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Theoretical Study of Intermolecular Energy Transfer of an Electronically Excited Diatomic Molecule by Atom Impact: He(1S) + H₂(B 1Σ⁺)

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ABSTRACT

An ab initio potential energy surface (pes) for He + H2(B 1Σ_u^+) has been determined using self-consistent field plus configuration interaction methods. The long-range interactions are described by a multipole expansion. The He–H2(B 1Σ_u^+) interaction energy is much more anisotropic than those of ground state systems studied to date.

As a first step in the dynamics studies, cross sections for rotational excitation at c.m. energies 0.015–0.105 eV have been computed in the rigid-rotator model using the space-fixed coupled-channel formalism and an analytical fit to the ab initio pes. Partial inelastic cross sections display a high degree of structure, which appears to be mainly due to the anisotropy of the interaction energy. The magnitudes of total cross sections for Δj = ±2 transitions are comparable to those for ion–molecule systems.
I. INTRODUCTION

Interest in the collision phenomena of electronically excited molecules has been stimulated by the greater availability of tunable lasers. One early experimental study focused on collisions of HD(B $1\Sigma^+_u$) with rare gas atoms [1]. Cross sections for rovibrational energy transfer and electronic quenching were measured for HD(B $1\Sigma^+_u, v=3, j=2$), excited by an argon lamp, in the presence of He, Ne, and HD(X $1\Sigma^+_g$). To further understand these processes, calculations of the potential energy surface (pes) of the closely related He + H$_2$(B $1\Sigma^+_u$) system have been carried out. To ascertain the origin of the quenching pathway, Schaefer, et. al. carried out ab initio Hartree-Fock (HF) and configuration interaction (CI) computations for perpendicular geometries (of He with respect to the H$_2$ midpoint) and found a long range attractive well but no surface crossing to explain the electronic quenching [2]. Römel, Peyerimhoff and Buenker (RPB) located an avoided crossing with He + H$_2$(B $1\Sigma^+_u$) using the ab initio multi-reference double-excitation CI (MRD-CI) method, but an unequivocal explanation of the quenching mechanism was not provided [3]. More recently, Farantos, Theodorakopoulos and Nicolaides (FTN) extended the pes of RPB by computing MRD-CI energies for the 45° approach and found an avoided crossing with the ground state He + H$_2$(X $1\Sigma^+_g$) pes that accounts for the quenching [4]. Farantos has performed quasi-classical trajectory studies of energy transfer and quenching using an analytic fit of a pes constructed from a combination of FTN's results and those of RPB [5].

The objective of the present effort is to provide a quantum mechanical description of rotational and rovibrational energy transfer in the B $1\Sigma^+_u$ state due to He impact using an accurate ab initio pes. In this paper, consideration is limited to rotationally inelastic collisions; the study of rovibrational energy transfer will be presented in a separate publication. In section II we briefly describe the method of calculation of the pes, and the features that are expected to strongly influence the energy transfer processes of interest. Section III summarizes the method used to compute rotational cross sections for the rigid-rotator model. In section IV we present conclusions and plans for future work.

II. POTENTIAL ENERGY SURFACE

Calculation of rotational energy transfer cross sections requires a highly accurate pes. In a separate study, it was shown that a correlated wavefunction is necessary to properly describe the charge distribution and polarizability of H$_2$(B $1\Sigma^+_u$) [6]. To satisfy these requirements, a variant of the iterative natural orbital (INO) method of Bender and Davidson [7] has been used in this study.
Gaussian basis sets are employed in all calculations. The H atom basis is that of RPB. It includes a very diffuse s function and one set of diffuse p functions which are necessary to describe the Rydberg character of H\(_2\)(B \(^1\Sigma_\uparrow\)). The near-HF-limit basis of Garrison, et. al. [8] is used for He.

