Trapping hydrogen atoms from a neon-gas matrix: A theoretical simulation

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I. INTRODUCTION

In the last decade there have been intense efforts to cool atoms leading to the study of states of the matter such as Bose–Einstein condensates and Bardeen–Cooper–Schrieffer order. In this study we simulate a recently proposed trap-loading mechanism for trapping hydrogen atoms released from a neon matrix. Accurate ab initio quantum calculations are reported of the neon-hydrogen interaction potential and the energy- and angular-dependent elastic scattering cross sections that control the energy transfer of initially cold atoms are obtained. They are then used to construct the Boltzmann kinetic equation, describing the energy relaxation process. Numerical solutions of the Boltzmann equation predict the time evolution of the hydrogen energy distribution function. Based on the simulations we discuss the prospects of the technique. © 2009 American Institute of Physics. [DOI: 10.1063/1.3180822]

II. THEORY

A. Elastic cross sections

The energy relaxation of hydrogen atoms in neon gas occurs due to elastic collisions. The radial part of the Schrödinger equation for center of mass (CM) scattering energy \( e \) satisfies the Schrödinger equation,

\[
\frac{d^2}{dR^2} + k^2 - \frac{U(R) - \ell(\ell + 1)}{R^2} j_{\ell}(R) = 0, \tag{1}
\]

where \( \mu \) is the reduced mass, \( \ell \) is the angular momentum, \( R \) is the internuclear distance, \( U(R) = 2\mu V(R)/\hbar^2 \) is the molecular potential, and \( k^2 = 2\mu V/\hbar^2 \). The asymptotic solution of Eq. (1) can be written in terms of the spherical Bessel \( j_{\ell}(r) \) and Neumann \( n_{\ell}(r) \) functions,

\[
u_{\ell}(R) = kR\left[j_{\ell}(kR)\cos \delta_\ell - n_{\ell}(kR)\sin \delta_\ell\right], \tag{2}
\]

where \( \delta_\ell \) is the phase shift. At large \( R \),

\[
u_{\ell}(R) = \sin(kR - \ell \pi/2 + \delta_\ell), \tag{3}
\]

and the differential cross section is given by

\[
\frac{d\sigma(e)}{d\Omega} = \frac{1}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \sin \delta_\ell e^{i\delta_\ell} P_{\ell}(\cos \chi)^2, \tag{4}
\]

where \( P_{\ell} \) denotes the \( \ell \)th Legendre polynomial and \( \chi \) is the CM scattering angle. Atomic units are used throughout this paper.
B. Kernel of Boltzmann equation

The energy evolution of atoms due to elastic and inelastic collisions with a uniform bath gas has been considered by Kharchenko et al.\textsuperscript{10,11} The rate of energy transfer of the projectile atoms from initial energy \( E' \) to final energy \( E \) in the laboratory frame (LF) is given by the kernel of the Boltzmann equation \( B(E'|E') \). In a uniform bath gas, whose density is much higher than that of the projectile atoms, collisions and energy exchange between projectile particles is negligible and the energy distribution \( f(E,t) \) of the projectile can be described by the linear Boltzmann equation,

\[
\frac{\partial}{\partial t} f(E,t) = \int B(E'|E',t)dE' - f(E,t) \int B(E'|E)dE' - \zeta(E)f(E,t) + Q(E,t),
\]

where \( Q(E,t) \) is the rate of production of the atoms with energy \( E \) and \( \zeta(E,t) \) is the rate of the sink reactions that remove them. For binary elastic and inelastic collisions, \( B(E'|E') \) can be derived analytically through the double differential cross section \( d^2\sigma/dOmega dE \) (Refs. 10 and 11), and in the case of elastic scattering, \( d^2\sigma/dOmega dE = \delta(E-E')d\sigma/dOmega \) and the energy relaxation \( B(E'|E) \) can be calculated using the differential cross section given by Eq. (4),

\[
B(E'|E) = \frac{n_p m^{3/2}}{2 \sqrt{2\pi \mu^2}} E \int \frac{d\sigma}{d\Omega} \rho(p_p') d\Omega_p d\Omega_{p'},
\]

