The He–CaH($^{2}\Sigma^{+}$) interaction. II. Collisions at cold and ultracold temperatures

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We present cross sections for rotational, vibrational, and fine-structure transitions in He–CaH($^{2}\Sigma$) collisions at cold and ultracold temperatures calculated using the ab initio potential energy surface reported in the preceding paper. Rotational quenching is fast, vibrational quenching is slow. The spin-rotational interaction, although small and having no influence at temperatures above 10 K, changes significantly the rate coefficients for rotational quenching at lower temperatures. The theoretical rotational, vibrational, and elastic cross sections are compared with the results of a buffer gas cooling experiment carried out at a temperature of about 0.4 K. The theoretical predictions for the vibrational and elastic cross sections are larger than the measured values. The sensitivity to the potential energy surface is explored. A modified surface diminishes but does not remove the differences between theory and experiment.

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I. INTRODUCTION

Recent advances in cooling and trapping atoms at ultracold temperatures have generated much interest in ultracold molecules1–7, although the complex structure of molecules makes it a more challenging task to cool and trap them. Methods developed for creating ultracold molecules include photoassociation of ultracold atoms,8–15 buffer gas cooling of paramagnetic molecules,16–18 electrostatic cooling of polar molecules,19–26 and supersonic expansion in a rapidly rotating molecular beam.27 Photoassociation produces molecules in highly excited vibrational levels and the efficiency of quenching of rovibrationally excited molecules by collisions with ultracold atoms has attracted considerable theoretical interest.28–34 Chemical reactivity in ultracold atom-molecule collisions has also been explored recently.35–37

While quantum scattering calculations of ultracold atom-diatom systems can be carried out without any approximations, large uncertainties may still be present due to inaccuracies in the intermolecular potential. It is not clear to what extent the uncertainties in the potential energy surfaces affect cross sections at ultracold temperatures and whether the best ab initio methods can provide reliable interaction potentials for ultracold collisional studies. The only atom-molecule system for which experimental measurements of inelastic energy transfer are available at sub-Kelvin temperatures is the He–CaH system. Doyle and co-workers17 cooled CaH molecules by elastic collisions with 3He buffer gas atoms and confined them in a magnetic trap at temperatures of around 0.4 K. Most CaH molecules were produced in the ground rovibrational level with a small fraction in the v = 1 vibrational level. Doyle and coworkers estimated cross sections for elastic and rovibrationally inelastic collisions between the trapped molecules and the 3He buffer gas atoms but no theoretical calculations were available for comparison with the experimental results.

Here we investigate the collisions between 3He atoms and CaH($^{2}\Sigma$) molecules using the potential energy surface developed in the preceding paper38 and compare the theoretical results with the experimental data of Weinstein et al.17,18 We also explore the effect of spin-rotational coupling in $^{2}\Sigma$ molecules and investigate how it modifies collision cross sections at cold (<1 K) and ultracold temperatures (<10−3 K). The energy splitting of rotational levels of CaH due to spin-rotational interaction is comparable to collision energies in cold collisions and it is important to understand whether spin-rotational interaction affects cross sections in cold and ultracold collisions. Our results show that spin-rotational coupling modifies the rotational quenching cross sections at ultracold temperatures and leads to interesting resonance structures in the cross section.

The paper is organized as follows: In Sec. II we briefly describe the methodology for close-coupled scattering calculations. Cross sections and rate coefficients for elastic and inelastic scattering and a discussion of the effect of spin-
II. THEORY

The theory for quantum calculations of cross sections for collisions of a diatomic molecule in the \( ^2\Sigma \) state with a structureless target has been described in detail by Alexander and Corey and McCourt. Our approach is different in that we perform calculations in the body-fixed basis and use an uncoupled representation of the wave function. The total Hamiltonian of the He–CaH\(^{2}\Sigma \) system can be written

\[
\hat{H} = -\frac{\hbar^2}{2\mu R} \frac{d^2}{dR^2} R + \frac{\hbar^2}{2\mu R^2} + V(R, r, \theta) + \hat{H}_{CaH} + \hat{V}_{SR},
\]

