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# Differential reaction cross sections from rotationally resolved quantum scattering calculations: application to gas-phase $S_{\rm N}2$ reactions

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Differential reaction cross sections have been computed based on previous rotationally resolved time-independent quantum-mechanical scattering calculations for the complex-forming  $S_N^2$  reaction  $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$ . The results show almost isotropic cross sections for reactant molecules with high rotational quantum numbers. Backward scattering is disfavoured for reaction out of states with small rotational excitation, in particular the rovibrational ground state. This is a quantum-mechanical effect (interference of partial waves) that can partly be rationalized by simple classical arguments. In particular for higher vibrational excitations, an umbrella effect can be observed that favours the backward direction. It can be explained by the strong enhancement of the reactivity by opening a direct mechanism. The ion–dipole interaction exerts a torque onto the molecule which carries out a rotation by about 90° and then completes the reaction.

# I. Introduction

Quantum-state resolved differential reaction cross sections provide angular distributions of the scattered products of a reactive process and thus contain information on a chemical reaction at a very detailed level. They provide the most stringent test for a quantitatively accurate theoretical model for elementary chemical reactions.<sup>1-6</sup> Only a few reactive systems could be studied with quantum-state resolution in a scattering experiment. So far, experimental results are available for reactions involving molecular hydrogen: the substitution reactions between open-shell atoms and hydrogen molecules H + H<sub>2</sub>, H +  $D_{2}$ ,<sup>7,8</sup> F +  $H_{2}$ ,<sup>9-11</sup> Cl +  $H_{2}$ ,<sup>12</sup> the four-atom reaction  $H_2 + OH^{13}$  and the insertion reactions of electronically excited atoms  $C(^{1}D)$ ,  $N(^{2}D)$ ,  $O(^{1}D)$  and  $S(^{1}D)$ into H2.14 In these experiments, the flux of the reaction products is measured that goes into different scattering angles and final rovibrational states for different initial levels. The differential cross section for a state-to-state reactive molecular collision often exhibits a complicated interference pattern. An important problem, which is discussed in recent reviews, 1-5,15 is how to analyse this scattering pattern in order to obtain sound information on the reaction dynamics.

Ion-molecule reactions can be studied experimentally by employing crossed-beam imaging.<sup>15</sup> Collisions between reactants with well-defined linear momenta are prepared, and the corresponding differential cross-sections are measured using angle- and velocity(*i.e.* energy)-resolved detection schemes. While this approach has been widely used for reactions

between neutral species,<sup>3,16</sup> it has also become a powerful tool for the investigation of reactions between neutrals and anions. In contrast to conventional crossed-beam experiments employing rotatable detectors, an imaging spectrometer allows not only for higher angular resolution, but also for a faster data acquisition. It can detect products within a  $2 \times 2\pi$  solid angle of acceptance. The underlying technique is that of velocity map imaging<sup>17</sup> where ions with the same velocity component parallel to the detector surface are projected onto the same spot on the detector. The finite size of the reaction volume avoids broadening of the product ion images. Wester et al. have constructed a velocity map imaging spectrometer in conjunction with a low-energy ion source<sup>18</sup> which has also been used to study gas-phase S<sub>N</sub>2 reactions. Here, slow ions (kinetic energy between 0.5 and 5 eV) collide with neutral molecules in a supersonic molecular beam in the centre of the velocity map imaging electrode stack. The electric field of the imaging spectrometer is rapidly pulsed on and the product ions are projected onto the position-sensitive imaging detector. A CCD camera records ion impact positions, which are proportional to the velocity components in the scattering plane parallel to the detector surface. The imaging data, *i.e.* the impact velocity vectors in the laboratory frame, need only little data processing (transformation to the centre-of-mass frame for each scattering event; correction for the loss of products with high laboratory velocities which leave the spectrometer volume that is imaged onto the detector).15

In this paper, we report on a detailed theoretical study of the effect of initial rotational excitation in a prototypical substitution reaction,  $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$ , at the quantum state-to-state level.

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From a theoretical point of view, it is necessary to extract converged *complex S*-matrix elements from a quantum scattering calculation, not only the squared moduli where the phase information is lost. While the latter are sufficient for the calculation of integral scattering cross sections (and can be obtained by averaging without taking into account the phases), differential cross sections are computed by first summing up the *S*-matrix elements weighted by Legendre polynomials and squaring the modulus of that sum afterwards. If the asymptotic wave function is projected onto channel Jacobi coordinates, the necessary complex *S*-matrix elements can be obtained from the scattering wavefunction.

In a general  $S_N^2$  reaction,  $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ (X, Y: halogen atoms)<sup>19-25</sup> several reaction mechanisms are possible. First, the attacking nucleophile X<sup>-</sup> directly hits the cone defined by the three hydrogen atoms and the central carbon nucleus. It then forms the new X-C bond in a direct collision while the other bond, C-Y, is broken. Second, a relatively long-living resonance state can be formed by virtue of intermolecular, i.e. long-range ion-dipole forces. This complex can perform many rotations before it dissociates back into the reactants or finally forms new products. It is thus interesting to investigate the importance of the different reaction channels. We have carried out comprehensive quantum-mechanical studies on  $S_N 2$  reactions<sup>26-31</sup> where reaction probabilities and total reaction cross section have been calculated and discussed in detail. We refer to these papers for details and extend our investigation towards differential cross sections that can give even more insight, in particular with respect to angular distributions and rotational-stateselected reactivity.

The present paper is organized as follows: in Section II we provide the particular theoretical background for the calculations of the differential reaction cross sections, while Section III contains the results and their discussion. Finally, Section IV presents our conclusions. Throughout, all energies are quoted in  $cm^{-1}$ .