where \( m \) is the mass of the projectile, \( \Omega_p' \) and \( \Omega_p \) are the solid angles of the initial and final momenta in the LF for fixed \( |p'| = \sqrt{2mE'} \) and \( |p| = \sqrt{2mE} \), \( n_p \) is the density of the bath gas, and \( \rho(p_p') \) is the Maxwellian–Boltzmann distribution function of the bath gas. The solution of Eq. (5) may be written as

\[
f(E,t) = \int_0^t \int_0^\infty K(E,t|E',t')Q(E',t')dE'dt',
\]

where the propagator \( K(E,t|E',t') \) describes the energy evolution of the projectile atoms created at the time \( t' \) with energy \( E' \). The propagator can be obtained from the solution of Eq. (5) in which the source function \( Q(E',t') \) is a delta function \( \delta(E-E')\delta(t-t') \) and there is no sink reaction to remove the projectile. If the initial function \( f(E',t'=0) \) is given, \( Q(E',t')=f(E',t'=0)\delta(t-t') \), \( f(E,t) \) at a later time \( t \) may be calculated from the propagator \( K(E,t|E',t') \) according to

\[
f(E,t) = \int K(E,t|E',0)f(E',0)dE'.
\]

Equation (8) can be solved numerically\textsuperscript{12,13} by defining the function \( f(E,t) \) in a given energy range \([0,E_{\text{max}}]\) and using a discretized kinetic equation for the kernel, defined as a \( N \times N \) matrix\textsuperscript{14} with the energy grid of \( \Delta E \),

\[
A_{ij} = \delta E[B(i\delta E|j\delta E) - \delta_{ij}\omega(i\delta E)],
\]

where \( \delta_{ij} \) is the Kronecker delta and

\[
\omega(E) = \int_0^\infty B(E'|E')dE'.
\]

In the present study, \( E_{\text{max}}=0.5 \text{ eV} \) and there are 20 energy grid points within 1\(kT\). The time-dependent distribution function is generated from the initial distribution function \( f(E,0) \),

\[
f(E,t) = e^{\omega E}f(E,0),
\]

and the time-dependent average translational energy is obtained from

\[
\langle E(t) \rangle = \int f(E,t)EdE.
\]

For an arbitrary time-dependent bath gas density, no general analytical expression for the solution of Boltzmann equation can be obtained. Nevertheless, a solution in closed form may be written for specific time dependence. Thus, for a time-dependent density \( N(t)g(t)N(t=0) \), Eq. (11) can be modified to a form with effective time \( \tau = \int_0^t dt'g(t') \),

\[
f(E,t) = e^{\omega_{\tau}E}f(E,0),
\]

where \( g(t) \) describes the time variation of the relative bath gas density and \( \omega_{\tau} \) is constructed with the density at \( t=0 \). No sink reaction is involved in the H trapping process and \( \zeta(E,t)=0 \).

C. Molecular potential: \textit{Ab initio} calculations

The interaction potential between Ne and H atoms has been evaluated using the partially spin restricted coupled cluster single and double\textsuperscript{15} method, augmented with triple excitations noniteratively,\textsuperscript{16} denoted as ROHF-RCCSD(T). All electrons were correlated in the RCCSD(T) calculation. A series of Dunning’s augmented polarized core/valence aug-cc-pCVnZ basis sets was used in the \textit{ab initio} calculation \((n=Q,5,6)\). Basis set superposition errors were corrected using the standard counterpoise approach of Boys and Bernardi.\textsuperscript{17} The final potential energies were extrapolated to the complete basis set limit by using the mixed exponential/Gaussian function,\textsuperscript{18}

\[
E(n) = E_{\text{CBS}} + Be^{-(n-1)} + Ce^{-(n-2)}.
\]

The MOLPRO2006.1 suite of programs\textsuperscript{19} was used throughout these electronic structure calculations.