(1)

where \( \mu \) is the reduced mass of the colliding particles, \( \hat{l} \) is the orbital angular momentum for the collision, \( V \) is the global potential for the He–CaH interaction, \( R \) is the center-of-mass separation between He and CaH, \( r \) is the interatomic distance in CaH, \( \theta \) is the angle between the vectors corresponding to \( R \) and \( r \), \( \hat{H}_{CaH} \) is the rovibrational Hamiltonian of the diatomic molecule and \( \hat{V}_{SR} \) is the operator describing the spin-rotation interaction in CaH\(^{2}\Sigma \). The spin-rotation operator is assumed to be independent of \( R \) and \( \theta \) and it is represented by the form

\[
\hat{V}_{SR} = \gamma \hat{S} \cdot \hat{N},
\]

(2)

where \( \hat{S} \) and \( \hat{N} \) are the electronic spin and nuclear rotational angular momenta of the diatomic molecule, respectively, and \( \gamma \) is the phenomenological spin-rotation constant equal to 0.0415 cm\(^{-1}\) in CaH.\(^{43}\)

The eigenfunction of the total Hamiltonian (1) is expanded in products of vibrational \( (\chi_{vN}) \), rotational \( (Y_{N\ell}) \) and spin functions of the diatomic molecule as follows:

\[
\Psi_{JM} = \frac{1}{R} \sqrt{\frac{2J+1}{4\pi}} \sum_{vN\ell\Sigma} F_{vN\ell\Sigma}(R) \chi_{vN}(r) \times Y_{N\ell}(\theta, \phi) \langle S\Sigma | J \rangle D_{\ell M\Omega}^{j}(\alpha, \beta, 0),
\]

(3)

where \( k \) and \( \Sigma \) are the projections of \( \hat{N} \) and \( \hat{S} \) on the body-fixed axis \( R \), \( \Omega = k + \Sigma \), \( J \) is the total angular momentum of the triatomic system with projection \( M \) on the space-fixed axis, \( D_{\ell M\Omega}^{j} \) are Wigner rotation functions, \( \phi \) is the polar angle of the diatomic axis in the body-fixed frame, and \( \alpha \) and \( \beta \) are polar coordinates of \( R \) with respect to a space-fixed frame.

Substitution of expansion (3) in the stationary Schrödinger equation with the Hamiltonian (1) leads to the following system of coupled equations for expansion coefficients \( F_{vN\ell\Sigma}^{j} \):

\[
\frac{d^2}{dR^2} F_{vN\ell\Sigma}^{j} + \left( \frac{k^2}{\hbar^2} R^2 - V(R, r, \theta) - \hat{H}_{CaH} + \hat{V}_{SR} \right) F_{vN\ell\Sigma}^{j} + \sum_{\ell'\Sigma'} \left( \langle S\Sigma | J \rangle D_{\ell M\Omega}^{j}(\alpha, \beta, 0) \langle J \ell' \Sigma' | M \rangle \right) F_{vN\ell'\Sigma'}^{j} = 0,
\]

(4)

where \( k^2 = 2\mu(E - \epsilon_{vN})/\hbar^2 \), \( E \) is the total energy and \( \epsilon_{vN} \) is the energy of the rovibrational level of CaH\((v,N)\) without the fine structure splitting.

The matrix of the interaction potential is diagonal in both the \( S \) and \( \Sigma \) quantum numbers and the elements \( \langle u'|Nk|V(R, r, \theta)|N'k'\rangle \langle u'|v \rangle \) are the same as for the case of a diatomic molecule in the \( ^1\Sigma \) state interacting with an atom. These elements were given in the body-fixed frame by T Pack.\(^5\) The elements of the matrices of \( \hat{l}^2 \) and \( \hat{V}_{SR} \) can be written directly in the basis (3) if one makes use of the relations:

\[
\hat{l}^2 = J^2 + N^2 \pm \frac{1}{2} (J^2 - \Sigma^2),
\]

\[
\hat{V}_{SR} = \gamma \frac{1}{2} (\hat{N}_z \hat{S}_z - \hat{\Sigma}_z \hat{\Sigma}_z),
\]

(5)

(6)

The set of equations (4) is solved numerically using the log-derivative method of Johnson and Manolopoulos. The log-derivative matrix is then transformed to the representation in which the \( \hat{l}^2 \) and the spin-rotation operators are diagonal using the following relation:

\[
\langle NS|jJM \rangle = \left( \frac{2J+1}{4\pi} \right)^{1/2} \sum_{\ell\Sigma} \langle j\Omega|\ell J\rangle \langle \Omega Nk\Sigma|\Omega\ell J \rangle D_{\ell M\Omega}^{j}(\alpha, \beta, 0),
\]

(7)

where \( j = N + \hat{S} \). The scattering S-matrix is constructed in the \( |j\rangle \) representation and the cross sections for elastic and inelastic collisions are computed from its elements as usual. A similar procedure was employed in a recent study of \( ^1\Sigma \) collisions by Krems and Dalgarno where more details of the method are given.

