Isotope effects in complex scattering lengths for He collisions with molecular hydrogen

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We examine the effect of theoretically varying the collision-system reduced mass in collisions of He with vibrationally excited molecular hydrogen and observe zero-energy resonances for select atomic "hydrogen" masses less than 1 u or a "helium" mass of 1.95 u. Complex scattering lengths, state-to-state vibrational quenching cross sections, and a low-energy elastic scattering resonance are all studied as a function of collision-system reduced mass. Experimental observations of these phenomena in the cold and ultracold regimes for collisions of ^{3}He and ^{4}He with H_2, HD, HT, and DT should be feasible in the near future.

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I. INTRODUCTION

Recent advances in creating dense samples of translationally cold molecules have generated much interest in understanding atomic and molecular interactions at temperatures close to absolute zero. Concurrently, collisions of rotationally and vibrationally excited molecules with cold atoms and diatomic molecules have received considerable theoretical and experimental attention [1–4]. Investigation of chemical reactivity in cold and ultracold atom-molecule collisions and how the reactivity could be influenced by external electric and magnetic fields are topics of ongoing research in this area [2–4].

A key aspect of ultracold collisions is that the collisional outcomes are generally sensitive to details of the interaction potential. At temperatures lower than 1.0 K, perturbations introduced by external electric and magnetic fields are comparable to the incident kinetic energy and external fields may strongly influence resulting collisional parameters. This is especially the case if the bound state energy levels of the molecule are modified by the presence of the external field inducing new resonances or eliminating existing ones [5]. There is also extensive literature on isotope effects in chemical reactions [6,7] and recent studies indicated that these effects are more pronounced in ultracold collisions, especially when tunneling or threshold resonances are present [3,8,9]. Indeed, it has been shown that varying the reduced mass of the collision complex in a scattering calculation is equivalent to adjusting the interaction potential [10]. Bodo *et al.* [9] demonstrated this for the $F + H_2$ reaction by artificially varying the mass of the hydrogen atom from 0.5 to 2.0 u. They found that for a fictitious "hydrogen" mass of 1.12 u, a zero-energy resonance is formed in this collision system yielding a zero-temperature rate coefficient that is about three orders of magnitude larger than the corresponding value for the $F + H_2$ reaction. This effect is somewhat akin to the Feshbach resonance method in which the scattering length is varied by sweeping a magnetic field across a Feshbach resonance that couples a bound state of the molecule to the energy of two colliding atoms [11–13].

Furthermore, reduced mass tuning of the complex scattering length near zero-energy resonances may be useful in constructing complex optical potentials for each rovibrational level. The resulting one-dimensional potentials would be easier to use in subsequent applications (e.g., molecules in an external field) than the corresponding coupled-channel potentials. In this approach, the zero-energy resonances would play a similar role to that of magnetic Feshbach resonances when an asymptotic bound state model [14–16] is used to construct model potentials.

Here, we show the effect of artificially varying the mass of the hydrogen atom or the He atom in He collisions with H_2, with an aim of understanding the sensitivity of the cross sections to small changes in the interaction potential as well as energies of quasibound triatomic complexes formed during the collision.

II. METHODOLOGY

Our analysis is primarily based on the behavior of cross sections in the Wigner threshold regime [17] where the scattering length approximation can be conveniently used to characterize elastic and inelastic scattering [18,19]. For multichannel binary collisions with more than one open channel, the scattering length is a complex quantity $a = \alpha - i\beta$, the imaginary part of which is a measure of the rate of decay of an excited

state; this quantity β may be derived from the inelastic cross sections [18]. A number of previous studies have obtained the complex components of the scattering length including calculations of H-H_2 [18] and He-H_2 [19–21] scattering. In this Brief Report we extend this analysis to scattering between He and a range of real and artificial isotopes of H_2. Specifically, we consider the three cases in which we set one atom in the diatom to be H, D, or T and vary the mass of the other atom giving collisions of the form ^{3}He-HX and ^{4}He-HX, ^{3}He-DX and ^{4}He-DX, and ^{3}He-TX and ^{4}He-TX, where X is varied over a large range of masses, excluding homonuclear cases. Thus the limit for the HX reduced mass as X approaches infinity is $\mu = m_{\rm H} = 1.00794$ u, that for DX is $\mu = m_{\rm D} = 2.0135532127$ u, and for TX it is $\mu = m_{\rm T} = 3.0160492$ u. The entrance channel in each case is selected to be $v = 1$, $j = 0$, and we consider only collisions in the ultracold limit (we adopt a collision energy of 10^{-6} cm^{-1}, except in the case of the elastic p-wave scattering resonance). Artificially varying the helium mass is also considered for collisions with HD.

