Integral and differential state-to-state cross-sections for the reactions F+D₂ (\(v_i = 0, j_i\)) → DF(\(v_f, j_f\)) + D: A comparison between three-dimensional quantum mechanical and experimental results

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In this letter we report quantum mechanical integral and differential cross sections for the title reactions as calculated on a new \textit{ab initio} potential energy surface. The calculations, all carried out in the reagents arrangement channel employing negative imaginary potentials, were done within the coupled-states approximation. The final vibrational state-to-state differential and integral cross sections were compared with experiment. Altogether, a very encouraging agreement was obtained. © 1996 American Institute of Physics. [S0021-9606(96)02207-7]

The F+H₂ system and its isotopic analogs are among the most important reactions in few-atom physical chemistry. The fact that they are exothermic reactions, with unique features that associate them with the strongest gaseous lasers, enhanced the interest of both experimentalists and theoreticians.¹–²⁷ The experimental studies were concentrated mainly on scattering experiments and rate constant measurements. The theoretical efforts were directed towards obtaining relevant potential energy surfaces (PESs) and performing dynamical calculations. Several PESs, some of them based on \textit{ab initio} calculations, were proposed. Among them are the M-5 (Ref. 12) the TSA [Ref. 15(a)] the 5SEC and 6SEC [Ref. 15(b),(c)] and the extended LEPS (Ref. 16) surfaces. A new \textit{ab initio} PES, recently introduced by Stark and Werner, was employed in the present calculations. It is important to mention that this PES was already used to calculate, for the title reaction\(^{15c}\) quasi-classical integral and differential cross sections, which were found to be in a good qualitative agreement with experiment.³ Here is reported the first three-dimensional quantum mechanical (QM) treatment of this system.

The present study is based on a QM time-independent approach, developed by Baer and co-workers.²⁸–³² This approach has four basic components.

(a) Application of the perturbative type Schrodinger equation (SE) to treat nonreactive collisions taking place in a given arrangement channel (AC) (Ref. 29)

\[
(E-H)\chi_{t,a} = V_{t,a}\psi_{t,a},
\]

where \(E\) is the total energy, \(H\) is the Hamiltonian, \(V_{t,a}\) is the \((t,a)\)-dependent perturbation, \(\chi_{t,a}\) is the short range part of the total wave function \(\Psi_{t,a}\), \(\psi_{t,a}\) is its unperturbed part representing, essentially, the asymptotic incoming component of \(\Psi_{t,a}\) (thus \(\Psi_{t,a} = \psi_{t,a} + \chi_{t,a}\)) and \(t,a\) (or more generally \(t_a\)) stands for a set of relevant quantum numbers namely

\[
t_a = (n_a l_a \Omega_a).\]

Here \(\lambda\) labels the incoming (reagents) AC, \(\alpha\) labels an outgoing (products) AC which may or may not be identical to \(\lambda\), \(n_a\), and \(j_{a}\) are the vibrational and the rotational quantum numbers, \(\Omega_a\) is the projection of \(J\) and \(j_{a}\) along the \(\alpha\)-AC \(z\)-body axis and \(J\) is the total angular momentum quantum number.

(b) Conversion of Eq. (1), which describes nonreactive processes, into an equation that describes reactive processes. This is achieved by adding to the Hamiltonian \(H\) in Eq. (1), in an \textit{ad hoc} way, a negative imaginary potential (NIP) (Ref. 30) in such a manner as to decouple the reactive ACs without affecting the form of \(\chi_i\) in the interaction region.

(c) Conversion of the scattering problem into a bound system-type problem by introducing one additional NIP in the asymptotic region, thus permitting the expansion of \(\chi_i\) in terms of \(L^2\) basis sets.²⁹,³²

(d) Application of the inelastic (i.e., nonreactive) coupled-states \((j_{\lambda}, l_{\lambda})\) approximation.³³,³⁴ It is important to emphasize that although exchange processes are considered, the coupled states approximation is applied only in the reagents AC, as is usually done in studies of inelastic (nonreactive) processes.

The aim of the calculation is to obtain the following (nonreactive) \(S\)-matrix elements

\[
S(t_a | t_{0a}) = \left\langle \delta_{\lambda_{a} l_{a} j_{a}} \delta_{\lambda_{0a} l_{0a} j_{0a}} + \frac{m}{\hbar^2} \langle \psi_{i_a} | V_{t,a} | \chi_{t_{0a}} + \psi_{t_{0a}} \rangle \right\rangle \times \exp(i \varphi_{t_a}),
\]

where \(\delta_{\lambda_{a} l_{a}}\) and \(\delta_{\lambda_{0a} l_{0a}}\) are Kronecker delta functions and \(\varphi_{t_a}\) is the \(t_a\)-th (elastic) phase shift related to \(\psi_{i_a}\). These matrix
elements, once derived as a function of various initial conditions, are used to calculate the reactive state-to-state differential cross sections according to the following formula:

\[ \frac{d\sigma(n_{aj}\rightarrow n_{0j}\alpha)}{d\omega} = \frac{1}{4k^2(n_{0j}\alpha)(2j_{0j}+1)} \sum_{(\alpha,\beta)} \sum_{(\beta,\gamma)} \left( \sum_{J} (2J+1) \right) \]

and state-to-state integral cross section according to

\[ \sigma(n_{aj}\rightarrow n_{0j}\alpha) = \frac{\pi}{k^2(n_{0j}\alpha)(2j_{0j}+1)} \sum_{J} (2J+1) \times \sum_{(\alpha,\beta)} \sum_{(\beta,\gamma)} |S(t_{\alpha}|t_{0\alpha})|^2. \]

Here the \( \tau \)'s stand for the expressions \( \tau = \min(J,j). \)

The advantage of performing the calculations only in the reagents AC becomes even greater when approximate treatments are applied. The various approximations will yield reasonable results for nonreactive systems, namely single AC systems, but they may become unreliable when applied to cases that require treating more than one AC. In the present study, we applied the coupled states approximation. This approximation was found in numerous (nonreactive) studies to yield correct results. For instance we applied this approximation in our recent studies of the \( \text{F} + \text{X}_2 \rightarrow \text{FX} + \text{X} \): \( \text{X} = \text{HLD} \) reactions performed on the TSA [Ref. 28(a)] and the 6SEC [Ref. 28(b)] PESs and compared the energy-dependent state selected integral cross sections with available exact results.\(^{19,a,22}\) For all practical purposes the two treatments yielded results which, along the whole energy range considered, were identical. Details regarding the numerical parameters employed in the present calculation will be given in a subsequent publication.

In this letter we report on a first comparison between experiment and a three-dimensional QM treatment for the title reaction. The calculations were done for \( E_{\text{tot}} = 0.277 \text{ eV} \) (which corresponds to \( E_{\text{ex}} = 0.087 \text{ eV} \)) and the results for the reactive vibrational state-to-state differential cross-sections

\[ F + D_2(v_i=0,j_f=0) \rightarrow \begin{cases} DF(v_f,\Sigma_{j_f}) + D \\ DF(\Sigma_{v_f,j_f}) + D \end{cases} \]

where \( v_f = 1 \rightarrow 4 \), are presented in Fig. 1. The units on the left-hand side of Fig. 1 refer to the QM cross sections; the experimental results were shifted in such a way as to fit a theoretical result at one angle (thus the fit is based on one single fitting parameter). The newly measured, high resolution experimental cross sections were evaluated by standard deconvolution procedures, as described in Ref. 10, for providing rotationally averaged data for the individual final vibrational states. It is important to emphasize that the experimental measurements were performed with converted deuterium (namely 90% orthodeuterium and only 10% para-deuterium) at low rotational temperatures (\( \sim 60 \text{°K} \)) so that 90% of the interacting deuterium molecules were at \( j_f = 0 \). As can be seen, except for \( v_f = 1 \), the fit between the two types of results, is very encouraging, in particular for the total differential cross section.

In addition, we also calculated the vibrational state-to-state integral cross-sections and the total cross section at this energy. The results are summarized in Table I where they are compared with the experimental ones. As before, a good agreement with experiment was obtained. More results related to this reaction as well as an extensive analysis will be published elsewhere.

In summary: This letter reports the first three-dimensional QM state-to-state integral and differential cross sec-
TABLE I. Quantum mechanical vibrational state-to-state and total cross sections ($\sigma$ A$^2$) for the F+D$_2$ reaction at $E_\text{c} = 0.087$ eV collision energy ($E_\text{c} = 0.277$ eV). The theoretical branching ratios (values in parentheses) are also listed and compared with the experimental values.

<table>
<thead>
<tr>
<th>State-to-state</th>
<th>$\nu_j = 1$</th>
<th>$\nu_j = 2$</th>
<th>$\nu_j = 3$</th>
<th>$\nu_j = 4$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory</td>
<td>0.16</td>
<td>1.25</td>
<td>1.55</td>
<td>0.63</td>
<td>3.58</td>
</tr>
<tr>
<td>(0.10)</td>
<td>(0.81)</td>
<td>(1.00)</td>
<td>(0.41)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment</td>
<td>0.16</td>
<td>0.61</td>
<td>1.00</td>
<td>(0.40)$^a$</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$Estimated value.

...employing an ab initio PES, for any of the F+H$_2$ reactions. The results for the F+D$_2$ system were compared with recent highly resolved experimental results and a very encouraging agreement was obtained.

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