The spin-rotation interaction is weak in \(^2\Sigma \) diatomic molecules and may be neglected in calculations of vibrational transitions. We verified that the loss of accuracy caused by its omission is negligible by carrying out selected calculations on rovibrational transitions in He–CaH collisions using the method developed for \(^1\Sigma \) molecules. The MOLSCAT program\(^9\) is used for these close-coupled (CC) scattering calculations which are performed in the space-fixed frame and the results will be referred to as the CC\(^1\Sigma \) data. The CC\(^1\Sigma \) results agree exactly with a calculation with the body-fixed program in which the spin-rotation constant \( \gamma \) was set to zero. The number of coupled equations in the accurate calculations is twice that of the CC\(^1\Sigma \) calculations.
so the omission of the spin-rotation interaction term in the Hamiltonian (1) increases the computational efficiency by a factor of eight.

III. RESULTS

A. Spin-rotation interaction in ultracold collisions

The term $\hat{V}_{SR}$ in the Hamiltonian (1) splits the rotational energy level with a given value of $N$ into two fine structure levels corresponding to the angular momenta $j=N \pm 1/2$. The splitting is small but it increases linearly with $N$. Because $\gamma$ is positive for CaH the states with $j=N+1/2$ are higher in energy. The splitting of the $N = 1$ level in CaH is 0.062 cm$^{-1}$. In the limit of zero energy, for $N=1, j=1/2$, only the rotational transition to $N=0, j=1/2$ is possible, while for the upper fine-structure level $N = 1, j=3/2$ both the rotational transition to $N=0, j=1/2$ and the fine-structure transition to $N=1, j=1/2$ may occur.

Figure 1 shows the cross sections for rotational relaxation of CaH($v=0,N=1$) in ultracold and cold collisions with $^3$He computed using the accurate approach and the CC$^1\Sigma$ approximation. At collision energies greater than 0.5 cm$^{-1}$ the cross sections for rotational relaxation of CaH($N=1$) in different fine structure levels are the same as the results of the CC$^1\Sigma$ calculations. All cross sections show a maximum at about 0.1 cm$^{-1}$. A partial wave analysis of the cross sections shows that the maximum arises from a shape resonance corresponding to the $l=2$ partial wave. The cross sections follow the Wigner behavior in the limit of vanishing collision velocity. The cross section for rotational relaxation of CaH($N=1, j=3/2$), however, shows a rapid decrease for collision energies below 0.02 cm$^{-1}$ and it is one order of magnitude smaller than that of CaH($N=1, j=1/2$) in the Wigner limit.

The suppression of the cross section for rotational relaxation of CaH($N=1, j=3/2$) in the Wigner regime can be understood by examining the behavior of the adiabatic potential curves obtained by diagonalizing the total coupling matrix at different values of $R$. We use quantum numbers $(N, S, j, I, J)$ with $J=j+I$, even though calculations were done in a body-fixed basis. At low energies $s$-wave scattering dominates and we consider only the $l=0$ partial wave in the incident ($N = 1, j=3/2, J=3/2$) channel. Thus, the total angular momentum $J$, which is a good quantum number, is equal to $j$ of the incident channel. For $s$-wave scattering in the incident ($N = 1, j=1/2, J=1/2$) channel only the $l=0$ partial wave is populated in the outgoing ($N=0, j=1/2, J=1/2$) channel, while for ($N=1, j=3/2, J=3/2$) the $l=1$ and $l=2$ partial waves are accessible in the outgoing channels of both rotational relaxation ($N=0, j=1/2, J=3/2$) and fine-structure transition ($N=1, j=1/2, J=3/2$). The adiabatic potential curves that correlate with ($N=1, j=3/2$) and ($N=1, j=1/2$) channels for $J=3/2$ are shown in Fig. 2 as functions of $R$. They cross twice at large values of $R$, at $\sim 25 a_0$ and $45 a_0$.

