On the Utility of Akima's Bivariate Interpolation Method: Rotational Energy Transfer in HF - M (M = Ar, He) and HCl - Ar Collisions

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We report state-to-state integral inelastic cross-sections for rotational energy transfer in collisions between rigid rotor HF and M (M = Ar, He) and rigid rotor HCl and Ar over a range of initial rotational states and relative translational energies using Akima's bivariate interpolated potential energy surfaces. The cross-sections have been fitted to power gap law in order to compare these with previously reported results. We have also computed the rotational rainbows in HF-He collisions.

Knowledge of potential energy surface (PES) for any system is of fundamental importance for theoretical studies of chemical reactions. Ab-initio potential energy (PE) values for different geometries are usually available in the form of table of numbers. However, for dynamical calculations the PES must be known in some convenient analytical or numerically interpolated form which is capable of generating potentials and its derivatives accurately and efficiently at any arbitrary geometry. Various methods for fitting the ab-initio PE values have been reviewed by Connon and more recently by Sathyamurthy. Recently, the accuracy of Akima's bivariate method of interpolation in fitting ab-initio potential energy surface has been tested and this method has been shown to be comparable in efficiency and reliability to 2D-cubic spline interpolation. Akima's method has also been shown to be fairly insensitive to choice of grids and to be applicable to sudden surfaces like that of LiFH.

We provide here a further test on the utility of Akima's interpolation method on the basis of our studies on non-reactive collisions such as rotational energy transfer (RET) processes. The RET processes were chosen for study because a wealth of information is available on these in the form of state-to-state integral inelastic cross-sections (IICS). Many fitting laws and scaling relationships have been proposed to compact these cross-sections. The most commonly employed such law is power gap law (PGL) proposed by Brunner et al.: 

\[ \sigma_{\Delta J} \propto (2J + 1) T_{\text{r}}^{\frac{1}{2}} |\Delta E_{\text{if}}|^{\gamma} \quad \ldots \quad (1) \]

where \( \sigma_{\Delta J} \) is the inelastic integral cross-section for transition from initial rotational state \( (J_i) \) to final rotational state \( (J_f) \), \( \Delta E_{\text{if}} \) the associated energy transferred and \( T_{\text{r}} \) is the final collision energy \( (= T_{\text{f}} - \Delta H_{\text{if}} \) with \( T_{\text{f}} \) the initial collision energy).

We have studied the rotational energy transfer in collisions between rigid rotor HF and M (M = Ar, He) and rigid rotor HCl and Ar using Akima's bivariate interpolated surfaces. The results have been analysed in terms of PGL. We have also computed the rotational rainbows in HF-He collisions at \( J_f = 1 \) and \( T_{\text{f}} = 0.492 \) eV and compared these with those obtained by Gianturco and Palma.

Methods

**Akima's interpolation method**

Let us consider a function \( y = f(x) \) for which the function values \( y_i \) are known at specific nodes \( x_i = 1, 2, ... \). Interpolation of \( y_i \) is achieved by constructing a piecewise function composed of a set of cubic polynomials applicable to successive intervals of \( x_i \). The polynomial representing a portion of the curve between two adjacent \( x_i \) is determined by the coordinates and slopes at these two nodes. The slope of curve at the node 3 for example is determined by Eq. 2,

\[ \frac{dy}{dx}_3 = \frac{|m_4 - m_3| m_2 + |m_2 - m_1| m_3}{|m_4 - m_3| + |m_2 - m_1|} \quad \ldots \quad (2) \]

where \( m_1, m_2, m_3 \) and \( m_4 \) are slopes of line segments \( 12, 23, 34 \) and \( 45 \) respectively. In the special case of
Potential energy surface

For HF-Ar and HF-He systems, the electron gas potentials computed by Detrich and Conn9 using the electron gas approximation of Gordon and Kim10 were used to generate the PE values over a \( R \times \theta \) grid where \( R \) is the centre of mass separation between HF and \( M \) (= Ar, He) and \( \theta \) is the angle between \( R \) and \( r \) (\( r \) being the internal coordinate of the diatom, HF). For HF-Ar system the grid \((23 \times 9)\) consisting of \( R \) from 1.0 to 10.0 bohr and \( \theta \) from 0° to 180° was used, while for HF-He system the grid \((21 \times 9)\) consisting of \( R \) from 1.0 to 8.0 bohr was used.

For HCl-Ar system, Green's Gordon-Kim11 potential were used to generate the PE values over a \( R \times \theta \) grid. The grid \((19 \times 7)\) consists of \( R \) from 1.0 to 12.0 bohr and \( \theta \) from 0° to 180° was used.

