A quasiclassical trajectory study of the heavy–light–heavy ClHCl and IHI reactions: Do three-dimensional partial cross sections oscillate as a function of energy?

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In this work we examined the possibility that characteristic heavy–light–heavy collinear oscillatory behavior of the reactive probability functions will also be apparent in three-dimensional partial cross sections. The study was carried out using the quasiclassical trajectory method for ClHCl and IHI. For this study the DIM-3C potential energy surfaces were employed. It was found that whereas in general the collinear features were reproduced in three dimensions, the prospects for them to be detected experimentally exist for only part of them.

I. INTRODUCTION

The heavy–light–heavy type reactions recently became a subject of major interest for various reasons, but the most intriguing one is the prospect of detecting characteristic energy-dependent oscillations for integral or differential cross sections. So far, none of the experimental studies or the three-dimensional quasiclassical trajectory (QCT) calculations ever revealed any particular structure for these functions other than monotonic behavior.

The heavy–light–heavy type systems are known to follow approximately, during an exchange process, certain physical laws, such as conservation of translational energy and orbital angular momentum. However, a novel feature was discovered in collinear calculations, namely, highly oscillatory reactive transition probability functions with the oscillation covering the whole available range between 0 and 1. This finding caused speculation whether this oscillatory behavior is strong enough to show up in some way also in three dimensions, so that it can be detected experimentally. First positive indications for this possibility were obtained in a reactive infinite or sudden approximation (RIOSA) study carried out for the Cl + HCl → HCl + Cl' reaction. It was found that whereas these oscillations were smoothed out in the calculation of integral cross sections, they were apparent when differential cross sections at certain angles were presented as a function of energy. However, due to its complexity this study was carried out for the threshold region only, i.e., \( E_\text{tot} = 0.32 - 0.40 \text{ eV} \) (in the tunnelling region). It was not clear whether this feature would show up at all or whether it would be strong enough at higher energy where the cross sections are also much larger.

Following this study, the present authors conducted a collinear and a three-dimensional QCT study for this system along a relatively large translational energy range, i.e., \( 0.3 < E_\text{r} < 2.0 \text{ eV} \). Again, the integral cross sections did not exhibit any of this oscillatory behavior but partial cross sections within the range of \( 0 < \theta < \pi \) showed an unusually deep minimum around \( E_\text{r} = 1.0 \text{ eV} \).

In this work, we extended this study to another heavy–light–heavy thermoneutral system, i.e., \( I + HI \rightarrow HI + I' \). The main purpose of the present work was to find out whether this unique structure can be detected in the laboratory. For this purpose we not only used the most up-to-date potentials to carry out the calculations but we also studied the sensitivity of these findings with respect to initial rotational states and angular range.

In Sec. II we describe the potentials employed in the calculations, in Sec. III results for the two heavy–light–heavy (HLH) systems are given, the sensitivity study is described in Sec. IV and conclusions are summarized in Sec. V.

II. THE POTENTIAL ENERGY SURFACE

To carry out the QCT calculations we used the DIM-3C potential constructed a few years ago for a hydrogen and two halogens. The DIM-3C method is an extension of the DIM method to which the missing three-center terms are added explicitly following the solution of the DIM eigenvalues. Thus

\[
E_\text{3D} = E_\text{DIM} + W_\text{SC},
\]

where \( E_\text{DIM} \) is the DIM (lowest) eigenvalue, \( W_\text{SC} \) is the three-center term and \( E_\text{3D} \) is the final three-dimensional energy surface. It was thus possible not only to obtain a correct description of all arrangement channels of a given system but also, by determining three adjustable parameters, to obtain the most up-to-date features of 17 different reactions including both abstraction and exchange reactions.

The main disadvantage in employing the DIM potential for QCT calculations is the complicated expression and the time consuming computations needed for both the potentials and the various derivatives. Therefore, one of the tasks we undertook before going into the actual study was to fit the DIM potential to an analytic expression from which one could easily get both the potential and the corresponding derivatives.

The representation we are suggesting is

\[
E_\text{DIM} = E_\text{LEP} + F,
\]

where \( E_\text{LEP} \) is the well known LEP potential which is identical to \( E_\text{DIM} \) for collinear arrangements and \( F \) is a bend potential which is novel and therefore will be described here to some extent (for more details see Ref. 17).