The computed potential energies at selected internuclear distances \( R \) were then fitted to an analytical expression of the Degli Espositi–Werner\textsuperscript{20} form composed of the short-range term \( V_{\text{sh}} \) and the asymptotic long-range part \( V_{\text{as}} \),

\[
V(R) = V_{\text{sh}}(R) + V_{\text{as}}(R),
\]

where

\[
V_{\text{as}}(R) = \sum_{i=0}^8 a_i R^i e^{-a(R-\beta)}.
\]

The long-range part was represented by the damped dispersion term,
\[ V_{\text{ad}}(R) = - \frac{1}{2} \left[ 1 + \tanh(\gamma + \lambda R) \right] \sum_{n=0}^{4} \frac{C_{6n+5}}{R^{2n+6}}. \] (17)

The nonlinear \( \alpha, \beta, \gamma, \) and \( \lambda \) and the linear \( a_i \) and \( C_n \) parameters were optimized using the Levenberg–Marquardt nonlinear least square algorithm with no constraints imposed. The maximum root-mean-square (rms) error is 0.3 cm\(^{-1}\), and the rms error averaged over the internuclear distance does not exceed 0.1 cm\(^{-1}\).

### III. RESULTS AND DISCUSSION

#### A. Potential energy curve

The calculated ground state potential energy curve is shown in Fig. 1 and the corresponding spectroscopic data are listed in Table I with other available experimental\(^{23}\) and theoretical\(^{22,25-27}\) results. The system is weakly bound and shows a minimum around 6.47 bohrs. The long-range dispersion coefficient \( C_6 = 5.80 \) derived from the \textit{ab initio} potential agrees closely with other theoretical values ranging from 5.688 to 6.2 and obtained by the dipole oscillator strength distribution,\(^{23}\) MBPT,\(^{22}\) and linear response density functional theory\(^ {24}\) methods. One bound state with energy of \(-0.035 \) cm\(^{-1}\) relative to the dissociation limit is found for the system with rotational angular momentum \( J=0 \) corresponding to masses of 19.992 440 175 9 and 1.007 825 amu for Ne and H, respectively.

#### B. Elastic differential and total cross sections

The calculated differential cross sections at selected energies are shown in Fig. 2. The system starts to enter the cold and ultracold regimes for collision energies below \( 10^{-3} \) eV. For energies smaller than \( 10^{-5} \) eV \( s \)-wave scattering dominates and the scattering length \( a \) may be obtained by fitting the effective range formula,\(^{28}\)

\[ k \cot \delta_0 = - \frac{1}{a} + \frac{1}{2} r_e k^2 + O(k^3). \] (18)

The derived \( a \) and \( r_e \) are 50.3 and 13.6 a.u., respectively. With increasing scattering energies more partial waves contribute and the differential cross sections demonstrate a detailed angular dependence which determines the energy transfer process. With further increase in energy, small angle scattering dominates.

The total and the momentum transfer cross sections as a function of the projectile energy are shown in Fig. 3. The momentum transfer cross section is defined as

![Fig. 1. Diatomic potential of H–Ne.](image1)

![Fig. 2. Differential cross sections at selected CM collision energies e.](image2)

![Fig. 3. Total and transport cross sections as a function of CM collision energy.](image3)

**TABLE I. Spectroscopic data for the diatomic molecule HNe.**

<table>
<thead>
<tr>
<th>( R_e ) (bohr)</th>
<th>( D_e ) (meV)</th>
<th>( C_6 ) (a.u.)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.466</td>
<td>1.497</td>
<td>5.80</td>
<td>Present</td>
</tr>
<tr>
<td>6.54</td>
<td>1.346</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>6.48</td>
<td>1.49</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>6.42</td>
<td>1.46</td>
<td>21 (expt.)</td>
<td></td>
</tr>
<tr>
<td>6.52</td>
<td>1.36</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.71 ± 0.07</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.227</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.688</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>
where the transport integral 

\[ \sigma_{\text{transport}}(E) = \int \frac{d\sigma(E, \chi)}{d\Omega}(1 - \cos \chi) d\Omega, \]

(19)

where \( d\sigma(E, \chi)/d\Omega \) is the differential cross section for scattering into the solid angle \( d\Omega \) given by Eq. (4). The classical diffusion coefficient \( D_{AB} \) can be evaluated from the momentum transfer cross sections,

\[ D_{AB} = \frac{3k_BT}{16\mu\Omega_{AB}} \frac{1}{(n_A + n_B)}, \]