The calculation of a point on the pes is performed in three steps. First, the self-consistent field (SCF) orbitals of He + H\(_2\)(C \(^1\Pi_\uparrow\)) are computed [9]. These orbitals are then used to define a set of reference configurations (RCs) as follows: (i) two electrons occupy the \(1\sigma\) orbital which is mainly He\((1S)\); (ii) the two remaining electrons are distributed in the \(2\sigma\) and \(3\sigma\) orbitals in all ways consistent with \(1\Sigma_\uparrow^+\) or \(1\Sigma^+\) symmetry. Second, a CI calculation including all single and double excitations from the RCs (SD-CI) is performed to obtain natural orbitals (NOs). A larger set of RCs is defined by allowing two electrons to occupy the \(2\sigma\), \(3\sigma\), \(4\sigma\) and \(5\sigma\) NOs in all ways consistent with \(1\Sigma_\uparrow^+\) or \(1\Sigma^+\) symmetry. This is followed by a final SD-CI over the RCs constructed from the NO basis. Table I shows the number of configurations and approximate CPU time, on a VAX 11/780, for the three steps and the four symmetries considered. The points calculated using the above prescription were combined with those of RPB and FTN to define the pes used for cross section calculations.

The pes has several noteworthy features. An attractive interaction with a minimum of \(-0.03\) eV is found at a He-to-H\(_2\) center-of-mass separation \((R)\) of \(-4.0\) a.u., H\(_2\) bond length \((r)\) at the equilibrium separation \((r_e)\) of 2.4 a.u. and angle \(\theta\) \((R\cdot r)\) of 90°. An avoided crossing with the He + H\(_2\)(B' \(^1\Sigma_\uparrow\)) pes causes a small barrier at \(R = 4.0\) a.u., \(r = 2.4\) a.u. and \(\theta = 0°\). This crossing arises when the He atom penetrates the very diffuse \(1\sigma_u\) orbital of H\(_2\)(B' \(^1\Sigma_\uparrow\)) and experiences a strong electrostatic attraction, while the He + H\(_2\)(B \(^1\Sigma_\uparrow\)) interaction is repulsive. The avoided crossing and attractive well combine to make the pes highly anisotropic and thus are expected to strongly influence translation-to-rotation energy exchange as well as rovibrational energy transfer. Another avoided crossing, this one with the He + H\(_2\)(X \(^1\Sigma_\downarrow\)) pes leads to a very deep (-1.5 eV) well at \(R = 1.5\) a.u., \(r = 4.0\) a.u., \(\theta = 45°\) and is the one mentioned in Sec. I that explains the experimentally observed fluorescence quenching [4]. Overall, the pes for electronically excited He-H\(_2\)(B \(^1\Sigma_\uparrow\)) is much more complex than those typically encountered in scattering of ground state systems.

As a first step in the dynamics studies, cross sections computed in the rigid-rotator model are being investigated. To this end, the rigid-rotator region of the pes was fit with an accurate function to simplify cross section calculations. A variant of the Sorbie-Murrell-type function [10], containing thirty adjustable parameters, describes the short-range \((R < 5.5\) a.u.) region. For very large \(R\) \((R > 15\) a.u.), the analytic multipole expansion:
\[ V_{\text{long range}}(R, \theta) = - \frac{3U_{\text{He}} U_{H_2} a_{\text{He}}}{2(U_{\text{He}} + U_{H_2})} \left[ a_{H_2} + \frac{1}{3}(a_{\|} - a_{\perp}) (\frac{3}{2} \cos^2 \theta - \frac{1}{2}) \right] R^{-6} \]

\[ - \frac{1}{3} a_{\text{He}} \Theta_{H_2} (105 \cos^4 \theta - 28 \cos^2 \theta + 9) R^{-8} \]

is used, where \( U \) is the ionization energy, \( a_{\|} \) and \( a_{\perp} \) are the parallel and perpendicular components of the polarizability, respectively, and \( \Theta \) is the quadrupole moment. The values used are given in Table II. A cubic spline interpolating function is used to link the short- and long-range functions. The general form of the pes is expressed in a Legendre expansion:

\[ V(R, \theta) = \sum_{\lambda} v_{\lambda}(R) P_{\lambda}(\cos \theta) \]

by projecting out the Legendre components of the analytic function. The \( R \) dependence of the Legendre coefficients is plotted in Figure 1. This diagram clearly shows the anisotropy near \( R = 4.0 \) a.u. It can also be seen that the \( v_2 \) term is larger than the \( v_0 \) term even for large \( R \). This is an indication of the very strong anisotropy of the He-H\(_2\)(B \( ^1\Sigma^+ \)) interaction.