Substituting Eq. (2) in Eq. (1) yields the equation of the
potential as it is used in this work, namely:

$$E_{3D} = E_{\text{LEP}} + W_{3C} + F.$$  (3)

Since the expressions for $E_{\text{LEP}}$ (and for $W_{3C}$) and for the corresponding derivations are relatively simple this choice fulfills our requirements and we are left with the problem of determining $F$.

The bend potential $F$ is assumed to be zero for all collinear configurations because for these the $E_{\text{DIM}}$ potential coincides with the $E_{\text{LEP}}$ potential. For $F$ we assume a certain analytic expression with a few free parameters which will be determined in such a way that $E_{\text{LEP}} + F$ will best fit $E_{\text{DIM}}$. Thus $F$ will be written as

$$F = \sum_{j=1}^{n} C_j Z_j,$$  (4)

where $Z_j$ are functions of interatomic distances and $C_j$ are coefficients to be determined by a least squares fit. $Z_j$ have to be equal to zero in the collinear arrangement and in all asymptotic regions. The $Z_j$ were taken as

$$Z_j = Y^n Y^l S,$$  (5)

$$n = 3, 4, \ldots, N,$$

$$l = 2, 3, \ldots, n - 1,$$

$$k = 1, 2, \ldots, l = 1,$$

where

$$Y_i = R_i + R_k - R_i,$$

$$i_1 \neq i_2 \neq i_3, i_1, i_2, i_3 = 1, 2, 3,$$  (7)

and

$$S = \exp \left[ - (\alpha_1 R_1 + \alpha_2 R_2 + \alpha_3 R_3) \right].$$  (8)

Here $N$ is the maximal power of the $Y$ functions in Eq. (5), and $\alpha_i$ ($i = 1, 2, 3$) are coefficients which are determined by trial and error. The important feature of $Z_j$ (and therefore also of $F$) is not only that they become zero in the various collinear arrangements but that they also behave in the vicinity of the collinear arrangements as $\sin^2 \chi$, where $\chi$ is the bend angle [Fig. 1(a)]. Due to the exponential function (8), the functions $Z_j$ decrease to zero when one of the atoms is shifted to infinity.

The potential energy surfaces calculated by the analytical expression (3) with the sum of the power series $F$ will be called LEP-3C-PS (London–Eyring–Polanyi + 3 center + power series). We shall not go into detail concerning the actual fitting calculations for HCl$_2$ and HI$_2$ since they have been described elsewhere. However in order to indicate the quality of the fit we list in Table I the LEP-3C-PS barriers and the corresponding interatomic distances for certain CIHCl and IHI configurations.

III. RESULTS

In this work we are interested in finding out whether the collinear oscillations will also show up in three-dimensional measurable quantities. It is not likely that that will happen for integral cross sections and therefore we decided to consider the partial cross sections.

Collinear reactive QCT always result in a center-of-mass scattering angle $\theta = \pi$. Therefore it seems reasonable to study the energy dependence of partial cross sections in the vicinity of, i.e., $0 < \theta < \pi$:

$$\sigma(E_i; \theta_0) = \int_{\theta_0}^{\pi} d\theta \int_{\theta_0}^{\pi} d\varphi \frac{d\omega}{d\Omega} \sin \theta,$$  (9)

where $\theta$ and $\varphi$ are the spherical center of mass scattering angles, $d\Omega$ is the solid angle, and $E_i$ is the translational energy. To derive $\sigma(E_i; \theta_0)$ employing QCT could be a time consuming process. However, it is known that in order to obtain collinear behavior, a necessary (but not sufficient) condition is the imposition of the value zero for $\eta$ [see Fig. 1(b)], defined as the angle between the molecular axis and the asymptotic direction of motion, and for the impact parameter $b$. Thus, the partial cross section $\sigma(E_i; \theta_0)$ can be presented as

$$\sigma(E_i, \theta_0) = \frac{1}{2} \pi b_{\theta_0}^2 \int_{\eta_{\theta_0}}^{\pi} d\eta \sin \eta P(\eta, E_i; \theta_0),$$  (10)

where $\eta_{\theta_0}$ and $b_{\theta_0}$ are the largest $\eta$ and $b$ values, respectively, for which a center-of-mass scattering $\theta$ in the range $\theta_0 < \theta < \pi$ is obtained and $P(\eta, E_i; \theta_0)$ is the reactive probability defined as