For an initial state with vibrational and rotational quantum numbers v and j, the imaginary part of the scattering length β_{vj} in the limit of zero initial kinetic energy is given by

$$\beta_{vj} = k\sigma_{vj}^{\rm in}/4\pi, \tag{1}$$

where k is the initial wave vector and $\sigma_{vj}^{\rm in}$ the sum of the inelastic cross sections of all open channels [18]. In the limit $k \to 0$, the relation between the elastic cross section $\sigma_{vj}^{\rm el}$ and the scattering length a_{vj} is given by [18]

$$\sigma_{vj}^{\rm el} = 4\pi\left(\alpha_{vj}^2 + \beta_{vj}^2\right) = 4\pi|a_{vj}|^2, \tag{2}$$

from which the magnitude of the real part of the scattering length is given by

$$|\alpha_{vj}| = \sqrt{\sigma_{vj}^{\rm el}/4\pi - \beta_{vj}^2}, \tag{3}$$

while the sign of α_{vj} is determined from the sign of the phase shift.

III. COMPUTATIONAL METHOD

Elastic and inelastic cross sections were obtained by performing close-coupling calculations using the nonreactive scattering program MOLSCAT [22]. The potential energy surface (PES) adopted here was that of Muchnick and Russek (MR) [23]; this surface, along with that of Boothroyd *et al.* (BMP) [24], was discussed previously by Lee *et al.* [25] who performed state-to-state rovibrational scattering calculations for He-H_2 and found that the MR surface gave the best agreement with available experimental data at thermal energies.

In the current work, the isotope dependencies are included by adjusting the collision-system reduced mass, the mass of the diatom in determining the rovibrational energies, and the location of the diatom center of mass for specifying the Jacobi coordinates. We do not consider mass-dependent adiabatic or nonadiabatic corrections to the PES [26]. The scattering calculations are performed using the close-coupling method with appropriate convergence tests performed for the basis set size, asymptotic matching distance, and number of quadrature points for evaluating the matrix elements of the interaction potential. Three partial waves were found to be adequate for convergence for the ultracold calculations while a larger number of partial waves was used for the elastic resonance studies.

IV. RESULTS

It was previously predicted by Balakrishnan *et al.* [19] in their study of collisions of H_2 with ^{3}He and ^{4}He that for each vibrational level of H_2 one should find an associated bound state of He-H_2 lying below the dissociation limit of the He-H_2 complex. In what amounts to an adjustment of the well depth of the interaction potential between the atom and molecule, we here varied the reduced mass of H_2. In Fig. 1 we show the real (elastic) part of the scattering length as a function of μ/μ_{H_2}, where μ_{H_2} is the reduced mass of H_2. Zero-energy resonances are identified for the case of HX with ^{3}He and ^{4}He at mass ratios of 0.94 and 0.78. The former value is smaller than, but very close to, the physical reduced mass limit of H_2 (i.e., of two H atoms). Possible resonances corresponding to bound states for the other isotopomer-He combinations may occur at much lower mass ratios than considered here. The effect of varying the helium mass for the He-HD case is shown in the inset of Fig. 1. It is seen that a zero-energy resonance occurs for a "helium mass" of ~1.95 u.

The imaginary part of the scattering length β_{10} is displayed in Fig. 2 for ^{3}He and ^{4}He where it is seen to generally increase with decreasing mass ratio below a value of ~2. Some oscillatory behavior is also evident below $\mu/\mu_{H_2} = 1$ for DX. For instance, a large resonance occurs near a mass ratio 0.58 for both ^{3}He-DX and ^{4}He-DX, and then another peak at ~0.75 followed by a much smaller one at 0.98. However, as discussed by Flasher and Forrey [27], the ratio β_{10}/α_{10}^2 is found to vary smoothly as the reduced mass is decreased through the zero-energy resonance for both cases. The inset shows the variation of β_{10} with the mass of the helium atom for He-HD collisions. For a "helium mass" of ~1.95 u, which corresponds to the zero-energy resonance in Fig. 1, β_{10} increases by about three orders of magnitude compared to the ^{3}He case and four orders of magnitude compared to the ^{4}He case.