# II. Theory

#### A. Coordinate systems and Hamiltonians

We refer to our previous paper<sup>31</sup> and treat the reaction as a pseudo-triatomic system with the methyl group as united atom, but with optimization of the internal geometry of this group for each set of Jacobi coordinates R, r and  $\gamma$ . In ref. 31, we started with the (exact) Hamiltonian operator in Jacobi coordinates:

$$\hat{H} = \hat{T}^{J=0} + \hat{T}^{J} + \hat{V}, \qquad (1)$$

consisting of the potential  $\hat{V}$  and the following expression for the kinetic energy<sup>32</sup>

$$\hat{T}^{J=0} = \delta_{j'j} \delta_{k'k} \left[ -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2} j(j+1) \left( \frac{1}{\mu_1 R^2} + \frac{1}{\mu_2 r^2} \right) \right],\tag{2}$$

$$\hat{T}^{J} = \delta_{j'j} \delta_{k'k} \frac{\hbar^2}{2\mu_1 R^2} [J(J+1) - 2k^2] - \delta_{j'j} \delta_{k'k\pm 1} \frac{\hbar^2}{2\mu_1 R^2} C^{\pm}_{Jk} C^{\pm}_{jk},$$
(3)

and

$$\hat{\gamma} = \delta_{k'k} \langle j'k | V(R, r, \gamma) | jk \rangle_{\gamma}, \tag{4}$$

where the coefficients  $C_{jk}^{\pm}$  are given by

I

$$C_{ik}^{\pm} = (j(j + 1) - k(k \pm 1))^{1/2}.$$

Here, J denotes the conserved total angular momentum (J) quantum number, while j = |k|, |k| + 1, ... is the angular momentum quantum number of the rotating diatom and k = -J, ..., J indicates the quantum number of the J-projection onto the body-fixed axis which is defined by the third atom and the center of mass of the diatom. The set  $|jk\rangle$  denotes a spherical harmonic function and  $\langle ... \rangle_{\gamma}$  indicates the integration over the Jacobi angle  $\gamma$ .

In ref. 31, we considered only the (J = 0) part to compute rotationally resolved S-matrices and therefrom reaction probabilities. For differential reaction cross sections, however, we need the S-matrices for nonvanishing total angular momenta (J > 0). In the above Hamiltonian, we restrict ourselves to vanishing helicity (k = 0) and consequently drop the Coriolis coupling term (centrifugal sudden approximation<sup>33,34</sup>). This approximation has been shown to yield acceptable results when compared to the data from calculations employing the full rotational Hamiltonian.<sup>35–38</sup>

The Hamiltonian for J > 0 used in the present work then reads

$$\hat{H}_{\rm CS} = \hat{T}^{J=0} + \hat{T}^{J}_{\rm CS} + \hat{V}, \tag{5}$$

with the influence of total angular momentum approximated in  $\hat{T}_{\rm CS}^J$  according to

$$\hat{T}_{\rm CS}^{J} = \delta_{j'j} \frac{\hbar^2}{2\mu_1 R^2} J(J+1).$$
 (6)

In the framework of time-independent quantum scattering theory as employed in ref. 31 we can therefore reuse the wave functions and overlap matrices, respectively, computed for J = 0 and add the above term as an energetic correction in the propagation of the wavefunction along the hyperradius. An additional approximation is required, however, when hyperspherical coordinates<sup>39–44</sup> are used in the interaction region. The full surface Hamiltonian reads<sup>31</sup>

$$\hat{H}_{\text{surf}} = \hat{T}_{\text{surf}}^{J=0} + \hat{T}_{\text{surf}}^{J} + \hat{V}$$
(7)

with

$$\hat{T}_{surf}^{J=0} = \delta_{j'j} \delta_{k'k} \left[ -\frac{\hbar^2}{2\mu\rho^2} \frac{\partial^2}{\partial\delta^2} + \frac{\hbar^2}{2\mu\rho^2} j(j+1) \left( \frac{1}{\cos^2 \delta} + \frac{1}{\sin^2 \delta} \right) \right],\tag{8}$$

$$\hat{T}_{surf}^{J} = \delta_{j'j} \delta_{k'k} \frac{\hbar^{2}}{2\mu\rho^{2}\cos^{2}\delta} [J(J+1) - 2k^{2}] - \delta_{j'j} \delta_{k'k\pm 1} \frac{\hbar^{2}}{2\mu\rho^{2}\cos^{2}\delta} C_{Jk}^{\pm} C_{jk}^{\pm}$$
(9)

and

$$\hat{V} = \delta_{k'k} \langle j'k | V(\delta, \gamma; \rho) | jk \rangle_{\gamma}.$$
 (10)

In the centrifugal sudden approximation for k = 0,  $\hat{T}_{surf}^{J}$  becomes

$$\hat{T}_{\text{surf,CS}}^{J} = \delta_{j'j} \frac{\hbar^2}{2\mu\rho^2 \cos^2 \delta} [J(J+1)].$$
(11)

This expression still contains the internal hyperspherical coordinate  $\delta$ . In the spirit of the rotating line approximation,<sup>45</sup> we drop this dependency and obtain

$$\hat{T}_{\text{surf,CS,RLA}}^{J} = \delta_{j'j} \frac{\hbar^2}{2\mu\rho^2} [J(J+1)] < \hat{T}_{\text{surf,CS}}^{J}.$$
 (12)

While this approximation will have a non-negligible quantitative effect, the dynamics is still retained in its essential characteristics, *i.e.* centrifugal barriers show up in the hyperspherical adiabatic curves.