The maximum of the centrifugal barrier due to the $l=2$ partial wave in the outgoing ($N=1, j=1/2$) channel is larger than the splitting between the fine-structure levels (0.062 cm$^{-1}$) but it is negligible compared to the energy gap of 8.4 cm$^{-1}$ between the $N=0$ and $N=1$ levels. Therefore, the centrifugal barrier in the outgoing ($N=0, j=1/2, J=3/2$) channel is not responsible for the suppression of the rotational relaxation of the ($N=1, j=3/2$) level. The suppression arises because the coupling between the fine-structure channels at large distances directs part of the initial flux to the ($N=1, j=1/2$) channel and the centrifugal barrier in the ($N = 1, j=1/2$) channel impedes penetration to smaller values of $R$ where the rotational transition occurs.

In Fig. 3 we plot the total cross sections and the $s$-wave contributions for rotational and fine-structure relaxations of the ($N=1, j=3/2$) channel. The $s$-wave contributions show a Feshbach-type resonance which is caused by trapping behind the barrier in the outgoing ($N=1, j=1/2$) channel. The resonances are not apparent in the total cross sections because the $s$-wave contribution is small compared to those from higher partial waves. We have verified that the suppression of the rotational relaxation in the Wigner regime and the resonances disappear when the centrifugal barrier in the final ($N=1, j=1/2$) state is artificially eliminated. Formation of Feshbach-type resonances due to trapping behind centrifugal barriers in the outgoing channels has also been observed in fine-
structure transitions in atom–atom collisions at ultracold temperatures.\textsuperscript{50} There is a factor of 1.9 between the cross sections for rotational relaxation of CaH\((N=1,J=1/2)\) and of CaH\((N=1)\) computed in the CC\(1\Sigma\) approximation in the ultracold limit because the coupling matrices corresponding to total angular momenta \(J=1/2\) and \(J=1\) are different. When CaH is in higher rotational levels the efficiency of rotational energy transfer is much larger than that of fine structure transitions at all collision energies including the ultracold \(s\)-wave limit.

Figure 4 presents a comparison of accurate and CC\(1\Sigma\) calculations of cross sections for elastic collisions of CaH\((N=0,j=1/2)\) with \(^3\)He at low and ultralow collision energies. All the features of the cross section including the resonant enhancement are reproduced with high accuracy by the CC\(1\Sigma\) calculations and the resonance again occurs for the \(l=2\) partial wave. Also shown in Fig. 4 are the CC\(1\Sigma\) results for the \(^4\)He–CaH system. Compared to the \(^3\)He–CaH system the resonance is shifted to the \(l=3\) partial wave and the limiting cross section is reduced by a factor of 2.

B. Vibrational relaxation at ultracold temperatures

Cross sections for vibrationally inelastic scattering were computed within the CC\(1\Sigma\) approximation using a large basis set. The energy gap between the \(v=0,N=0\) and \(v=1,N=0\) levels is 1258 cm\(^{-1}\). There are 17 rotational levels \((N=0-16)\) between the \(v=0\) and \(v=1\) vibrational levels. We included levels \(v=0,1,\) and 2 in our basis set with rotational levels \(N=0-19\) in \(v=0\) and 1 and \(N=0-9\) in \(v=2\) forming a total of 50 rovibrational levels. The highest energy represented in the basis set is 2792 cm\(^{-1}\) with respect to the \(v=0,N=0\) level. Calculations are reported for total energy values ranging from zero to 2258 cm\(^{-1}\). Thus a large number of closed channels is present even at the highest energy in the calculations. We used the hybrid modified log-derivative Airy propagator method of Manolopoulos and Alexander\textsuperscript{51} to solve the coupled equations. The highest value of \(J\) retained in our calculations is 40 for which the number of coupled equations is 475. To obtain converged rotational populations, terms in the Legendre polynomial expansion of the interaction potential up to the 16th order were needed.

Cross sections for quenching of the \(v=1,N=0\) level of the CaH molecule by collisions with \(^3\)He are shown in Fig. 5 as functions of the kinetic energy. The cross section passes through a minimum at an energy of about 8 cm\(^{-1}\) and then increases with subsequent decrease of temperature. The increase is due to the attractive van der Waals interaction which accelerates the colliding particles into the interaction region. The peak at an energy of about 0.02 cm\(^{-1}\) is due to the \(l=2\) shape resonance. It is broader than in the elastic scattering cross section in the \(v=0,N=0\) channel and the cross section varies by about three orders of magnitude through the resonance.