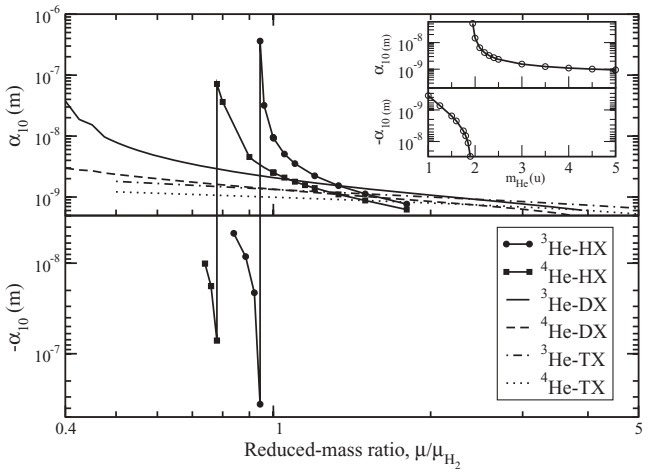

FIG. 1. Real part α_{10} of the scattering length for ^{3}He and ^{4}He collisions with HX, DX, and TX as a function of the ratio of the reduced masses of the hydrogen isotopomer and H_2. (Inset) α_{10} for a variation of the He mass for He-HD collisions.

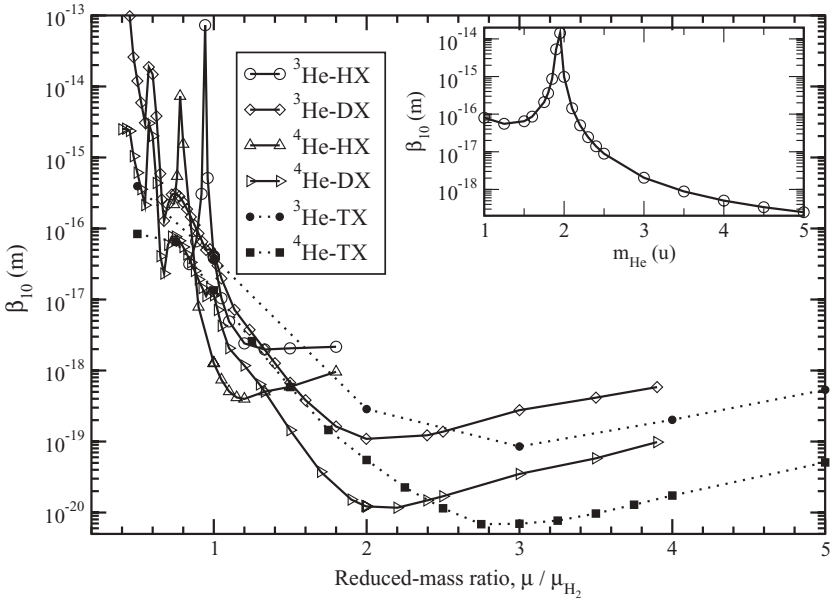

FIG. 2. Same as Fig. 1, but for the imaginary part β_{10} of the scattering length.

The oscillatory behavior in β_{10} can be understood by considering the state-to-state cross sections for ^{3}He-DX, for example, given in Fig. 3. For H_2, rotational levels up to $j' = 8$ are open in the ultracold limit. As the mass is decreased, the highest rotational state is not energetically accessible at the collision energy considered here. For example, the $j' = 7$ state is only accessible for mass ratios greater than about 0.58, which is the location of a resonance in β_{10}. However, its cross section decreases sharply to a minimum at a mass ratio of 0.68. Further, the state-to-state cross section for $j' = 7$ has a maximum at 0.75, which corresponds to a maximum in β_{10}. The maximum for the mass ratio of 0.98 is then caused by the appearance of the $j' = 8$ state as it becomes energetically open.

In their study of He-H_2 transitions with initial state ($v = 1$, $j = 0$) using the BMP surface, Lee *et al.* [25] observed a similarly acute dependence of particular state-to-state rate coefficients on reduced mass. In increasing the molecular reduced mass, the $j' = 8$ rate coefficient was seen to decrease exponentially while other rotational states showed a much less sensitive dependence, with the $j' = 10$ channel only becoming exoergic and contributing at a relatively high reduced mass. A somewhat similar situation can be seen in Fig. 3, though using the MR PES.