#### B. Reactive scattering formalism

The time-independent Schrödinger equation at fixed total energy E and fixed J,

$$\hat{H}\psi_n^J(R,\mathbf{x}) = E\psi_n^J(R,\mathbf{x}), \qquad (13)$$

is solved by employing an expansion of the wavefunction,

$$\psi_{n}^{J}(R, \mathbf{x}) = \frac{1}{R} \sum_{m=1}^{\infty} g_{nm}^{J}(R) \phi_{m}^{J}(\mathbf{x})$$
(14)

where the  $g_{nm}^{J}(R)$  denote the translational functions, while the  $\phi_{m}^{J}(\mathbf{x})$  are eigenfunctions of the surface Hamiltonian depending on all other coordinates collectively denoted by  $\mathbf{x}$ (in this work: r and  $\gamma$ ).

Asymptotically,  $\psi$  represents an incoming free plain wave (initial reactant states *n*) and a scattered spherical wave (product states *m*), and we impose the boundary condition

$$g_{nm}^{J}(R) \sim \delta_{nm} e^{-i(k_{n}R - (J+j_{n})\pi/2)} - \left(\frac{k_{n}}{k_{m}}\right)^{1/2} S_{nm}^{J} e^{i(k_{m}R - (J+j_{m})\pi/2)}$$
(15)

for  $R \to \infty$ ,  $j_n$  is the angular momentum quantum number of the diatom for state *n* and total angular momentum *J*.

The (complex) S-matrix elements  $S_{nm}^J$  not only yield reaction probabilities  $P_{nm}^J = |S_{nm}^J|^2$ , but also contain additional information on time delays<sup>48</sup> and differential cross sections. Note that the phase factors  $e^{\pm iJ\pi/2}$  in eqn (15) lead to alternating signs of  $S_{nm}^J$  with increasing J and thus are important when different J are involved in the calculation. The factors  $e^{-ig_n\pi/2}$  and  $e^{ig_m\pi/2}$  drop out in the computation of many real quantities obtained from  $S_{nm}^J$ , like reaction probabilities and cross sections.

The numerical solution of the scattering problem makes use of the technique of *R*-matrix propagation<sup>46</sup> (in what follows, all matrices are *J*-dependent, but superscripts are suppressed for clarity). From such an asymptotic matrix  $\mathbf{R}_{\infty}$ , we obtain the *S*-matrix *via* 

$$\boldsymbol{S} = (\boldsymbol{R}_{\infty} \boldsymbol{\tilde{O}}' - \boldsymbol{\tilde{O}})^{-1} (\boldsymbol{R}_{\infty} \boldsymbol{\tilde{I}}' - \boldsymbol{\tilde{I}}), \quad (16)$$

where  $\tilde{I}$  and  $\tilde{O}$  are diagonal matrices representing the incoming and outgoing waves, respectively, according to eqn (15). For the construction of  $R_{asym}$ , we start in the interaction region with the hyperspherical reaction coordinate  $\rho$  being divided into small sectors with midpoints  $\rho_i$ .<sup>†</sup> For each  $\rho_i$ , the wavefunction is expanded in a finite product basis similar to the infinite expansion (14),

$$\psi_n(\rho;\rho_i) = \frac{1}{\rho} \sum_{m=1}^{N_{\rm ch}} g_{nm}(\rho;\rho_i) \phi_m(\boldsymbol{x};\rho_i).$$
(17)

If the surface functions  $\phi_m(\mathbf{x};\rho_i)$  are chosen to be eigenfunctions of  $\hat{H}_{\text{surf}}(\rho_i)$  with eigenvalues  $\varepsilon_m(\rho_i)$ , insertion of the finite expansion (17) into the Schrödinger equation yields decoupled equations for the sector translational functions  $g_{nm}(\rho;\rho_i)$ :

$$\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} \tilde{\boldsymbol{g}}_n(\rho;\rho_i) + \boldsymbol{W}(\rho_i) \tilde{\boldsymbol{g}}_n(\rho;\rho_i) = \boldsymbol{0}. \tag{18}$$

Here, the column vector  $\tilde{g}_n$  contains the elements  $g_{nm}/\rho$  and the matrix W is given by

$$W_{mn}(\rho_i) = \left(\frac{2\mu}{\hbar^2} (E - \varepsilon_n(\rho_i)) - \frac{1}{4\rho_i^2}\right) \delta_{mn}.$$
 (19)

Eqn (18) is easily solved to give a local *R*-matrix in each sector and an assembled global *R*-matrix (*cf.* ref. 46). For that purpose, the surface eigenfunctions  $\phi_m(\mathbf{x};\rho_i)$  for adjacent sectors  $\rho_{i-1}$  and  $\rho_i$  are mapped onto each other by virtue of their energy-independent intersector overlap matrix elements  $O_{mm}^{(i-1,i)}$ ,

$$O_{mm}^{(i-1,i)} = \langle \phi_m(\boldsymbol{x};\rho_{i-1}) | \phi_n(\boldsymbol{x};\rho_i) \rangle$$
(20)

which need to be computed only once for each J. For the asymptotic region, we proceed in a similar manner, with eqn (19) being replaced by

$$W_{mn}(\rho_i) = \left(\frac{2\mu}{\hbar^2} (E - \varepsilon_n(\tilde{R}_i))\right) \delta_{mn}.$$
 (21)

#### C. Step size algorithm

In the different regions of the potential, the size of the sectors needed to achieve convergence largely differs. In the interaction region, small sizes are necessary to account for the rapid changes of the eigenfunctions; in the intermediate region, the sector size is limited by the geometric changes in the hyperspherical coordinates whereas in the asymptotic region, large sector sizes can be chosen. We used a step size algorithm similar to ref. 46 to determine appropriate sector sizes during runtime depending on the wave functions computed.