At incident energies lower than 10\(^{-3}\) cm\(^{-1}\) only \(s\)-wave scattering occurs and the cross section varies inversely as the velocity in accordance with the Wigner law.\textsuperscript{52} The scattering length is real for single channel scattering where only elastic scattering occurs but it has an imaginary part when two or more channels are open. The complex scattering length for the \(v=1,N=0\) level is \(a=(a-i\beta)=(8.16-i9.18\times10^{-7})\times10^{-8}\) cm. The imaginary part \(\beta\) is related to the zero-

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FIG. 3. Cross sections for rotational (broken curves) and fine structure (full curves) relaxation in CaH\((N=1,j=3/2)\)–\(^3\)He collisions. Thin curves are the \(s\)-wave cross sections and bold lines are total cross sections.

FIG. 4. Cross section for elastic CaH\((v=0,N=0)\)–\(^3\)He collisions: Open circles—calculations for \(^3\)He–CaH with the spin-rotation interaction; solid curve—CC\(1\Sigma\) calculation for \(^3\)He–CaH; dotted curve—CC\(1\Sigma\) calculation for \(^4\)He–CaH.

FIG. 5. Cross sections for quenching of the \(v=1,N=0\) level of CaH by collisions with \(^3\)He as functions of the incident kinetic energy.
temperature quenching rate coefficient according to 

$$k_b(T \to 0) = 4\pi \beta h/\mu.$$

The zero-energy limiting value of the elastic scattering cross section is given by

$$\sigma_{el}(E_k \to 0) = 4\pi(\alpha^2 + \beta^2)^2$$

where $E_k$ is the incident kinetic energy. The scattering length for $^4$He–CaH($v=1, N=0$) is $a = (5.75 - i3.80 \times 10^{-7}) \times 10^{-8}$ cm. The elastic cross section at zero energy is $4.16 \times 10^{-14}$ cm$^2$ and the zero-temperature quenching rate coefficient is $2.6 \times 10^{-17}$ cm$^3$ s$^{-1}$.

Cross sections for transitions from the $v=1,N=0$ state of CaH to rotational levels $N_f = 0, 1, 2, 12,$ and 13 of CaH($v=0$) are shown in Fig. 6 as functions of the incident energy. Each of the individual cross sections exhibits a similar energy dependence to that of the total cross section shown in Fig. 5. However, there are subtle differences in the magnitudes of the partial cross sections at collision energies above 1000 cm$^{-1}$. High rotational states are favored at low energies but this preference tends to disappear at energies above 1000 cm$^{-1}$. The inversion in rotational populations in the ultracold limit is illustrated in Fig. 7 at an incident energy of $10^{-6}$ cm$^{-1}$. Such inversions in rotational populations have been observed in Ar+HF and Ar+HCl collisions at higher incident energies between 300 and 3000 cm$^{-1}$ by Krems et al.$^{53,54}$ who suggested that they are due to the large anisotropy of the interaction potential. The rotational level in $v=0$ that is closest in energy to the initial $v=1,N=0$ level is $N=16$. The enhancement of such near-resonant transitions may be limited because the conservation of classical action is also significant in determining the final rotational populations.$^{31,53,54}$

The rate coefficient for the quenching of the $v=1,N=0$ level is shown in Fig. 8 as a function of the temperature in the range $10^{-5}$ to 100 K. As the temperature decreases from 100 K, the rate coefficient passes through a minimum value of about $2 \times 10^{-16}$ cm$^3$ s$^{-1}$ at 4 K and then increases to reach a maximum value of $10^{-14}$ cm$^3$ s$^{-1}$ at 2 $\times 10^{-2}$ K. The rate coefficient decreases with further decrease of temperature, and at zero temperature attains the finite limiting value of $2.6 \times 10^{-17}$ cm$^3$ s$^{-1}$. The dramatic increase in the rate coefficient by a factor of 50 in the temperature range from 4 to $10^{-2}$ K is due to a combination of the attractive van der Waals interaction and the shape resonance shown in Fig. 5. The temperature dependence of the rate coefficient is similar to that observed for the vibrational relaxation of CO($v=1,N=0$) by collisions with $^4$He (Ref. 32) but the rate coefficient for the present system is orders of magnitude larger due to the greater anisotropy of the interaction potential as the bond is stretched compared to CO. The equilibrium bond distances of CaH and CO are 3.795 $a_0$ and 2.132 $a_0$, respectively.

