. As we might expect, the expression for the degeneracy averaged cross section [Eq. (17)] is identical in both the laboratory and collision frames.

As discussed above, the passage from Eq. (5) to Eq. (11) was inspired by the construction of statistical tensors from $|J'M'\rangle$ and $\langle JM|$ states. An alternative approach follows the more usual expansion of the state density matrix in terms of statistical tensors formed by coupling the $|JM\rangle$ with $\langle JM|$ states,[5,22,34-39] and the $|J'M'\rangle$ with $\langle J'M'|$ states. The connection between the two approaches can be shown as follows: In analogy with Eq. (7), but following the coupling scheme outlined at the beginning of this paragraph, we can define an irreducible generalized cross section $\sigma^{KK'}_{JJ'}$ as

$$\sigma^{KK'}_{JJ'}=\frac{1}{4\pi k_J^2}\int\sum_{\substack{MM'\\M''M'''}}(2K+1)^{1/2}(2K'+1)^{1/2}(-1)^{K+K'-J-J'-Q-Q'-M-M'}\times\begin{pmatrix}J & J & K\\ -M & M'' & -Q\end{pmatrix}\begin{pmatrix}J' & J' & K'\\ -M' & M''' & -Q'\end{pmatrix}f_{JM,J'M'}f^{*}_{JM'',J'M'''}\,d\hat{R}\,d\hat{R}_{\rm lab}\,. \tag{22}$$

Integration and substitution of Eq. (5) gives, after some angular momentum algebra,

$$\sigma^{KK'}_{JJ'}=\delta_{KK'}\frac{\pi}{k_J^2}\sum_{\substack{\mathcal{J}\mathcal{J}'\\LL'}}(2\mathcal{J}+1)(2\mathcal{J}'+1)(-1)^{L+L'-J-J'+2\mathcal{J}}\times\begin{Bmatrix}J & J & K\\ \mathcal{J} & \mathcal{J}' & L\end{Bmatrix}\begin{Bmatrix}J' & J' & K'\\ \mathcal{J} & \mathcal{J}' & L'\end{Bmatrix}T^{\mathcal{J}}_{JL,J'L'}T^{\mathcal{J}'*}_{JL,J'L'}\,. \tag{23}$$

This expression is seen to be similar to the generalized collision cross sections discussed by Fitz and Marcus[36] and Coombe and Snider.[38] As discussed by Rowe and McCaffery[5] $\sigma^{KK}_{JJ'}$ is the cross section for the collisional transfer of the Kth multipole moment of the density matrix.

Reversal of the transformation contained in Eq. (22) gives a generalized integral cross section,[32] namely,

$$\sigma_{JMM''-J'M'M'''}=\sum_{KQ}(2K+1)(-1)^{-J-M-J'-M'}\times\begin{pmatrix}J & J & K\\ -M & M'' & -Q\end{pmatrix}\begin{pmatrix}J' & J' & K\\ -M' & M''' & -Q\end{pmatrix}\sigma^{KK}_{JJ'}\,. \tag{24}$$

Inserting Eq. (23) into Eq. (24) and then setting $M''=M$ and $M'''=M'$, we find the expression first derived by Kinsey *et al.*,[34] namely,

$$\sigma_{JM-J'M'}=\frac{\pi}{k_J^2}\sum_{\substack{\mathcal{J}\mathcal{J}'L\\L'K}}(2\mathcal{J}+1)(2\mathcal{J}'+1)(-1)^{L+L'-M-M'}\times\begin{pmatrix}J & J & K\\ -M & M & 0\end{pmatrix}\begin{pmatrix}J' & J' & K\\ -M' & M' & 0\end{pmatrix}\begin{Bmatrix}J & J & K\\ \mathcal{J} & \mathcal{J}' & L\end{Bmatrix}\begin{Bmatrix}J' & J' & K\\ \mathcal{J} & \mathcal{J}' & L'\end{Bmatrix}\times T^{\mathcal{J}}_{JL,J'L'}T^{\mathcal{J}'*}_{JL,J'L'}\,. \tag{25}$$