To be more specific, if  $\rho_i$  is the hyperradius for sector *i* and  $\Delta \rho_i$  its size, the hyperradius  $\rho_{i+1}$  for sector i + 1 is chosen to obtain a sufficiently good overlap of the vector spaces spanned by the surface functions in both sectors. This, in turn, is anticipated by the deviation from unitarity of the overlap matrix for sector *i*,  $O^{(i-1,i)}$ : let  $N^{\text{sec}} = \min(N^{\text{sec}}_{i-1}, N^{\text{sec}}_i)$  be the minimum number of channels in sectors i - 1 and *i*. Then, if  $N^{\text{sec}}_i > N^{\text{sec}}_{i-1}$ ,

$$\bar{q} = \frac{1}{N^{\text{sec}}} \sum_{n=1}^{N^{\text{sec}}} \sum_{j=1}^{N^{\text{sec}}_{j}} (O_{nj}^{(i-1,i)})^{2}$$
(22)

<sup>&</sup>lt;sup>†</sup> This puts some restriction on the distribution of the  $\rho_i$  values and the equations should be rewritten if arbitrary  $\rho_i$  are needed, *e.g.* when avoided crossings are traced.

and in the other case

$$\bar{q} = \frac{1}{N^{\text{sec}}} \sum_{n=1}^{N^{\text{sec}}} \sum_{j=1}^{N^{\text{sec}}} (O_{jn}^{(i-1,i)})^2.$$
(23)

The value  $\rho_{i+1}$  results from

$$\rho_{i+1} = \rho_i + (\rho_i - \rho_{i-1})\bar{q}, \qquad (24)$$

where we impose additional constraints to avoid a rapid growth/shrinking:

$$\begin{split} \bar{q} &\leq \min \bigg( \frac{\text{stpmax}}{\rho_i - \rho_{i-1}}, \bar{q}_{\max} \bigg), \\ \bar{q} &\geq \max \bigg( \frac{\text{stpmin}}{\rho_i - \rho_{i-1}}, \bar{q}_{\min} \frac{\Delta \rho_i}{\rho_i - \rho_{i-1}} \bigg). \end{split}$$

The value  $\bar{q}_{\min}$  needs to be chosen to be at least 0.5 to have  $\rho_{i+1}$  outside of the outer boundary of sector *i* (note that  $\Delta \rho_i \neq \rho_i - \rho_{i-1}$  for varying sector sizes).

#### D. Wavefunction projection

In the asymptotic region of configuration space, we continue the propagation of the wave function in the specific Jacobi coordinates for reactant ( $\alpha$ ) and product ( $\beta$ ) configurations. For that purpose, the eigenfunctions need to be projected from hyperspherical coordinates onto those in Jacobi coordinates; following the approach described in ref. 47 we obtain the *R*matrix in Jacobi coordinates from the one in hyperspherical coordinates by

$$\boldsymbol{R}_{ja} = (\boldsymbol{I}^{(1)}\boldsymbol{B}_{M} + \boldsymbol{I}^{(2)})(\boldsymbol{I}^{(3)}\boldsymbol{B}_{M} + \boldsymbol{I}^{(4)})^{-1}, \qquad (25)$$

where  $B_{\rm M}$  describes the "propagation" of the hyperspherical *R*-matrix  $R_{\rm hyp}$  to the outer boundary  $\rho_{\rm M}^+$  of the sector centered at hyperradius  $\rho_{\rm M}$ ,

$$\boldsymbol{B}_{\rm M} = [\boldsymbol{t}^{(1)}(\rho_{\rm M}^{+}) - \boldsymbol{R}_{\rm hyp}(\boldsymbol{t}^{(1)})'(\rho_{\rm M}^{+})]^{-1}[\boldsymbol{R}_{\rm hyp}(\boldsymbol{t}^{(2)})'(\rho_{\rm M}^{+}) - \boldsymbol{t}^{(2)}(\rho_{\rm M}^{+})]$$
(26)

with the diagonal matrices  $t^{(1)}$  and  $t^{(2)}$  defined by ( $\tau = 1,2$ )

$$t_{ij}^{(\tau)}(\rho) = \begin{cases} \delta_{ij} f_{\tau}^{\text{op}}(k_i(\rho - \rho_{\rm M})) & \text{channel } i \text{ open} \\ \delta_{ij} f_{\tau}^{\text{cl}}(k_i(\rho - \rho_{\rm M})) & \text{channel } i \text{ closed} \end{cases}$$
(27)

with  $f_1^{\text{op}}$ : = sin,  $f_1^{\text{cl}}$ : = sinh,  $f_2^{\text{op}}$ : = cos and  $f_2^{\text{cl}}$ : = cosh. Note that eqn (26) contains a sign error in ref. 47.

The matrices  $(t^{(\tau)})'$  are the corresponding derivatives with respect to  $\rho$  evaluated at  $\rho_{\rm M}^+$ . As usual, the wavenumber  $k_i$  is given by

$$k_i = \hbar^{-1} (2\mu (E - \varepsilon_i))^{1/2}$$
(28)

for internal state *i* (with  $\varepsilon_i$  being the eigenvalue of the surface Hamiltonian). The block-diagonal matrices  $I^{(n)}$ , n = 1, ..., 4,

$$\boldsymbol{I}^{(n)} = \begin{pmatrix} \boldsymbol{I}_{\alpha}^{(n)} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{I}_{\beta}^{(n)} \end{pmatrix}$$
(29)

with integrals ( $\tau = 1,2$ )