We have also considered vibrational and rotational quenching from excited rotational levels in $v=1$. Cross sections for pure rotational quenching from excited rotational levels of $v=1$ are comparable to those shown in Fig. 1 for $v=0$. Vibrational quenching from excited rotational levels of $v=1$ depends only weakly on $N$. We obtain limiting values of $3.7 \times 10^{-17}$, $2.9 \times 10^{-17}$, and $2.1 \times 10^{-17}$ cm$^3$ s$^{-1}$, respectively, for the rate coefficients of vibrational relaxation of CaH($v=1,N=1–3$) in collisions with $^3$He at zero temperature.

### C. Sensitivity to interaction potential

The experimental data on $^3$He–CaH collisions were obtained at a temperature of about 0.4 K. The computed cross sections exhibit a resonance at about 0.02 cm$^{-1}$ which significantly enhances the rate coefficients at temperatures near 0.4 K. Resonance positions are often sensitive to the interac-

![FIG. 6. Cross sections for relaxation of CaH($v=1,N=0$) to individual rotational levels $N_f$ of $v=0$ as functions of the incident kinetic energy.](image)

![FIG. 7. Rotational populations of the CaH molecule in the $v=0$ level after quenching from the $v=1,N=0$ level at an incident energy of $10^{-6}$ cm$^{-1}$.](image)

![FIG. 8. Rate coefficient for the quenching of the $v=1,N=0$ level of the CaH molecule as a function of the temperature.](image)
We carried out a series of calculations in which the interaction potential was slightly modified to explore the sensitivity of the cross sections to small changes in the interaction potential. The modified potential is defined as

\[ \tilde{V} = V_{\text{CCSD}}(T) + f \left( V_{\text{CCSD}}(T) - V_{\text{CCSD}} \right), \]

where \( V_{\text{CCSD}}(T) \) is the original potential computed with perturbative triples and \( V_{\text{CCSD}} \) is the interaction potential computed without the triples contribution. We extrapolate the contribution of the triples by taking \( f \) equal to 0.10 and 0.15. For \( f = 0 \) we recover the original potential. The effect of the triples contribution is to make the entire attractive part of the potential more attractive and the entire repulsive part less repulsive. For \( f = 0.10 \)– 0.15 the van der Waals minimum becomes more attractive by 2%–3%. This change is of the same order as the uncertainty in the \textit{ab initio} potential, which was estimated in Paper I to be a few percent.

Figure 9 shows the spherically symmetric parts of the original potential and the modified potential with \( f = 0.15 \) averaged over the \( v = 0 \) vibrational wave function of the CaH molecule. The modified potential with \( f = 0.10 \) would be almost indistinguishable in this plot and is not shown.

Elastic scattering cross sections obtained from the modified potential with \( f = 0.10 \) and 0.15 and the original potential are shown in Fig. 10. For \( f = 0.10 \), the resonance shifts to 0.004 cm\(^{-1}\) with a sharper peak, and for \( f = 0.15 \), the resonance goes away. The background cross sections on which the resonances structures are superposed and the zero energy limits are nearly identical for all three potentials.

A comparison of the results for vibrational quenching collisions for the three potentials is shown in Fig. 11. As for the elastic collisions, the resonance moves to a lower energy for \( f = 0.10 \) and disappears for \( f = 0.15 \). Outside the energy region of the resonances the cross sections merge smoothly with those corresponding to the original potential. The cross sections in the Wigner regime are the same for all three potentials.

Changes within the uncertainty of the \textit{ab initio} potential can shift or eliminate resonances. In the following section, we compare our results obtained with the modified potential and the original potential with the experimental data.