(20)

where the transport integral \( \Omega_{AB} \) is given in terms of binary collisions between species A and B by

\[ \Omega_{AB} = \frac{2}{\sqrt{\pi\mu}} \left( \frac{1}{2k_BT} \right)^{5/2} \int_0^{\infty} e^2 \exp\left(-\frac{e}{k_BT}\right) \sigma(e) de, \]

(21)

where \( k_B \) is the Boltzmann constant, \( \sigma(e) \) is given by Eq. (19), and \( (n_A + n_B) \) is the total molecular number density. \( D_{\text{HNe}} \) can be reproduced within 1% by the following expressions:

\[ D_{\text{HNe}} = \frac{1 \times 10^{16}}{n_H + n_{\text{Ne}}} \times \left[ 39.505 - 13.817 \times e^{-0.046561T} \right. \]
\[ - 33.071 \times e^{-0.552087T} ] (cm^2 s^{-1}), \quad T \leq 40 \text{ K}, \]

\[ D_{\text{HNe}} = \frac{1 \times 10^{16}}{n_H + n_{\text{Ne}}} \times \left[ 38.641 - 0.011209 \times T + 1.1869 \right. \]
\[ \times 10^{-7} \times T^{2.5624} + 18.681 \times \ln(0.00822997) \]
\[ + 29.29 \times e^{-0.011038T} ] (cm^2 s^{-1}), \quad T > 40 \text{ K}. \]

C. Energy transfer kinetics

The calculated differential cross sections were used to construct \( B(E|E’) \) at characteristic bath gas temperatures of 10 and 15 K with various densities of the Ne gas. In Fig. 4 we show the kernel at 15 K for a density of \( 10^{15} \text{ cm}^{-3} \) for initial energies of \( 8.5 \times 10^{-4} \) and 0.28 eV. At both energies, sharp maxima occur at \( E \sim E’ \) because collisions are dominated by small angle scattering involving small energy losses.

In applications the hard-sphere approximation (HSA) is often adopted because of its analytical simplicity. Although it lacks angular and energy dependence, an appropriately selected HS cross section provides a realistic account of the physical processes. We found that a HS cross section of 18 Å² reproduces the kernel of the Boltzmann equation at an initial LF energy of 0.28 eV, whereas the kinetics of the thermalization were recovered by a HS cross section of 58 Å². The larger HS cross section for the thermalization is a consequence of the absence of angular dependence and the suppression of the peaks in the kernel of the Boltzmann equation obtained with the HSA, indicated in Fig. 4. At the lower energy of \( 8.5 \times 10^{-4} \text{ eV} \), the difference between the HSA kernel and the purely quantum mechanic kernel is less because of the slower variation with scattering angle.

In the proposed experiment the hydrogen is initially held in a magnetic trap with a thermal energy of about 1 K. The hydrogen atoms are heated through collisions with the flowing neon gas at temperatures between 13 and 17 K. The density of the neon gas is much larger than that of the hydrogen atoms and decays exponentially with time. The feasibility of this trapping proposal depends on the energy transfer rate from neon gas to hydrogen. To gain a better understanding of the kinetics, we investigated the energy transfer process at different bath gas densities and temperatures.