$$\left[\boldsymbol{I}_{\alpha}^{(\tau)}\right]_{ij} = \int_{0}^{\infty} \int_{0}^{\pi} F_{i}(r,\gamma) \rho^{-1/2} t_{jj}^{(\tau)}(\rho) H_{j}(\delta,\gamma) \sin \gamma \, \mathrm{d}\gamma \, \mathrm{d}r,$$

$$\begin{bmatrix} \boldsymbol{I}_{\alpha}^{(\tau+2)} \end{bmatrix}_{ij} = \int_{0}^{\infty} \int_{0}^{\pi} F_{i}(r,\gamma) \rho^{-1/2} \left( \left( t_{jj}^{(\tau)} \right)'(\rho) H_{j}(\delta,\gamma) \cos \delta \right. \\ \left. - \rho^{-1} t_{jj}^{(\tau)}(\rho) \frac{\partial}{\partial \delta} H_{j}(\delta,\gamma) \sin \delta \right) \sin \gamma d\gamma dr$$

with analogous equations for the  $\beta$  channel give the overlap of the hyperspherical,  $F_i(r,\gamma)$ , and Jacobi surface functions,  $H_j(\delta,\gamma)$ . The integrals are calculated at a value  $R_M$  obtained from  $\rho_M$  and an average value of  $\delta$ . Employing these equations within the *R*-matrix propagation scheme is not straightforward as the integrations are energy dependent, thus re-introducing all degrees of freedom considered to the otherwise one-dimensional *R*-matrix propagation. Both functions  $H_j(\delta,\gamma)$  and  $\frac{\partial}{\partial \delta}H_j(\delta,\gamma)$  are expressed in the potential-optimized discrete variable representation (PODVR) basis of the Jacobi surface functions  $F_i(r,\gamma)$ . The computation of the integrals is then reduced to matrix–matrix multiplications in that basis (after multiplication with the additional factors in each of the integrals).

While handling the  $\gamma$  coordinate is straightforward, the transformation of the surface functions from  $\delta$  to *r* needs more consideration. The underlying PODVR basis functions in  $\delta$  can be expressed in the Jacobi coordinate *r* as

$$\Phi_i^{\text{hyp}}(r_j) = \left(\frac{\Delta r}{\Delta \delta}\right)^{1/2} \sum_{k=1}^{N_{\delta}} \Phi_i^{\text{hyp}}(\delta_k) \text{sinc}(\pi(\delta(r_j) - \delta_k)) \quad (30)$$

where  $r_j = r_{\min} + j\Delta r$  and  $\delta_k = \delta_{\min} + k\Delta\delta$  are the values of rand  $\delta$ , respectively, corresponding to the sinc-DVR-basis. The overlap matrix elements with the PODVR basis functions  $\Phi_i^{ja}(r_j)$  in the Jacobi coordinate setting can then be computed which in turn transform each  $H_j(\delta,\gamma)$  and  $\frac{\partial}{\partial\delta}H_j(\delta,\gamma)$  to the basis in which the  $F_i(r,\gamma)$  are described. To compute the derivate  $\frac{\partial}{\partial\delta}H_j(\delta,\gamma)$  we make use of the sinc-DVR-derivative operator

$$\boldsymbol{D}_{ij} = \begin{cases} \frac{(-1)^{i-j}}{(i-j)\Delta\delta} & i \neq j\\ 0 & \text{otherwise,} \end{cases}$$
(31)

which, after transformation into the PODVR-basis, can be applied to each of the  $H_i(\delta, \gamma)$  to yield  $\frac{\partial}{\partial \delta} H_i(\delta, \gamma)$ .

The projection onto Jacobi coordinates is very difficult at an arbitrary value of the hyperradius  $\rho$  because the eigenfunctions in the two coordinate systems will deviate too much for small values of  $\rho$ . The projection scheme presented above requires the same number of surface functions in both coordinate systems and the matrices  $I^{(n)}$  close to their asymptotic values  $(I^{(1)} \rightarrow 0, I^{(2)} \rightarrow 1, I^{(3)} \rightarrow k, I^{(4)} \rightarrow 0$ , where 0 and 1 are the zero and unit matrix, respectively, and k is the diagonal matrix with entries  $\delta_{ij} k_i$ ) to obtain a sufficiently symmetric  $R_{ja}$ . Apart from symmetrization of  $R_{ja}$ , we need to project at a sufficiently large value of  $\rho$  and, for that purpose, check for overlap of the vector spaces spanned by the two sets of surface functions: if

$$\boldsymbol{\mathcal{Q}}_{ij} = \int_0^\infty \int_0^\pi F_i(r, \gamma) H_j(\delta, \gamma) \sin \gamma \, \mathrm{d}\gamma \, \mathrm{d}r \tag{32}$$

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defines the intrasector overlap matrix, we demand

$$R_{\mathrm{M}}^{-1}(\boldsymbol{Q}\boldsymbol{Q}^{\dagger})_{ii}/(\boldsymbol{Q}\boldsymbol{Q}^{\dagger})_{11} - 1| \leq \varepsilon_{\mathrm{hypjac}}$$
(33)

with  $R_{\rm M}^{-1}$  accounting for the change of the integration variable and  $(\mathbf{Q}\mathbf{Q}^{\dagger})_{11}$  for a common offset. Jacobi eigenfunctions are computed until the asymptotic configuration is reached. This requires all states to be assigned a rotational quantum number *j*. Surface functions are therefore computed until for each *i* 

$$\int_{0}^{\infty} \left(F_{i}(r, j_{i})\right)^{2} \mathrm{d}r \geq 1 - \varepsilon_{\mathrm{asym}}$$
(34)

for a given rotational quantum number  $j_i$ . Here,  $F_i(r,j_i)$  denotes the Jacobi surface function  $F_i(r,\gamma)$  transformed into the variational basis representation (VBR) of the Legendre polynomials.