Results and Discussion

We report the results of a quasiclassical trajectory (QCT) study of the rotationally inelastic collisions between a rigid rotor HF and Ar atom for \( J_i = 0, T_i = 0.3767 \) eV; \( J_i = 1, T_i = 0.39 \) eV and 0.65 eV; \( J_i = 6, T_i = 0.65 \) eV. In the case of rigid rotor HF and He atom we have chosen \( J_i = 0, T_i = 0.3767 \) eV; \( J_i = 1, T_i = 0.492 \) eV and \( J_i = 20, T_i = 0.20 \) eV. In case of collisions between rigid rotor HCl and Ar atom the studies have been made at \( J_i = 0, T_i = 0.0774 \) and 0.3767 eV. In our trajectory program we followed the methodology given in ref. 12. The initial rotor state \( J_i \) was fixed and for each \( J_i \) we varied the impact-parameter \( b \) systematically from 0 through \( b_{\text{max}} \). All other variables were chosen randomly with the aid of the random number generator subroutine GGUB of IMSL13. The individual trajectories were started and terminated at the centre-of-mass separation of 14 a.u. Conservation of total energy and total angular momentum was used to check the accuracy of integration of the trajectory. We computed 50 trajectories at each \( b \) and the resulting probabilities of transition \( P_{J_i \rightarrow J_f} \) were converted to \( \sigma_{J_i \rightarrow J_f} \) using Eq. 4,

\[
\sigma_{J_i \rightarrow J_f} = \int_0^{b_{\text{max}}} 2\pi b P_{J_i \rightarrow J_f}(b) \, db
\]

\[
= 2\pi b \sum_i b_i P_i(b) \quad \ldots (4)
\]

We have shown the plots of \( \ln[\sigma_{J_i \rightarrow J_f}/(2J_i+1)] T_i^{(2)} \) as a function of \( \ln|\Delta E_{\text{id}}| \) for HF-Ar, HF-He and HCl-Ar systems in Figs 2, 3 and 4, respectively.

The slope \( \gamma \) computed from power gap law i.e. the plots of \( \ln[\sigma_{J_i \rightarrow J_f}/(2J_i+1)] T_i^{(2)} \) as a function of \( \ln|\Delta E_{\text{id}}| \) are summarised in Table 1. We have also re-
We have also analysed our results for the presence of rotational rainbows in HF-He collisions at $J_i = 1$ and $T_i = 0.492$ eV in order to compare these with those reported by Gianturco and Palma. We have run 200 trajectories at each impact parameter. The

Table 1—A Summary of $\gamma$ Values Obtained by PGL Fit of IICS

<table>
<thead>
<tr>
<th>System</th>
<th>Ref</th>
<th>$V_i$</th>
<th>$J_i$</th>
<th>$T_i$ (eV)</th>
<th>$\gamma$</th>
</tr>
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<tbody>
<tr>
<td>HF-Ar</td>
<td>5(a)</td>
<td>1</td>
<td>1</td>
<td>0.17-0.69</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>5(b)</td>
<td>2,4,6</td>
<td>6,10</td>
<td>0.65</td>
<td>1.80±0.1</td>
</tr>
<tr>
<td></td>
<td>Present</td>
<td>—</td>
<td>0</td>
<td>0.3767</td>
<td>1.80±0.3</td>
</tr>
<tr>
<td></td>
<td>study</td>
<td>—</td>
<td>1</td>
<td>0.39</td>
<td>1.9±0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>—</td>
<td>1</td>
<td>0.65</td>
<td>1.8±0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>—</td>
<td>6</td>
<td>0.65</td>
<td>1.5±0.2</td>
</tr>
<tr>
<td>HF-He</td>
<td>5(c)</td>
<td>4</td>
<td>20</td>
<td>0.2</td>
<td>2.4±0.3</td>
</tr>
<tr>
<td></td>
<td>Present</td>
<td>—</td>
<td>20</td>
<td>0.2</td>
<td>2.5±0.5</td>
</tr>
<tr>
<td></td>
<td>study</td>
<td>—</td>
<td>0</td>
<td>0.3767</td>
<td>2.4±0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>—</td>
<td>1</td>
<td>0.492</td>
<td>2.3±0.3</td>
</tr>
<tr>
<td>HCl + Ar</td>
<td>5(g), 5(h)</td>
<td>0.5</td>
<td>8</td>
<td>0.216</td>
<td>2.0±0.5</td>
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<tr>
<td></td>
<td></td>
<td>—</td>
<td>8</td>
<td>0.65</td>
<td>1.6±0.2</td>
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<tr>
<td></td>
<td></td>
<td>—</td>
<td>8</td>
<td>1.3</td>
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<tr>
<td></td>
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<td>0,4,8</td>
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<tr>
<td></td>
<td>Present</td>
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<td>0</td>
<td>0.3767</td>
<td>1.3±0.2</td>
</tr>
<tr>
<td></td>
<td>study</td>
<td>—</td>
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<td>0.0774</td>
<td>1.4±0.2</td>
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Acknowledgement

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References