Although this equation bears little obvious similarity with Eqs. (14) and (15), an interesting connection can be made by setting $M''=M$ and $M'''=M'$ in Eq. (24) to give

$$\sigma_{JM-J'M'}=\sum_{K}(2K+1)(-1)^{-J-M-J'-M'}\times\begin{pmatrix}J & J & K\\ -M & M & 0\end{pmatrix}\begin{pmatrix}J' & J' & K\\ -M' & M' & 0\end{pmatrix}\sigma^{KK}_{JJ'}\,, \tag{26}$$

an expression equivalent to that given earlier by Brechignac *et al.*[22] The differences between Eqs. (14) and (26) reflect the different nature of the tensorial coupling. In each case $(2J_{\rm min}+1)$ values of the tensor order contribute, where $J_{\rm min}=\min(J,J')$. The allowed tensor orders are given by $0\le K\le(2J_{\rm min}+1)$ for Eq. (26) and $|J-J'|\le K\le J+J'$ for Eq. (14). We can sum over the projection quantum numbers to obtain a relation equivalent to Eq. (16), namely,

$$\sigma_{J\to J'}=\frac{1}{2J+1}\sum_{MM'}\sum_{K=0}^{2J_{\rm min}+1}(2K+1)(-1)^{-J-M-J'-M'}\times\begin{pmatrix}J & J & K\\ -M & M & 0\end{pmatrix}\begin{pmatrix}J' & J' & K\\ -M' & M' & 0\end{pmatrix}\sigma^{KK}_{JJ'}\,. \tag{27}$$

III. IMPLICATIONS FOR M CONSERVATION

Equation (14) contains some important implications for the development of models for M conservation in rotationally inelastic collisions. First we note that a *necessary* condition for the validity of a strict $\Delta M=0$ selection rule, as advocated by McCaffery, Pritchard, and their co-workers,[1-3] is the vanishing of the $3j$ symbol

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

for Q not equal to zero. Since this does not occur, it is clear that *under no circumstances will M be rigorously conserved in a collision cell experiment.* A similar conclusion was reached by Elbel.[28]

Secondly, since the triangular condition on the arguments of the $3j$ symbol restricts K to the values $|J-J'|\le K\le J+J'$, we see that the entire $(2J+1)\times(2J'+1)$ ma-

trix of cross sections is determined by only $2J_{\min}+1$ independent parameters, the $P^K_{JJ'}$ tensor opacities. An identical conclusion follows from Eq. (28), as was discussed by Brechignac, Launay, and co-workers.[22] Since the expression for the $J\bar{M}\to J'\bar{M}'$ cross sections [Eqs. (20) and (21)] appropriate to a molecular beam experiment does not reduce to a summation over quantities which are independent of $\bar{M}$ and $\bar{M}'$, it follows that this type of experiment contains, in principle, more information than could be accessible in a collision cell experiment, even if, in the latter, all M states were resolved.

We stress that the analysis of this section does not involve any explicit consideration of the tensor opacities, which contain, through the T-matrix elements in Eq. (15), all the effects of the interaction potential, reduced mass, and collision energy of a given system. Thus the implications that have been drawn here are completely general and will apply to any system, independent of the choice of interaction potential or dynamical limit. In the next section we shall examine some further relationships that can be derived within a sudden treatment of the dynamics.

IV. ENERGY SUDDEN LIMIT

If the collision time is shorter than the time which characterizes the dephasing of the initial and final rotational levels, then an energy sudden limit[38,52,53] is appropriate. Khare[53] has shown how within this approximation the entire T matrix can be expressed in terms of the $J=0\to J'$ elements. We have[53]

$$T^{\mathcal{J}}_{JL,J'L'}=(-1)^{-\mathcal{J}+L}[(2J+1)(2J'+1)(2L+1)]^{1/2}\sum_l(-1)^l \times(2l+1)^{1/2}\begin{pmatrix}J & l & J'\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}L & J & \mathcal{J}\\ J' & L' & l\end{Bmatrix}T^L_{lL',0L}\,. \tag{28}$$

Substitution of Eq. (28) into Eq. (13) gives, after some angular momentum algebra,

$$(J'L'||T_K||JL)=(-1)^{K-J+L-L'}[(2J+1)(2J'+1) \times(2L+1)(2K+1)]^{1/2}\begin{pmatrix}J & K & J'\\ 0 & 0 & 0\end{pmatrix}T^L_{KL',0L}\,, \tag{29}$$

and for the tensor opacity

$$P^K_{JJ'}=(2J+1)(2J'+1) \times\begin{pmatrix}J & K & J'\\ 0 & 0 & 0\end{pmatrix}^2\sum_{LL'}(2L+1)|T^L_{KL',0L}|^2\,. \tag{30}$$

From the presence of the $3j$ symbol we observe that within the energy sudden limit the tensor opacities will be nonvanishing only for K values such that

$$(-1)^K=(-1)^{J+J'}\,. \tag{31}$$

This would reduce the number of independent quantities needed to describe the full matrix of cross sections. For collisions of homonuclear diatomics, where only even changes in J will occur, the tensor order K will obviously be restricted to even values.