In Fig. 4(a), we present the elastic cross section in the cold to ultracold regimes for ^{4}He collisions with H_2 and three physical isotopes. At ultracold energies, the elastic cross section decreases with increasing target mass. Also, a p-wave resonance occurs near $\sim$1 cm^{-1} for H_2. Figure 4(a) shows that this resonance shifts to lower energies with increasing molecular target mass with the peak becoming broader and having a maximum at a value of $\sim$0.07 cm^{-1} for DT, but the magnitude of the resonance is largest for HT. Resonances for larger values of J are also present, but difficult to discern from the background cross section. However, as illustrated

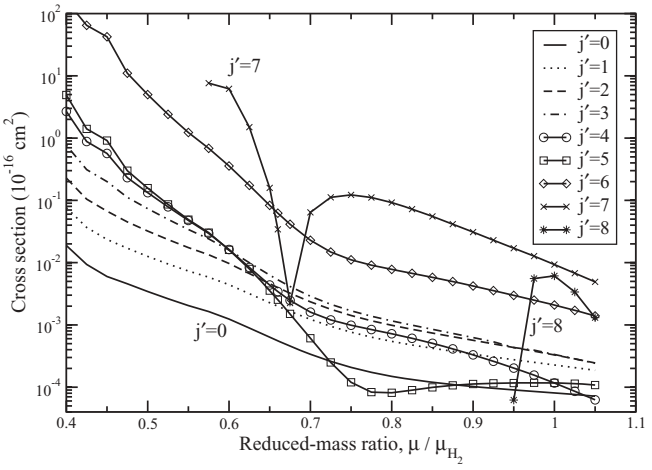

FIG. 3. State-to-state quenching cross sections for ^{3}He-D$X(v = 1, j = 0) \rightarrow {}^3$He-D$X(v = 0, j')$ as a function of the DX/H_2 reduced-mass ratio.

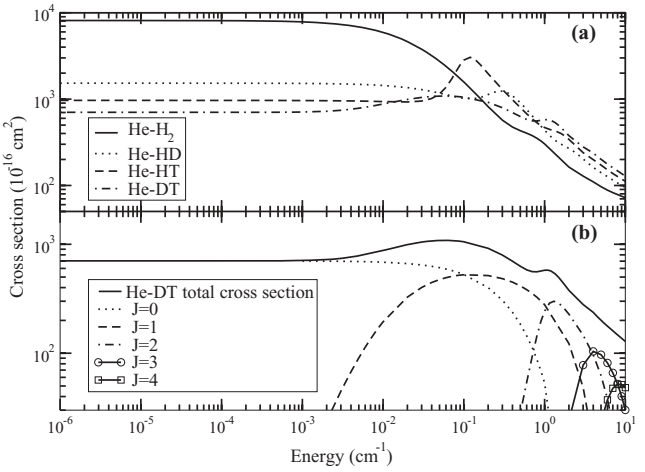

FIG. 4. Low-energy elastic cross sections for ^{4}He collisions with molecular hydrogen isotopomers with $v = 1$, $j = 0$. (a) Total cross sections for H_2, HD, HT, and DT. (b) Partial cross sections for the dominant partial waves for ^{4}He-DT.

in Fig. 4(b), the $J = 2$ resonance for DT is prominent near $\sim$1.5 cm^{-1}. The experimental detection of this low-energy resonance in the cold regime for the physical isotopomers would provide critical tests of the spherical component of the He-H_2 interaction potential.

An avenue for the measurement of low-energy He-H_2 cross sections is suggested by recent studies of Barletta *et al.* [28] who proposed the possibility of creating ultracold H_2 through collisions with ultracold rare gas atoms. In their method, cold molecules created by optical Stark deceleration [29] are subjected to sympathetic cooling by thermal contact with laser-cooled rare gas atoms. Compared to other rare gas atoms, the inelastic cross sections for He with para-H_2 are largest, making it a favorable case for such an experimental study [28].

V. CONCLUSIONS

We have explored the sensitivity of elastic and inelastic scattering in ultracold He-H_2 collisions for a range of physical and artificial isotopes of H_2 and He. The purpose of these calculations was to explore how changes in bound state energy levels of H_2 and those of the triatomic He-H_2 van der Waals complexes influence scattering at low energies. We have shown that by varying the molecular (or helium) mass, a zero-energy resonance appears for the ^{4}He-H_2 and ^{3}He-H_2 collision systems with $v = 1$, $j = 0$, but for reduced masses corresponding to nuclear masses less than that of the proton (or ^{3}He). For reduced mass ratios $\mu/\mu_{H_2} < 1$, the imaginary part of the scattering length for collisions with ^{3}He and ^{4}He displays a number of oscillations and resonances that are attributable to energetically open rotational levels as the reduced mass is increased. An elastic resonance in the cold regime due to p-wave scattering is seen to shift to lower energies as the target mass is increased. For He-HD, a zero-energy resonance is found to occur for a "helium mass" of $\sim$1.95 u.

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