# E. Differential reaction cross sections

Inserting eqn (12) in the propagation algorithm of the J = 0 wave functions and employing the proper (*J*-dependent) boundary conditions, we finally obtain state resolved, energyand total angular momentum-dependent *S*-matrices  $S_{nm}^{J}(E)$ . State-resolved differential cross sections for vanishing helicity can then be computed by the usual formula

$$\frac{\mathrm{d}\sigma_{nm}}{\mathrm{d}\Omega}(E,\theta) = \frac{1}{4k_n^2} \left| \sum_{J=0}^{\infty} \left( 2J + 1 \right) S_{nm}^J(E) P_J(\cos(\theta)) \right|^2, \quad (35)$$

with  $k_n$  being the wavenumber of the initial state and  $P_J$  the Legendre polynomial of order J. Here,  $\theta = 0$  denotes forward scattering, and  $\theta = \pi$  corresponds to backward scattering. In a numerical calculation, this sum needs to be cut off at a value  $J_{\text{max}}$  which is chosen to be large enough to include all significant contributions to this sum. In practice, we select the total reaction probability  $P_{\text{tot}}^J(E) = \sum_{n,m} P_{nm}^J(E)$  as a reference and terminated the summation when  $P_{\text{tot}}^J(E)$ dropped to a negligible value in comparison with the J = 0total reaction probability:

$$J_{\max} = \min\{J: P_{\text{tot}}^{J}(E) \le \varepsilon_{\text{sum}} P_{\text{tot}}^{J=0}(E)\}.$$
 (36)

# F. Numerical parameters

We used the same parameters as employed in ref. 31. The cutoff criterion for the summation of the total angular momenta was set to  $\varepsilon_{sum} = 10^{-8}$ . State-resolved differential cross sections have been computed at energies  $E_{dif} = 350$ , 850, 1400 and 1900 cm<sup>-1</sup>; to smoothen the many fluctuations that are characteristic for this type of reaction, for each energy  $E_{dif}$ , differential cross sections were actually computed at 21 equidistant values  $E_{dif} - 1.0 \text{ cm}^{-1}$ ,  $E_{dif} - 0.9 \text{ cm}^{-1}$ , ...,  $E_{dif} + 1.0 \text{ cm}^{-1}$ and then averaged.

As in our previous work on rotational effects,<sup>31</sup> we employ the analytical potential energy surface proposed by Wang, Zhu and Hase.<sup>49</sup>

# III. Results and discussion

#### A. Differential reaction cross sections

In Fig. 1–4, the initial-state selected differential reaction cross sections are graphically displayed. They are summed over all



**Fig. 1** Differential reaction cross sections for the reaction  $\text{Cl}^- + \text{CH}_3\text{Br}(v,j) \rightarrow \text{ClCH}_3 + \text{Br}^-$ , for different initial rovibrational states (v,j), summed over all product states, at total energy 350 cm<sup>-1</sup>.



**Fig. 2** Differential reaction cross sections for the reaction  $\text{Cl}^- + \text{CH}_3\text{Br}(v,j) \rightarrow \text{ClCH}_3 + \text{Br}^-$ , for different initial rovibrational states (v,j), summed over all product states, at total energy 850 cm<sup>-1</sup>.

product states for total energies  $E_{tot}$  of 350, 850, 1400 and 1900 cm<sup>-1</sup>. Shown is  $\sin(\theta)(d\sigma/d\Omega)(E_{tot})$  which is the integrand for the total cross section  $\sigma_{tot}(E_{tot})$ . Thus, the contributions to  $\sigma_{tot}$  become visible. Consequently, the data for  $\theta = 0$  and  $\theta = 180^{\circ}$  are exactly zero, as long as the differential cross section remains finite. However this cannot be seen in the plots, first because this occurs only at these two exact angles and second because of data averaging. The data are smoothly averaged over intervals of 5° (for  $E_{tot} = 350 \text{ cm}^{-1}$ ) and 10° (for all other energies), each with the exception of 0 and 180°. Forward scattering corresponds to  $\theta = 0$ , while backward scattering is associated with  $\theta = 180^{\circ}$ . The finer averaging intervals in the case of 350 cm<sup>-1</sup> are due to the fact that the cross sections are very isotropic here.

Fig. 1 shows the differential reaction cross sections for a total energy of 350 cm<sup>-1</sup> and different initial rotational excitations (v = 0; j = 0, ..., 4). At this small energy, it can be seen clearly that  $(d\sigma/d\Omega)\sin(\theta)$  increases with *j* and becomes increasingly more isotropic. Many oscillations typical of resonance features can be observed. Here, the increasing cross sections with *j* can be traced back mainly to an energetic effect. Rotationally excited initial states are higher in energy, and



**Fig. 3** Differential reaction cross sections for the reaction  $Cl^- + CH_3Br(v,j) \rightarrow ClCH_3 + Br^-$ , for different initial rovibrational states (v,j), summed over all product states, at total energy 1400 cm<sup>-1</sup>. Top: rotational excitation only; bottom: one quantum in the C–Br stretching mode.

thus have – at a given total energy – less translational energy which, however, enters the equation for the calculation of the cross section (see eqn (35)) in the denominator. Only for the initial state (0, 0) and (0, 2), back scattering is slightly less effective. A remarkable observation is that the differential cross sections for (0, 2) are below that for (0, 1). This is the result from two contrary effects, the increase of the reactivity with the energy of the initial level and a decrease with rotational excitation (see below). Note that the ordinate in Fig. 1 starts at 3.0  $a^2$  sterad<sup>-1</sup>.