| TABLE I. The DIM-3C and LEP-3C-PS saddle point coordinate $R_{\text{HX}}$ (Å) and potential barrier $E_b$ (eV) for HXH arrangement [Fig. 1(a)]. |
|---|---|---|---|
|   | DIM-3C |   | LEP-3C-PS |
|   | $X$ | $R_{\text{HX}}$ | $E_b$ | $R_{\text{HX}}$ | $E_b$ |
| CIHCl |   |   |   |   |   |
| 0° | 1.51 | 0.36 | 1.51 | 0.36 |
| 30° | 1.52 | 0.41 | 1.52 | 0.40 |
| 60° | 1.54 | 0.64 | 1.53 | 0.66 |
| 90° | 1.67 | 1.64 | 1.66 | 1.63 |
| IHI |   |   |   |   |   |
| 0° | 1.84 | 0.14 | 1.84 | 0.14 |
| 30° | 1.85 | 0.21 | 1.85 | 0.20 |
| 60° | 1.91 | 0.54 | 1.91 | 0.55 |
| 90° | 2.12 | 1.56 | 2.11 | 1.54 |
\[ P(\eta, E; \theta_0) = n(\eta, E; \theta_0)/N(\eta, E). \]  
(11)

Here, \( N(\eta, E) \) is the total number of trajectories calculated for given values of and \( E \), and \( n(\eta, E; \theta_0) \) is the number of reactive trajectories for which the center-of-mass scattering angle \( \theta \) is in the range \( \theta_0 < \theta < \pi \).

Expression (10) was employed to calculate the Cl + HCl partial cross section. The I + HI partial cross section was calculated for the whole range of the orientation angle \( (0 < \eta < \pi) \), i.e., by using the expression

\[ \sigma(E; \theta_0) = \pi b^2 \rho n(E; \theta_0)/N(E), \]  
(12)

where \( N(E) \) is the total number of trajectories for a given translational energy \( E \), and impact parameter \( b < b_0 \), and \( n(E, \theta_0) \) is the number of reactive trajectories with the scattering angle in the range \( \theta_0 < \theta < \pi \).

Here the study of the \( X + HX \) (\( X = \text{Cl}, \text{I} \)) collisions is restricted to the initial states without HX rotation (\( j = 0 \)). The excited rotational states will be considered in the next section.

Partial integral cross section \( (E, \theta_0 = 160^\circ) \) for both IHI and CIHCl are presented as a function of \( E \), in Fig. 2. In order to see to what extent the collinear behavior is preserved we also derived the collinear probability functions and presented them in the same figures.

The main features to be noticed are the following:

(a) In contrast to what is always expected from energy dependent integral (and even differential) cross sections, the partial cross sections presented here behave in an entirely different way; they are strongly oscillating functions without having, even in general, a well defined trend.

(b) From a comparison with the collinear probability functions, it is noticed that the collinear characteristics were preserved during the transition to three dimensions. The single minimum in the CIHCl case is well reproduced, except that the decrease towards the minimum is not so sharp as in the collinear case. For IHI the collinear probability function possesses, in the studied energy range, two minimum values, one at \( E = 0.2 \) eV and the other at \( E = 0.7 \) eV. Both are well noticed also in \( \sigma(E; 160^\circ) \), except that they seem to have sharper edges and also the position of the second minimum is somewhat shifted towards higher energies (from 0.7 to 0.8 eV).

(c) The minimum cross sections are much smaller than the maximum values. In the CIHCl case the minimum value is 0.02 \( \text{Å}^2 \) vs the maximum value 0.03 \( \text{Å}^2 \) [Fig. 2(a)]. In the IHI case the cross section in the second minimum point \( E = 0.8 \) eV is 0.05 \( \text{Å}^2 \) whereas in the maximum points, around \( E = 0.3 \) and 1.0 eV the cross sections are 0.095 and 0.08 \( \text{Å}^2 \) [Fig. 2(b)]. The cross section becomes much larger in the low energy region where the maximum value (at \( E = 0.05 \) eV) is as large as 0.18 \( \text{Å}^2 \) (Fig. 3).

(d) As far as the prospect for experimental detection of these minimum values is concerned it seems that the IHI system is more promising, not only because the minimum values are more pronounced in this case but also because all cross sections are more than twice as large as in the CIHCl case.