From Eq. (17) we know that the degeneracy averaged cross section for the $J=K\to J'=0$ transition is given by

$$\sigma_{K\to 0}=\frac{\pi}{(2K+1)k_K^2}\sum_{LL'}(2L+1)|T^L_{KL',0L}|^2\,. \tag{32}$$

By inserting Eq. (32) into the right-hand side of Eq. (30), we find

$$P^K_{JJ'}=\frac{(2K+1)(2J+1)(2J'+1)k_K^2}{\pi}\begin{pmatrix}J & K & J'\\ 0 & 0 & 0\end{pmatrix}^2\sigma_{K\to 0}\,. \tag{33}$$

Substitution of this into Eq. (14) gives

$$\sigma_{JM\to J'M'}=(2J+1)(2J'+1)\sum_{KQ}(2K+1) \times\begin{pmatrix}J & J' & K\\ -M & M' & -Q\end{pmatrix}^2\begin{pmatrix}J & J' & K\\ 0 & 0 & 0\end{pmatrix}^2\sigma_{K\to 0}\,. \tag{34}$$

We see that Eq. (34) relates the M dependent cross sections for a particular $J\to J'$ transition to a vector of degeneracy averaged inelastic cross sections into the $J=0$ level. This is one more example of the powerful scaling relations which are possible within an energy sudden limit.[49,50,52–56] Equation (34) also implies that a measurement of M dependent cross sections for a particular $J\to J'$ transition can, in principle, be deconvoluted to yield the set of degeneracy averaged cross sections for the $J=K\to J'=0$ transitions. Consistent with the discussion following Eq. (30), it would be necessary to use two sets of $J\to J'$ transitions to obtain the $J=K\to 0$ cross sections for both odd and even values of K. These $K\to 0$ cross sections could then be used to obtain the entire matrix of $J\to J'$ cross sections by means of the well known sudden scaling relation for degeneracy averaged integral cross sections[54–56]

$$\sigma_{J\to J'}=(2J'+1)\sum_K(2K+1)\begin{pmatrix}J & K & J'\\ 0 & 0 & 0\end{pmatrix}^2\sigma_{K\to 0}\,. \tag{35}$$

In fact, as we might expect, Eq. (34) reduces to Eq. (35), if we sum and average over M and M'.

The use of any energy sudden scaling relation[49,53–56] involves some ambiguity with respect to the translational energy. As written Eq. (34) involves cross sections at the same total energy. An alternative interpretation, after DePristo and co-workers,[56] would restrict Eq. (34) to downward transitions ($J>J'$) and assume a constant translational energy in the initial channel. Cross sections for upward transitions could then be obtained by microscopic reversibility.[56]

We reiterate that Eqs. (29), (30), and (34) were obtained by imposition of the energy sudden limit, and do not depend for their validity on the additional centrifugal decoupling which underlies the well known infinite order sudden (IOS) method.[54,57–59] Of course, Eqs. (29), (30), and (34) will also be valid within the full IOS approximation.

We recall that Eq. (34) has been derived by substitution of the sudden limit of the T matrix [Eq. (28)] into Eq. (14) and (15). Alternatively, as has been done by Launay and Brechignac,[22] in the formulation where the

TABLE I. Tensor opacities for CO–He collisions at $E = 60$ cm^{-1}.[a]

J	J'	$K=0$	1	2	3	4	5	6	7	8
1	1	2009.4	3.3	78.6						
2	2	2945.4	7.3	82.3	1.1	18.3				
3	3	3076.0	43.0	97.0	10.5	11.6	1.0	5.3		
4	4	2152.3	6.9	78.2	1.1	11.0	0.2	3.6	0.3	1.8
5	5[b]	493.9	0.9	25.8	0.7	3.1	0.3	0.8	0.0	0.0
1	2		66.5	1.7	15.8					
1	3			118.8	2.7	18.4				
1	4				21.0	0.5	3.2			
2	3		81.6	8.1	11.4	0.9	3.4			
2	4			162.2	1.9	16.5	0.3	5.8		
3	4		92.6	9.1	11.4	1.3	1.8	0.2	1.3	

[a]Tensor opacities defined by Eq. (15).
[b]The $K = 10$, 11 values, which occur for this transition, are < 0.05 in magnitude.

statistical tensors are created by coupling the $|JM\rangle$ states with their own Hermitian conjugates (Sec. II), Eq. (28) could be substituted into Eq. (23) to obtain sudden limit expressions for the $\sigma^{KK}_{JJ'}$ cross sections. In work not yet published, Derouard[60] has used this approach, along with Eq. (26), to relate the $JM \to J'M'$ cross sections to the degeneracy averaged $J \to 0$ cross sections. His resulting expressions are equivalent to Eqs. (33) and (34).