In agreement with our previous results,<sup>30</sup> the cross sections are largest for small energies.<sup>30</sup> At higher total energies (850 cm<sup>-1</sup>, Fig. 2), the (0, 0) differential cross section shows a similar behaviour (back scattering is slightly less probable), and the average differential cross section has become smaller by a factor roughly of two. Also, the oscillations in the differential cross sections are less pronounced. For initial rotational excitation (shown are angular momentum quantum numbers j = 1, 2, 3, 10, 20, 30), the differential cross sections decrease and become more isotropic, so that for the highest *j*-states shown (20 and 30) almost no anisotropy can be observed. Isotropic cross sections point to the existence of long-living resonance states which cause that the correlation with the initial angle disappears.



**Fig. 4** Differential reaction cross sections for the reaction  $Cl^- + CH_3Br(v,j) \rightarrow ClCH_3 + Br^-$ , for different initial rovibrational states (v,j), summed over all product states, at total energy 1900 cm<sup>-1</sup>. Top: rotational excitation only; middle: one quantum in the C–Br stretching mode; bottom: two quanta in the C–Br stretching mode.

For even higher total energy (Fig. 3, top panel),  $1400 \text{ cm}^{-1}$ , a similar trend can be observed. However, the coarse oscillations for (0, 0) are again more pronounced. Fig. 3 (bottom panel) shows the same for additional initial vibrational excitation, which is possible at this given total energy. The differential cross sections increase as expected from our previous studies,<sup>30</sup> while the behaviour with respect to angular excitation remains as before (note the scaling). The dip for backward scattering becomes more pronounced and the oscillations are coarser.

Again, for energies of 1900 cm<sup>-1</sup> (Fig. 4), the differential cross sections tend to be more isotropic for larger values of *j*. The initial state (0, 0) becomes more and more interesting: the peak for backward scattering ( $\theta = 180^{\circ}$ ) is only one-third as high as the maximum value which found in the range between 100 and 160°. The features become even coarser and the typical resonance structure is lost. Additional vibrational excitation shifts this range to 90–140° with backward scattering less than one-third of the maximum cross section. Two quanta in the vibrational mode cause a further shift down to 80–115°.

The state-dependent peak relation  $((d\sigma/d\Omega)(0)/(d\sigma/d\Omega)(\pi))$ is shown in Fig. 5. The peaks for forward and backward scattering are not contained in the data sets presented above because  $\sin(0) = 0 = \sin(\pi)$ . A general slight preference for forward scattering can be observed. Initial states with small *j* show a considerably larger forward peak. The other oscillations are due to nearly closed channels, *i.e.* small translational energies. Other reaction channels show up at higher energies, in agreement with recent results by Wester *et al.*<sup>24</sup>

How can the calculated behaviour of the differential reaction cross sections be explained? The isotropy for large *i*-values can be rationalized by a simple classical-mechanical argument. If the target molecule is fastly rotating, all directions for dissociation of the intermediate complex are possible and equally probable. If the lifetime of the complex is long enough (i.e. if the resonance is narrow), it can carry out several rotations before the products break apart, and no direction is favoured. The smaller cross sections for backward scattering, however, need to be considered separately. In our previous collinear studies,<sup>28–30</sup> backward scattering was the only possible event. The chloride anion hits the centre of the methyl group, forms a bond to the carbon atom, and after the umbrella flip of the hydrogen atoms the CH<sub>3</sub>Cl moiety bounces back to the direction where the chloride ion came from. This direction is disfavoured in the full three-dimensional picture. Here, the chlorine anion approaches the CH<sub>3</sub>Br molecule off from the collinear axis. Due to the strong ion-dipole interaction a torque is exerted onto the molecule, and it begins to carry

out a rotation. However, due to the potential, no full rotational cycle is performed, and an angle of about  $90^{\circ}$  seems most probable. This explains why exact backward scattering is such a disfavoured event, the strong electrostatic forces are responsible for the differential cross sections in the cases without initial rotational excitation.

#### B. Product distributions

To display the product distribution for a given initial rovibrational state it appears to be convenient to use velocity maps that come out of an experiment,<sup>24</sup> so that our results can thus directly be compared to the results of dynamical measurements.

In Fig. 6 and 7 the velocity of the product bromide anions in the centre-of-mass system is graphically displayed. The centre of each image denotes zero velocity in the centre-of-mass frame. The circles represent constant product velocities with the largest circle showing the maximum possible product velocity based on the known total energy in the reaction system. Thus, each concentric circle corresponds to a product quantum state with a well-defined energy. The translational energy and the speed are constant on each circle. Along the circles, the colours indicate the percentage amount (with respect to the total cross section at the respective initial state), with a threshold value of  $10^{-5}$  (ref. 24). The diagrams are symmetric with respect to the axis  $v_y = 0$ . Forward scattering corresponds to the left-hand side, backward scattering to the right-hand side of the diagrams.

In Fig. 6, the initial state (0, 0) is considered at total energies of  $E = 350 \text{ cm}^{-1}$  (A),  $E = 850 \text{ cm}^{-1}$  (B) and  $E = 1400 \text{ cm}^{-1}$ (C). In case (A) one state close to the energetic limit is populated, corresponding to the small circle (low translational energy). For the higher energy (B), the radii of the circles become larger because more translational energy is available. The final states are energetically close to the reactant state, in agreement with our previous findings; thus, no further inner circles show up. When the total energy is increased, the circles are narrowing, showing that less energy is transferred to rotational excitation. In panel (D), the initial state is vibrationally excited, (1, 0), at  $E = 1400 \text{ cm}^{-1}$ . Two circles (*i.e.*, different vibrational product states) display a significant anisotropy in the differential cross section (cf. Fig. 4), corresponding to the overall anisotropic cross section. It is remarkable that the two product vibrational states show a different forward scattering behaviour.