IV. COMPARISON WITH EXPERIMENTAL RESULTS

A. Elastic scattering

In the experiments of Doyle and co-workers\textsuperscript{17,18,55} CaH molecules were produced by laser ablation of a solid sample of CaH\(_2\). The CaH molecules in the low field seeking states were trapped after thermalizing collisions with the \(^3\)He buffer gas atoms at a temperature of about 0.4 K. The molecules were mostly produced in their ground state except for a small fraction in the excited \( v = 1 \) level. By measuring the diffusive loss of the molecules in the absence of the trapping field, Weinstein \textit{et al.}\textsuperscript{17} obtained a lower limit of \( 10^{14} \) cm\(^{-2}\) for the elastic momentum transfer collision cross section between \(^3\)He and CaH at a temperature of about 0.4 K. This limit was revised to a cross section of \( 1.5 \pm 0.6 \times 10^{14} \) cm\(^{-2}\) in the thesis of Weinstein.\textsuperscript{55}

The elastic cross sections for the collisions of CaH with \(^3\)He are shown in Fig. 10 as a function of the energy. The
measurement refers to the momentum transfer or transport cross section for a thermal population of molecules. The transport cross section is defined as

$$\sigma_T(E) = 2\pi \int_0^\pi d\chi \frac{d\sigma(E)}{d\chi} (1 - \cos \chi) \sin \chi \, d\chi,$$  \hspace{1cm} (9)

where $d\sigma(E)/d\chi$ is the differential cross section and $\chi$ is the scattering angle. They were computed explicitly from Eq. (9) by first evaluating the differential cross sections. By integrating the product of the transport cross sections and the relative velocity over a Maxwellian velocity distribution and dividing by the average thermal velocity we obtain effective transport cross sections. Figure 12 compares our results obtained on the original potential and the potential with $f = 0.15$ with the experimental result. The results obtained from the modified potential with $f = 0.10$ are almost the same and are not included. The effect of the resonance on the transport cross section is very small, because the contributions from small angle scattering is suppressed by the $(1 - \cos \chi)$ factor in Eq. (9). Theory and experiment are consistent in finding a large cross section but the theoretical cross sections exceed the measured cross sections by a factor of 3 at 0.4 K.

B. Rotational relaxation

Because of the very high rates of rotational relaxation rotationally excited CaH molecules were not directly detected in the experiments. A lower limit of $10^{-15} \text{ cm}^3 \text{ s}^{-1}$ was reported for the rate coefficient for the rotational relaxation of CaH($v=0,N=1$) by collisions with $^3$He at 0.4 K. The predicted values of the rate coefficients are given in Table I for temperatures up to 100 K. They are several orders of magnitude larger than the experimental lower limit. These rate coefficients are reported only for the original potential.

C. Vibrational relaxation

For the quenching of the vibrational level $v=1$, Weinstein et al.\textsuperscript{55} reported an upper limit of $10^{-16} \text{ cm}^3 \text{ s}^{-1}$. Theory and experiment are consistent in finding a large cross section but the theoretical cross sections exceed the measured cross sections by a factor of 3 at 0.4 K. Theoretical rate coefficients for vibrational quenching obtained using the original potential are listed in Table I. The rate coefficient at 0.5 K is $6.4 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$, a factor of 6 larger than the experimental upper limit. A major contribution to the rate coefficient arises from the $J=2$ shape resonance shown in Fig. 11. For the $f=0.15$ case for which there occurs no resonance we obtain a value of $2.4 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ at 0.5 K which is about a factor of two larger than the upper limit given by experiment. For both elastic and vibrational quenching collisions, our cross sections are a factor of two or more larger than the experimental values.

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by a factor of 50 between 4 and 0.01 K due to a $d$-wave shape resonance. The vibrational quenching rate coefficients are four to five orders of magnitude smaller than pure rotational quenching rate coefficients. Because vibrational quenching is so slow, as long as the molecules are in the $N = 0$ rotational level, they can be trapped in excited vibrational levels without significant trap loss. We drew similar conclusions for CO (Ref. 32) and $O_2$. 33

Our calculations yield momentum transfer cross sections larger by a factor of 2 or 3 from the measurements. Vibrational relaxation rate coefficients are found to be more sensitive to the presence of resonances in the cross section. The resonance position is very sensitive to small changes in the interaction potential. Because the position of the resonance is close to the energy regime explored by the experiment, it makes a large contribution to the rate coefficient near 0.4 K. We get a rate coefficient larger than the experiment by a factor of 8. The uncertainties in the potential energy surface make a large contribution to the rate coefficient near 0.4 K.

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