III. ROTATIONAL ENERGY TRANSFER CROSS SECTIONS

The standard space-fixed frame formulation of the coupled-channel (CC) equations has been used to calculate rotational energy transfer cross sections [11]. Vibrational motion of \( H_2 \) has been neglected; however, the energy levels of the rigid-rotator have been corrected to more nearly approximate the true rotational levels of \( H_2(B \ ^1\Sigma^+, v=0) \). The energy levels are given by the expression [12]:

\[ \epsilon_j = B_0[j(j+1)] - D_0[j(j+1)]^2 + H_0[j(j+1)]^3 \]

Gordon's method is used to solve the CC equations for energies in the range 0.015-0.105 eV. For these energies, at least three closed rotational levels must be included to converge inelastic cross sections to three significant figures.

The partial cross sections are displayed in Figures 2-5. The large number of peaks in \( \sigma(H_2) \) is unusual. The peaks appear at energies below the threshold for excitation of \( j = 4 \) (0.047 eV) so they are not caused by interference between different inelastic transitions. The structure of the curves remains remarkably constant aside from a shift.
to larger J with increasing energy. This seems to rule out resonances, which are strongly energy dependent. The main features of $\sigma_{0 \rightarrow 2}$ can be reproduced using a two-state (two rotational states of H$_2$) calculation which samples only the $v_0$, $v_2$ and $v_4$ terms of the Legendre expansion. It appears that the structure is mainly due to the anisotropy of the pes.

Total inelastic cross sections are given in Table III. The magnitude of the cross sections for $\Delta j = \pm 2$ transitions are comparable to those for ion-molecule systems [13], but the dominant interactions causing transitions are, of course, much shorter ranged and reflect the large anisotropy of the present system.

IV. CONCLUSION

Collisional energy transfer in electronically excited molecules holds much interest but few quantum mechanical studies have been done because of their difficulty. We have performed ab initio large basis set SCF-CI calculations to determine energies on the He-H$_2$(B 1Σ$^+$) pes needed to augment those of RPB and FTN to generate a pes which can be used for accurate quantitative estimates of rotational energy transfer cross sections. This pes is very anisotropic, much more so than those of ground state atom-diatom systems studied to date. Rotational energy transfer cross sections have been calculated for the atom-rigid-rotator model. The high degree of structure in the partial cross sections for the 0$\rightarrow$2 transition appears to be mainly due to the change in anisotropy with center-of-mass separation. Total inelastic cross sections for energies in the range 0.015-0.105 eV are found to be large, with magnitudes comparable to those of ion-ground state molecule systems.

These preliminary results provide an indication of the differences that can be expected for rovibrational energy transfer involving electronically excited target molecules. We are currently extending this work to include rovibrational energy transfer processes concomitant with electronic quenching.
REFERENCES


5. S. C. Farantos, private communication.


9. The He-H\textsubscript{2}(C \textsuperscript{1}Π\textsubscript{u}) state was used because of convergence problems encountered with He-H\textsubscript{2}(B \textsuperscript{1}Σ\textsuperscript{+}\textsubscript{u}).


12. B\textsubscript{0} = 19.4537, D\textsubscript{0} = 0.01541, and H\textsubscript{0} = 1.1x10^{-5} taken from G. Herzberg and L. L. Howe, Can. J. Phys. 37, 636 (1959).

TABLE I.

Number of Configurations and CPU time\(^a\) for PES Calculations\(^b\)

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>First CI</th>
<th>Second CI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Average</td>
</tr>
<tr>
<td></td>
<td>RCs</td>
<td>CSFs CPU (hr.)</td>
</tr>
<tr>
<td>D(_{oh})</td>
<td>1 1553 0.75 4 4002 2.0</td>
<td></td>
</tr>
<tr>
<td>C(_2v)</td>
<td>1 2017 0.75 4 5162 3.0</td>
<td></td>
</tr>
<tr>
<td>C(_{4v})</td>
<td>3 3172 1.25 10 8105 8.5</td>
<td></td>
</tr>
<tr>
<td>C(_S)</td>
<td>3 4100 1.75 10 10425 12.0</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) See text for description of CI calculations.