Fig. 7 contains velocity maps at a total energy of  $E = 1900 \text{ cm}^{-1}$ , for the initial ground state (0, 0) (E) and two vibrationally excited states, (1, 0) (F) and (2, 0) (G). Moreover, Fig. 7 contains – at the same total energy – two rotationally excited states, (0, 3) (H) and (0, 65) (I), as well as one highly rovibrationally excited state (2, 25) (J). Again, when the reactants are not rotationally excited, the products are close to their rotational ground state (narrow circles) and display a remarkable anisotropy. Initial rotational excitation, in contrast, leads to a broad distribution of angular momenta in the products (broad circles) and isotropic scattering. These findings agree well with the considerations from the previous section: with high initial rotational excitation, long-lived

and backward ( $\theta = 180^{\circ}$ ) scattering





Fig. 6 Velocity maps for the Br<sup>-</sup> product ion in the reaction Cl<sup>-</sup> + CH<sub>3</sub>Br (v,j)  $\rightarrow$  ClCH<sub>3</sub> + Br<sup>-</sup> at different total energies and for selected initial rovibrational states (v,j). Colours indicate the relative amount in the differential cross sections. A:  $E = 350 \text{ cm}^{-1}$ , (0,0); B:  $E = 850 \text{ cm}^{-1}$ , (0,0); C:  $E = 1400 \text{ cm}^{-1}$ , (0,0); D:  $E = 1400 \text{ cm}^{-1}$ , (1,0).

intermediate complexes lead to the final direction of the products being almost independent from the initial direction. When the reactants are not rotationally excited, the chlorine anion exerts a torque on the CH<sub>3</sub>Br molecule, causing a partial rotation and favouring scattering angles from  $100^{\circ}$  to  $160^{\circ}$ .

For a comparison, in Fig. 8(A) the corresponding most pronounced circles resulting out of the initial ground state (0,0) are displayed separately. At the two lowest energies, 350 and 850 cm<sup>-1</sup>, strong oscillations are observed, while no clear trend is seen. For E = 1400 cm<sup>-1</sup> a weak decrease towards backward scattering is discernible, while for E = 1900 cm<sup>-1</sup> we find a strongly favoured scattering into the backward direction. Fig. 8(B) shows the same results for vibrationally excited initial states, (1, 0) at 1400 and 1900 cm<sup>-1</sup> and (2, 0) at 1900 cm<sup>-1</sup>.

With their ion-molecule crossed-beam imaging spectrometer Wester *et al.* studied the  $S_N$ 2-reaction of  $Cl^- + CH_3I$  at relative scattering energies between 0.4 and 2 eV<sup>24</sup> and obtained cross-sections in the centre-of-mass frame for various relative energies. At 0.39 eV, isotropic scattering of the  $I^-$  product ions is observed, which indicates an indirect reaction involving long-living complexes. Much of the available energy is used to excite internal modes of the CH<sub>3</sub>Cl product. This is in good agreement with our computational results. In contrast, at 1.9 eV the I<sup>-</sup> ions are scattered preferentially backward with respect to the incoming CH<sub>3</sub>I, with a velocity close to the maximum possible value.<sup>24</sup> This can be rationalized by a fast and direct reaction mechanism where the I<sup>-</sup> ion leaves the reaction approximately collinearly with the incoming Cl<sup>-</sup> anion. While most of the flux indicates this direct scattering with large product velocities, also small product velocities both forward and backward scattered are observed which are explained by an indirect 'roundabout' mechanism. Wester *et al.* could explain this behaviour by means of classical trajectory calculations.<sup>24</sup>

The aim of our future theoretical studies is to extend the underlying potential surfaces and perform quantum scattering calculations that take into account both the direct mechanism at higher energies as well as the postulated roundabout



Fig. 7 Velocity maps for the Br<sup>-</sup> product ion in the reaction Cl<sup>-</sup> + CH<sub>3</sub>Br (v,j)  $\rightarrow$  ClCH<sub>3</sub> + Br<sup>-</sup> at different total energies and for selected initial rovibrational states (v,j). Colours indicate the relative amount in the differential cross sections. E:  $E = 1900 \text{ cm}^{-1}$ , (0,0); F:  $E = 1900 \text{ cm}^{-1}$ , (1,0); G:  $E = 1900 \text{ cm}^{-1}$ , (2,0); H:  $E = 1900 \text{ cm}^{-1}$ , (0,3); I:  $E = 1900 \text{ cm}^{-1}$ , (0,65); J:  $E = 1900 \text{ cm}^{-1}$ , (2,25).





**Fig. 8** Product distributions for some of the most prominent states (*i.e.* circles) in Fig. 6 and 7.

pathway. Another promising experimental approach could be to use molecular traps, allowing for the study of chemical reactions at ultracold temperatures.<sup>50</sup>

# IV. Conclusions

We have calculated quantum-mechanical differential reaction cross sections for the nucleophilic bimolecular reaction Cl<sup>-</sup> + CH<sub>3</sub>Br  $\rightarrow$  ClCH<sub>3</sub> + Br<sup>-</sup>. The results show almost isotropic cross sections for high rotational quantum numbers of the reactant molecule. Backward scattering is disfavoured for reaction out of the rovibrational ground state and out of states with small rotational excitation. This is a quantummechanical effect (interference of partial waves) that can partly be rationalized by simple classical-mechanical arguments. In particular for higher vibrational excitations, an umbrella effect can be observed, that favours the backward direction. It can be explained by the strong enhancement of the reaction by opening up a direct mechanism. The ion-dipole interaction exerts a torque onto the molecule which rotates it by about 90° and then completes the reaction.

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