(e) There is of course the question whether these oscillations are real and not due to statistical sampling. The

![FIG. 2. Three dimensional partial cross sections, \( \sigma(E; \theta_0 = 160^\circ) \), and collinear probability as a function of translational energy for the heavy–light–heavy system. (The error bars stand for one standard deviation.) O, three-dimensional results, - - - , collinear results. (a) Cl + HCl' \rightarrow HCl + Cl'; (b) I + HI' \rightarrow HI + I'.](image)

![FIG. 3. Partial and integral cross sections for the IHI reactive system as a function of translational energy: \( \Phi, \sigma(E; \theta_0 = 160^\circ); \sigma(E; \theta_0 = 150^\circ); O, \sigma(E; \theta_0 = 140^\circ); \) (note scale on the left-hand side); \( \Delta, \sigma(E; \theta_0 = 100^\circ); \) (note scale on the right-hand side).](image)
strongest evidence for them being real is given in case of CIHCl in Fig. 2(a), where the error bars are significantly smaller than the amplitude of the oscillation. A less convincing situation is encountered for IHI in Fig. 2(b). However the error bars associated with the two maxima at $E_t = 0.3$ and 1.0 eV and the one with the maximum value at $E_t = 0.8$ eV are well separated and do not mask the real oscillation.

The sensitivity of the oscillations with respect to variations in $\theta_0$ is studied for the IHI system in Fig. 3. Here are presented the partial cross sections $\sigma(E_t; \theta_0)$ for three values of $\theta_0$, i.e., $\theta_0 = 160^\circ$, $150^\circ$, $140^\circ$, as well as the integral cross section $\sigma(E_t)$ which is equal to $\sigma(E_t; \theta_0 = 0^\circ)$ (the curve $\theta_0 = 160^\circ$ is the same as in Fig. 2 but with two more points in the low energy region). As expected, the $\sigma(E_t; \theta_0)$ increases with $\theta_0$ but simultaneously slowly loses its collinear character. In fact the absolute size of the oscillations increase as $\theta_0$ varies from 160° to 140° but the relative values decrease from 50% at $\theta_0 = 160^\circ$ to 20% at 140°. The integral cross section, as expected, behaves monotonically and is a decreasing function of the energy, after it reaches the maximum at the low energy point $E_t = 0.2$ eV. There are some small oscillations in the integral cross section (as well as in the partial cross section for $\theta_0 = 140^\circ$), however these oscillations do not exceed the statistical error.

The preservation of the collinear behavior in the three-dimensional partial cross section ($E_t; \theta_0 = 160^\circ$) can be explained by the fact that most of the reactive trajectories with the scattering angle $160^\circ < \theta < 180^\circ$ have small initial impact parameters $b$ and orientation angles $\eta$, i.e., the conditions are close to those of the collinear collision ($b = \eta = 0$ in the absence of rotation). This feature of the reactive I + HI trajectories with the scattering angle $160^\circ < \theta < 180^\circ$ is demonstrated by their $b$ and $\eta$ distribution (Fig. 4). The orientation angle distribution [Fig. 4(b)] has a complicated structure. According to this distribution a small number of trajectories which have large initial orientation angles $\eta$ around 90° are separated from the group of trajectories with small orientation angles by an angle gap. For the translational energy interval $E_t = 1.0 - 1.4$ eV this gap extends from 53° to 86°. A similar gap was found also in the CIHCl case. The close-to-collinear character of the reactive trajectory with small $b$ and $\eta$ is demonstrated in Fig. 5 where the time dependence of the interatomic distances is presented. The collinearity of the process is seen (before the exchange takes place namely $R_{IH} < R_{YH}$) from the fact that $R_{IH} + R_{YH} = R_{II}$. This relation does not hold any more once the exchange took place but this fact hardly affects the final outcome.

IV. PROSPECTS FOR EXPERIMENTAL DETECTION OF THE OSCILLATIONS

In order to be able to examine the prospects for experimental detection of collinear oscillations found in the partial cross sections $\sigma(E_t; 160^\circ)$, is it important to have information on their sensitivity to variations in the initial rotational states. In Figs. 6 and 7 are shown $\sigma(E_t; 160^\circ)$ as a function of $E_t$ for different $j$ values. The CIHCl system is shown in Fig. 6 and the IHI in Fig. 7. As for the CIHCl system, the prospects of detecting experimentally the minimum at $E_t = 1.0$ eV are slim, due to the sharp decrease of $\sigma(E_t; 160^\circ)$ for $E_t = 0.4$ eV when $j$ becomes larger than zero. A similar behavior was found for other energy values on the lower energy wing of

**FIG. 4.** Impact parameter $b$ (a) and orientation angle $\eta$ (b) distributions of the partial cross section $\sigma(E_t; \theta_0 = 160^\circ)$. $0.05 \text{ eV} < E_t < 0.2 \text{ eV}$, $0.1 \text{ eV} < E_t < 1.4 \text{ eV}$.