V. TENSOR OPACITIES FOR He-CO COLLISIONS

As discussed in the Introduction, the calculation of Green[31] of cross sections for the He–CO system at $E = 60$ cm^{-1} represents, to our knowledge, the only instance where orientation averaged cross sections have been determined for an atom colliding with a molecule in a $^1\Sigma$ electronic state. From these calculated cross sections we determined the appropriate tensor opacities by a least squares procedure, where, for each $J \to J'$ transition, the square deviation, defined by

$$\sum_{MM'} \left[\sigma_{JM \to J'M'} - \frac{\pi}{k_J^2} \sum_{KQ} \begin{pmatrix} J & J' & K \\ -M & M' & -Q \end{pmatrix}^2 P^K_{JJ'} \right]^2 = \Delta(P^1_{JJ'}, P^2_{JJ'}, \ldots) \tag{36}$$

was minimized with respect to each $P^K_{JJ'}$. This resulted in a set of linear equations which was easily solved.

The resulting tensor opacities are listed in Table I. It is clear from this table that for a given transition either even *or* odd tensor orders make the dominant contribution. It is interesting to note that even at this low collision energy, where we do not expect the energy sudden limit to be valid, this alternation in magnitude of the $P^K_{JJ'}$ is in accord with our prediction from Eq. (31). Table I also illustrates the economical way in which a few tensor opacities can describe the full array of M dependent cross sections. For instance, for the $J = 1 \to J' = 2$ transition there are eight different M dependent cross sections, even after taking symmetry into account; but only three tensor opacities are required.

The reader should note that an entirely analogous least squares procedure could be used to extract the tensor cross sections $\sigma^{KK}_{JJ'}$ from the $\sigma_{JM \to J'M'}$ cross sections, by means of Eq. (26).

We have attempted to use the M dependent cross sections for low J, where the relative kinetic energies will be largest and, as a result, the sudden limit most appropriate, to extract the degeneracy averaged $J = K \to 0$ cross sections from the tensor opacities (Table I), by means of Eq. (33). The results are displayed in Table II, and are compared with integral cross sections from close coupling calculations.[14,31] The agreement is excellent, even at this very low collision energy. This implies that it would be possible to extract an entire matrix of inelastic cross sections from experimental values of M dependent cross sections for a few $J \to J'$ transitions.

We reiterate that the extraction of the tensor opacities (Table I) is entirely rigorous, independent of any dynamical limit. On the other hand, the extraction of the degeneracy averaged $K \to 0$ cross sections (Table II) is strictly rigorous only in the energy sudden limit.

TABLE II. He–CO degeneracy averaged $J'' \to 0$ cross sections (Å^2) at $E = 60$ cm^{-1}, extracted from $JM \to J'M'$ cross sections.[a]

		$J''=0$	1	2	3	4
J	J'	Extracted values[a]				
1	1	197		4.8		
2	1		3.5		0.84	
3	1			4.8		0.84
2	2	173		4.2		1.2
3	2		2.9		0.56	
		CC values				
Green[b]		178	3.1	4.2	0.75	1.2
Fitz *et al.*[c]		•••	3.2	4.1	0.72	1.5

[a]Calculated from Eq. (33) with tensor opacities (Table I) extracted from CC $JM \to J'M'$ cross sections (Refs. 27 and 31). In line with the discussion following Eq. (30), the extraction of $J'' \to 0$ cross sections is only meaningful for values of J'' such that $(J + J' + J'')$ is an even number.
[b]References 27 and 31; individual values supplied by L. Monchick (private communication, 1982).
[c]Reference 14; the $0 \to J''$ cross sections were converted to $J'' \to 0$ cross sections by microscopic reversibility.