\(^b\) CPU times are for a DEC VAX 11/780. Nomenclature: RCs (Reference Configurations); CSFs (Configuration State Functions).
TABLE II.

<table>
<thead>
<tr>
<th></th>
<th>( U )</th>
<th>( \alpha_\parallel )</th>
<th>( \alpha_\perp )</th>
<th>( \alpha )</th>
<th>( \Theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2(\text{B} \ 1\Sigma_u^+) )</td>
<td>0.1557 ( b )</td>
<td>259 ( d )</td>
<td>51 ( d )</td>
<td>121 ( d )</td>
<td>-5.63 ( f )</td>
</tr>
<tr>
<td>( \text{He} )</td>
<td>0.9033 ( c )</td>
<td>-</td>
<td>-</td>
<td></td>
<td>1.3845 ( e )</td>
</tr>
</tbody>
</table>

a. All values are given in atomic units.
c. C. E. Moore, Atomic Energy Levels, NBS Circ. 467 (1949).
d. See [6].
f. R. M. Grimes, M. Dupuis and W. A. Lester, Jr. unpublished results.
<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>0.015</th>
<th>0.030</th>
<th>0.045</th>
<th>0.060</th>
<th>0.075</th>
<th>0.090</th>
<th>0.105</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition (j_i \rightarrow j_f)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 \rightarrow 2</td>
<td>1.43(-1)</td>
<td>1.37</td>
<td>3.04</td>
<td>4.66</td>
<td>5.87</td>
<td>6.85</td>
<td>7.4</td>
</tr>
<tr>
<td>0 \rightarrow 4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.08(-2)</td>
<td>5.46(-2)</td>
<td>1.17(-1)</td>
<td>2.1 (-1)</td>
</tr>
<tr>
<td>0 \rightarrow 6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.3 (-5)</td>
</tr>
<tr>
<td>2 \rightarrow 4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.43(-1)</td>
<td>6.50(-1)</td>
<td>1.45</td>
<td>2.6</td>
</tr>
<tr>
<td>2 \rightarrow 6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.9 (-4)</td>
</tr>
<tr>
<td>4 \rightarrow 6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.3 (-2)</td>
</tr>
</tbody>
</table>

a. Numbers in parenthesis denote powers of ten, i.e. 1.93(+2) = 193.
FIGURE CAPTIONS

Fig. 1  Legendre expansion coefficients $v_0 - v_{18}$ for the rigid-rotator pes.

Fig. 2  Energy dependence of partial integral cross sections for the $0 \rightarrow 2$ transition: 0.015-0.060 eV.

Fig. 3  Energy dependence of partial integral cross sections for the $0 \rightarrow 2$ transition: 0.075-0.105 eV.

Fig. 4  Energy dependence of partial integral cross sections for the $2 \rightarrow 4$ transition: 0.060-0.105 eV.

Fig. 5  Energy dependence of partial integral cross sections for the $0 \rightarrow 4$ transition: 0.060-0.105 eV.
Legendre Coefficients for Rigid-Rotator PES
Partial Integral Cross Sections

\[ \sigma_{J \rightarrow 2} (\text{\AA}^2) \]

\( J - \text{Total Angular Momentum} \)

- 0.060 eV
- 0.045 eV
- 0.030 eV
- 0.015 eV
Partial Integral Cross Sections

\[ \sigma_{0 \rightarrow 2} (\text{Å}^2) \]

\( J - \text{Total Angular Momentum} \)

- 0.075 eV
- 0.090 eV
- 0.105 eV
Partial Integral Cross Sections

\[ \sigma_{2\rightarrow 4} (\AA^2) \]

\[ J - \text{Total Angular Momentum} \]

- 0.105 eV
- 0.090 eV
- 0.060 eV
- 0.075 eV
Partial Integral Cross Sections

\[ \sigma_{J \to 4} (\text{Å}^2) \]

- 0.105 eV
- 0.090 eV
- 0.075 eV
- 0.060 eV

J - Total Angular Momentum
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