**FIG. 5.** Trajectory of $I^+ + HI \rightarrow HI^+ + I$ reaction as a function of time. Initial parameters: $E_t = 0.5$ eV, $j = 0$, $b = 0.398$ Å. $\eta = 18^\circ$. $I^-I$ distance, $\cdots$ $I^-I$ distance.
the minimum, which leads to a monotonous increase of \( \sigma(E_r; 160^\circ) \) with \( E_r \) for \( j > 1 \) (Fig. 6). Thus unless the rotational temperature of the reagents is close to zero \( (T \sim 10 \text{ K}) \) this minimum will be smoothed out.

As for IHI the situation is much more promising. Although the partial cross section depends on \( j \) in a complicated way the minimum at \( E_r = 0.8 \text{ eV} \) is preserved for any \( j \) value up to \( j = 6 \), at least. Only in the \( j = 10 \) state does this minimum disappear. This implies that the \( E_r = 0.8 \text{ eV} \) minimum is detectable for rotational temperatures \( (\text{of the reagents}) \) which are as high as 300 K. As for the minimum at \( E_r = 0.2 \text{ eV} \) here the situation is somewhat similar to that encountered in the CHCI case but for different reasons. As is seen from Fig. 7 any change in \( j \) from \( j = 0 \) to \( j = 3 \) causes the partial cross section to increase abruptly. Similar behavior was encountered at other energy values in close vicinity to that minimum. Thus, from additional calculations, it was found that this minimum \( (E_r = 0.2 \text{ eV}) \) cannot be detected unless the rotational temperature is less than 5 K.

V. CONCLUSIONS

In this work the energy dependence of the partial cross sections \( \sigma(E_r; \theta_0) \) for the two thermoneutral heavy–light–heavy CHCI and IHI systems was studied in the (translational) energy range \( 0.05 \text{ eV} < E_r < 1.8 \text{ eV} \). The study centered on the possible extension of the characteristic collinear oscillatory reactive probability function to three dimensions. Indeed we found that these oscillations were reproduced when considering \( \sigma(E_r; \theta_0) \) with \( \pi > \theta_0 > 160^\circ \). In the studied energy range, one oscillation was found for CHCI with the minimum position at \( E_r = 1.0 \text{ eV} \) and two oscillations for IHI with the minimum positions at \( E_r = 0.2 \text{ eV} \) and \( E_r = 0.8 \text{ eV} \). A similar structure was encountered in the collinear case. It was shown that when \( \theta_0 = 160^\circ \) these oscillations are strong enough to be eventually detectable also in experiment: the amplitude of the oscillation in the case of CHCI is 0.015 Å\(^2\) (this might be too small) and for IHI 0.035 Å\(^2\). As for IHI, we found that decreasing \( \theta_0 \) to 150\(^\circ\) causes the first oscillation to become weaker, but it seems that the second is enhanced because the amplitude increased from 0.035 to 0.05 Å\(^2\). A further decrease in \( \theta_0 \) to 140\(^\circ\) caused the oscillative structure to be diminished.

As for the dependence on the initial rotational states, it was found that the CHCI oscillation disappears once \( j \) becomes larger than zero. A similar situation is encountered for the first IHI oscillation, but the second oscillation seemed to be unaffected by changes in \( j \). This was found to be the case up to \( j = 6 \) which means that the second oscillation will survive even if the rotational temperature is as high as 300 K.

It should be emphasized that these findings are subject to a certain extent to the kind of potential energy surfaces employed in the calculations. Because we used the most up-to-date potential available, it is our hope that the findings are relevant. However, it could very well be that other potential energy surfaces will yield somewhat different results. Still the source of the features studied here are the mass effects\(^\text{3,10}\) and therefore the potential energy surfaces are expected to be of secondary importance only.

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