VI. M DEPENDENCE IN INELASTIC COLLISIONS OF Na_2 ($A\,^1\Sigma_u^+$) MOLECULES

The original suggestion of M conservation advanced by Pritchard and co-workers[3] arose from the analysis of experiments on Na_2. The molecules are excited by a laser to the particular rovibrational level of the $A\,^1\Sigma_u^+$ state. Collisions subsequently transfer population to neighboring rotational levels, which then fluorescence. The intensity of the fluorescence provides a measure of the rate constant for inelastic energy transfer. Recently, Pritchard and collaborators[7] have used a sophisticated composite scaling relation to obtain rate constants for $J \to J' = 0$ transitions in collisions of $Na_2(A\,^1\Sigma_u^+)$ with various noble gases.

Provided the energy sudden limit is valid, the M dependence of rotationally inelastic collisions of Na_2^* can be simulated using an expression for the thermal $JM \to J'M'$ rate constants, equivalent to Eq. (34), namely,

$$k_{JM\to J'M'}(T) = (2J+1)(2J'+1)\sum_{KQ}(2K+1) \times \begin{pmatrix} J & J' & K \\ -M' & M' & -Q \end{pmatrix}^2 \begin{pmatrix} J & J' & K \\ 0 & 0 & 0 \end{pmatrix}^2 k_{K\to 0}(T)\,. \tag{37}$$

If we follow the convention of DePristo *et al.*,[56] this equation will be restricted to downward transitions; the rates for upward transitions can be obtained by detailed balance. We have used the experimental $K \to 0$ rate constants to predict M resolved cross sections for Na_2^*–He collisions. Pritchard and co-workers[7] have reported values of $k_{K\to 0}$ for $K = 2$, 4, 6, 8, and 10. Only even K indices occur since Na_2 is homonuclear. The sudden approximation is certainly appropriate for the collision of the light, fast He with the massive, slowly rotating Na_2 molecule. As confirmation of this, Pritchard and co-workers[7] were able to fit well all the experimentally determined Na_2^*–He degeneracy averaged cross sections with the sudden scaling relation [Eq. (35)].

Rather than present tables of $JM \to J'M'$ rate constants, it is perhaps more instructive to investigate the overall M dependence by calculating moments of the change in the projection quantum number. These we define as

$$\Delta M^n_{JJ'} = \sum_{MM'} k_{JM\to J'M'}(M'-M)^n \Big/ \sum_{MM'} k_{JM\to J'M'}\,. \tag{38}$$

Several close-coupling calculations[10,11,15] of M dependent cross sections in the collision frame as well as Monchick's study of He–CO collisions in a laboratory frame[27] suggest that an appropriate model for M changes might be based on conservation of θ, the classical angle between J and $\hat{z}$, rather than conservation of M. This model was initially advanced by Jeyes *et al.*[2] to explain their experimental data on rotational energy transfer in I_2^*, but was rejected in favor of the M conservation model. To examine this model we can also determine moments of the change in θ, defined by

$$\Delta\theta^n_{JJ'} = \sum_{MM'} k_{JM\to J'M'}[\theta(J'M') - \theta(JM)]^n \Big/ \sum_{MM'} k_{JM\to J'M'}\,, \tag{39}$$

where

$$\theta(JM) = \cos^{-1}\{M/[J(J+1)]^{1/2}\}\,, \tag{40}$$

TABLE III. Standard deviations of the ΔM and $\Delta\theta$ distributions for downward $J \to J - \Delta J$ transitions in $Na_2(A\,^1\Sigma_u^+)$ + He collisions, simulated from experimental degeneracy averaged rate constants.[a]

J	σ_M[b]	σ_θ[c]
	$\Delta J = 2$	
4	2.18	36.7
16	2.36	9.17
26	2.34	5.57
38	2.34	3.79
66	2.34	2.17
	$\Delta J = 4$	
4	2.58	97.9
16	3.43	12.2
26	3.42	7.17
38	3.42	4.81
66	3.42	2.73
	$\Delta J = 6$	
16	4.40	14.2
26	4.39	8.03
38	4.39	5.30
66	4.39	2.96

[a]The input rate constants [Eq. (37)] are $k_{2\to 0} = 102$, $k_{4\to 0} = 33$, $k_{6\to 0} = 15$, $k_{8\to 0} = 8$, and $k_{10\to 0} = 6$, all in units of 10^{-12} cm^3 molecule^{-1} s^{-1} (see Ref. 7 for details of the experiment).
[b]Defined as $(\Delta M^2_{JJ'})^{1/2}$ [Eq. (38)].
[c]Defined as $(\Delta\theta^2_{JJ'})^{1/2}$ [Eq. (39)], in degrees.