The energy distribution functions of hydrogen atoms were obtained numerically according to Eq. (11). In Fig. 5 we present the translational energy distribution functions at selected times for hydrogen atoms in neon gas with a density of \( 10^{15} \text{ cm}^{-3} \) and a temperature of 15 K. At \( t=0 \) the energy distribution function of hydrogen atoms is a delta function peaked at 1 K. As time progresses its amplitude at high energies increases only slowly due to the small cross sections. Gradually the distribution function assumes a Maxwellian-
independent bath gas density, the dependence of the average kinetic energy evolution curve to the Boltzmann equation. The relaxation kinetics from a time-dependent density varying as $n(t) = n_0 e^{-t/t_0}$, where $t_0$ is the inverse of the rate of change of the bath gas density, estimated to be less than 60 $\mu$s. Three trial values of 60, 40, and 20 $\mu$s are adopted for our simulation for which we used three initial bath gas densities of $1.22 \times 10^{13}$, $8.11 \times 10^{13}$, and $4.01 \times 10^{15}$ $\text{cm}^{-3}$. The calculated trapping efficiencies expressed as percentages of the spin-up hydrogen atoms at times of 60 and 100 $\mu$s are listed in Table II. Multiplication of the percentages by the product of the initial Ne density, the H to Ne density ratio, and the fraction of the initially trapped H atoms to total number of atoms yields the number density of trapped H atoms. The factors of 0.28 and 0.74 correspond to the fractions of initially trapped H atoms in 1T and 3T traps, respectively. They are given by $f_{\text{tr}} = f(E) dE$, where $f(E)$ is the initial Maxwell distribution and normalized to unity. After 100 $\mu$s, the Ne density for all three conditions is less than $10^{14}$ $\text{cm}^{-3}$, and it continues to decay with a slower change until 1 ms when the density becomes $10^{11}$ $\text{cm}^{-3}$. The small Ne density in this time period causes a slow energy transfer between H and Ne atoms and a slow decrease in the trapping percentage as shown by the small changes in the trapping percentage from $t=60$ $\mu$s to $t=100$ $\mu$s. For the fastest decay rate, $t_0=20$ $\mu$s, the decay is slowest.
crease is \( \sim 2\% \). For the slower density decay rate, the largest decrease does not exceed 20\%, and, in general, it is \( \sim 15\% \). Therefore, the further decrease in trapped H atoms will be less than 10\% even for the slowest density decay rate in our simulations.

The dependence of the trapping percentage on the initial density \( N_0 \) and on the decay rate \( t_0^{-1} \) is not linear. The trapped percentage increases with the decrease in \( N_0 \), but the number density of trapped H atoms decreases from \( 1.22 \times 10^{10} \) to \( 1.11 \times 10^{10} \) \( \text{cm}^{-3} \) for a 1T trap with \( t_0 = 60 \) \( \mu \text{s} \). On the other hand, the fastest density decay, \( t_0 = 20 \) \( \mu \text{s} \), increases the number density of trapped H atoms by a factor of \( \sim 2 \) for the same 1T trap. For the intermediate decay rate, \( t_0 = 40 \) \( \mu \text{s} \), the increase is less than 30\% for both of the 3T and 1T traps compared to \( t_0 = 20 \) \( \mu \text{s} \). The deeper trap will also help to retain the H atoms. Compared to the 1T trap, the 3T trap generally increases the number density of trapped H atoms by a factor of \( \sim 4 \) for the same conditions.

It seems there is no optimal condition such that the trapped number density is a maximum with respect to the initial density and decay rate, but the fast density decay and deeper trap will certainly help to trap the H atoms. Our simulations suggest that a trapped number density on the order of \( 10^8 \) \( \text{cm}^{-3} \) could be achieved. No magnetic field is considered in the Boltzmann equation, but the estimated order of magnitude will not change much.

**IV. SUMMARY AND CONCLUSION**

*Ab initio* calculations of the time-dependent thermalization of initially cold hydrogen atoms in a buffer gas of neon atoms were performed. The atomic interaction potential was constructed at the coupled cluster level of theory with extrapolation to the complete basis limit. Elastic differential cross sections were evaluated quantum mechanically. The derived scattering length and effective range are 50.3 and 13.6 a.u., respectively. The diffusion coefficient was evaluated at temperatures between 1 and 1000 K. The kernels of the Boltzmann equation, describing the rate of energy change collisions in the LF, were constructed using the elastic differential cross sections, and the corresponding time-dependent solutions of the Boltzmann equation were used to simulate a proposed experiment for trapping hydrogen atoms. A number density of trapped H atoms on the order of \( 10^9 \sim 10^8 \) \( \text{cm}^{-3} \) was obtained in our simulation. It supports the proposed experiment in which a hydrogen density of the order of \( 10^8 \) \( \text{cm}^{-3} \) was estimated, based on approximations and a simplified kinetic theory.

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19 H.-J. Werner, P. J. Knowles, R. Lindh et al., MOLPRO is a package of \textit{ab initio} programs.