and similarly for $\theta(J'M')$. It is easy to show, using the symmetry of the first $3j$ symbol in Eq. (37), that only the even moments are nonvanishing, both for M and θ. Since the first moment vanishes, the standard deviations of the M and θ distributions are just the square roots of the second moments.[61]

The standard deviations, predicted using the experimental[7] $K \to 0$ rate constants as input into Eq. (37), are listed in Table III for Na_2^*–He collisions, for all transitions with $\Delta J = 2$, 4, and 6 originating in the $J = 4$, 16, 26, 38, and 66 rotational levels, which are the rotational levels initially populated in the experiments analyzed. We see that the average change in M, in a root-mean-square sense, is significant, only slightly less than the change in J, and appears to approach an asymptotic limit as J increases, for a given ΔJ. Thus M conservation does not appear to be a reasonable model. If all values of ΔM were equally probable, as would be predicted by a purely statistical model, then the standard deviation in M would be equal to $(2J+\frac{3}{2})/3^{1/2}$. A binomial distribution would predict a standard deviation of[61] $(J+\frac{3}{4})^{1/2}$. Thus, although the sizable values of σ_M indicate that complete M conservation is not a physically reasonable model, nevertheless some dynamical constraints on the changes in the projection quantum number do exist. This is, of course, consistent with the more recent qualitative conclusions of Rowe and McCaffery[5] and Pritchard and co-workers.[7]

Table III indicates that the concept of θ conservation,

in a laboratory frame, becomes increasingly valid as J increases, at least for the Na_2^*–He system. We note also in Table III that as ΔJ increases for a fixed J the standard deviations in θ increase more slowly than the standard deviations in M, which is another confirmation of the appropriateness of a θ-conserving model. Monchick has demonstrated[27] that in a semiclassical large-J limit θ conservation in the collision frame is a sufficient condition for θ conservation in a laboratory frame, so that the values of σ_θ in Table III are consistent with the earlier conclusions based on close-coupling calculations in the collision frame.[10,11,15]

VII. CONCLUSIONS

In this article we have applied to collisions of a diatomic molecule the rotationally invariant tensor operators used by Grawert[40] in the study of atomic collisions. We have compared the resulting expressions for M dependent cross sections with those arising from an alternative irreducible tensor expansion. The main conclusions are as follows:

(1) The orientation averaging which occurs when the quantization is referred to a laboratory frame washes out all interference terms between various tensor orders. As a result, the entire matrix of $M \to M'$ cross sections can be expressed in terms of a much smaller number of tensor opacities.

(2) Within the energy sudden limit each tensor opacity is proportional to the degeneracy averaged cross section for the $J \to 0$ transition. For a given $J \to J'$ pair, only even or odd tensor orders will contribute. This effect was even seen in an analysis of He–CO collisions at low energy, where the energy sudden limit is not justified. A further consequence is that within the energy sudden limit many of the $J \to J'$ degeneracy averaged cross sections can be predicted from the knowledge of the complete M dependence of a few $J \to J'$ transitions.

(3) Strict M conservation in a laboratory frame, as postulated in early interpretations[1–3] of experimental data, can definitely be ruled out by a formal analysis of the expressions for the M dependent cross sections.

(4) Use of the sudden limit expressions to simulate the M dependence of $Na_2(A\,^1\Sigma_u^+) + He$ collisions suggests that the average changes in the projection quantum number can be as large as the changes in the rotational angular momentum itself. By contrast, conservation of the classical alignment angle θ appears to provide an accurate model for the description of the dynamics.

We feel that the formal analysis presented here will provide a useful framework for the interpretation of further experiments on alignment effects in rotationally inelastic collisions. In particular, one could use the energy sudden limit expressions to simulate intensity ratios in experiments in which polarized lasers are used for state selection and/or detection.[1,2,4,5,9] From a theoretical point of view one could use the cross section expressions arising from the Grawert tensor coupling within dynamical approximations other than the energy sudden limit. Along these lines Elbel[28] has already published a semiclassical analysis of atom–diatomic collisions. Another approach would be to extend the present treatment to collisions of molecules with two (or more) internal angular momenta (diatomics in electronic states with nonzero S and/or Λ, molecular tops). As will be seen in a future publication,[62] this will allow us to discuss the range of validity in the laboratory frame of a selection rule for M transitions which we have recently derived in the collision frame.[29]

Note added in proof: After this paper was accepted, J. Derouard brought to our attention that Eq. (34) has been already given, without derivation, by A. Varshalovich and V. K. Khersonsky [Astrophys. Lett. **18**, 167 (1977)].

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