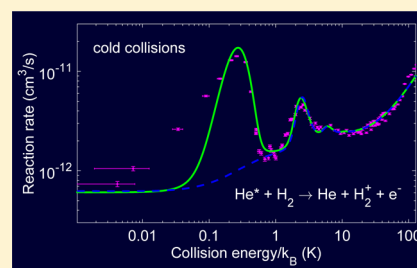


Adiabatic Variational Theory for Cold Atom–Molecule Collisions: Application to a Metastable Helium Atom Colliding with *ortho*- and *para*-Hydrogen Molecules

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Supporting Information

ABSTRACT: We recently developed an adiabatic theory for cold molecular collision experiments. In our previous application of this theory (Pawlak, M.; et al. *J. Chem. Phys.* **2015**, *143*, 074114), we assumed that during the experiment the collision of an atom with a diatom takes place when the diatom is in the ground rotational state and is located in a plane. In this paper, we present how the variational approach of the adiabatic theory for low-temperature collision experiments can be used for the study a SD collision between the atom and the diatomic molecule with no limitations on its rotational quantum states and no plane restrictions. Moreover, we show here the dramatic differences in the measured reaction rates of $\text{He}(2^3\text{S}_1) + \textit{ortho}/\textit{para}\text{-H}_2 \rightarrow \text{He}(1s^2) + \textit{ortho}/\textit{para}\text{-H}_2^+ + e^-$ resulting from the anisotropic long-range interactions in the reaction. In collisions of metastable helium with molecular hydrogen in the ground rotational state, the isotropic potential term dominates the dynamics. When the collision is with molecular hydrogen in the first excited rotational state, the nonisotropic interactions play an important role in the dynamics. The agreement of our results with the latest experimental findings (Klein, A.; et al. *Nat. Phys.* **2017**, *13*, 35–38) is very good.



INTRODUCTION

The adiabatic approach has a long history in the theory of van der Waals complexes and molecular scattering. It goes back at least to the “best local” approximation developed in a space-fixed formulation by Levine et al.^{1–3} Later, it was rederived using body-fixed coordinates by Holmgren et al.⁴ Recently, inspired by the latter work, we developed an adiabatic theory for anisotropic cold collisions of slow atoms with cold diatomic molecules using well-known perturbational and variational techniques.⁵ Within the framework of adiabatic variational theory (AVT), couplings between different angular momentum states (associated with diatomic and with atom–diatom relative rotations) and different angular momentum projection states during an experiment are taken into consideration. It provides us with physical insight into dynamics of reactions and enables us to study the role of anisotropy. The effect of anisotropy in cold atom–molecule collisions via quantum scattering resonances has just been experimentally observed.⁶ It was found that a low-energy resonance (below 1 K) takes place in the measured Penning ionization reaction between metastable helium and molecular hydrogen only in the rotational excited state. Consequently, by changing the molecular rotational state, one can turn the anisotropy of the atom–molecule interaction on/off.

In order to understand the experimental excited atom–molecule collision results, one can carry out calculations within the framework of quantum defect theory.^{7–10} A more accurate

approach is based on sophisticated and rigorous, but more time-consuming, quantum-mechanical scattering calculations.^{6,11–15} In turn, the conventional variational approach including all internal degrees of freedom provides an extremely large Hamiltonian matrix that has to be diagonalized. Our method, similarly to ref 16, reduces the complexity without losing essential physics and significantly enhances the computational efficiency even several orders of magnitude. The five degrees of freedom problem, where the bond length in the diatomic molecule is kept fixed and all rotations are included, is replaced with a set of uncoupled one-dimensional subproblems.

In this paper, we present how to use AVT for cold collision experiments when not all products are in ground states. We apply the theory to calculate the Penning ionization reaction rates of the excited metastable helium atom with *ortho*-H₂ (*o*-H₂) as well as with *para*-H₂ (*p*-H₂) and compare them with the recent cutting-edge experimental findings.⁶ Moreover, we do not limit the rotation of the molecule to a plane as we did in our previous application of AVT for He(2³S₁)–HD in the rotational ground state.⁵ Note that the restriction of the dynamics to be in a plane might introduce artificial structures in the cross sections (see, for example, the study of the collision between a hydrogen atom and an Ar–Cl complex in ref 17).

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We clearly show here that the isotropic part of the interaction dominates the dynamics when molecular hydrogen is in the rotational ground state. When the diatom is rotationally excited, the strong anisotropic effect occurs, causing the appearance of a new resonance in the millikelvin regime in the collisional reaction rate.

THEORY

We study the Hamiltonian for collision an atom (A) with a two-nuclear molecule (M) in the form

$$\hat{H} = -\frac{\hbar^2}{2\mu_{A/M}} \frac{\partial^2}{\partial R^2} + \frac{\hat{L}^2(\theta_1, \phi_1)}{2\mu_{A/M}R^2} + \frac{\hat{L}^2(\theta_2, \phi_2)}{2\mu_M r^2} + V(R, \theta) \quad (1)$$

where $\mu_{A/M}$ is the reduced mass of the complex, μ_M is the reduced mass of the diatom, three components of $\vec{R} = (R, \theta_1, \phi_1)$ point to the atom from the center of mass of the diatom, $d\vec{R} = \sin \theta_1 dR d\theta_1 d\phi_1$, and the angles θ_2 and ϕ_2 show the orientation of the molecular axis in the same laboratory coordinate frame. For simplicity, we consider the diatomic molecule to be a rigid rotor; thus, the distance between nuclei r is fixed. The intermolecular potential expanded in Legendre polynomials is as follows^{4,18}

$$V(R, \theta) = \sum_k V_k(R) P_k(\cos \theta) \\ \cong V_0(R) + V_1(R) \cos \theta + V_2(R) \frac{1}{2}(3 \cos^2 \theta - 1) \quad (2)$$

The angle θ between \vec{R} and the molecular axis can be expressed in terms of the angles $\theta_1, \phi_1, \theta_2$, and ϕ_2 ⁵

$$\cos[\theta(\theta_1, \phi_1, \theta_2, \phi_2)] = \cos \theta_1 \cos \theta_2 \\ + \sin \theta_1 \sin \theta_2 \cos \phi_1 \cos \phi_2 \\ + \sin \theta_1 \sin \theta_2 \sin \phi_1 \sin \phi_2 \quad (3)$$

We use products of spherical harmonics as basis functions^{5,12}

$$\psi_\alpha(\theta_1, \phi_1, \theta_2, \phi_2) = Y_{j_1, m_1}(\theta_1, \phi_1) Y_{j_2, m_2}(\theta_2, \phi_2) \quad (4)$$

where α denotes a superindex containing quantum numbers j_1, m_1, j_2, m_2 ($j_1 = 0, 1, \dots, j_{\max}^{(1)}$; $m_1 = -j_1, -j_1 + 1, \dots, j_1 - 1, j_1$; $j_2 = 0, 1, \dots, j_{\max}^{(2)}$; $m_2 = -j_2, -j_2 + 1, \dots, j_2 - 1, j_2$). We expect our solutions to conserve the total angular momentum \vec{J} and its projection on the z -axis \vec{M} . Note that we do not limit the calculations to specific J and M states, although it is clear that during every one of the collisions J and M are conserved. The reason that we do not limit ourselves to a specific value of J and M is due to the fact that in the experiments for any value of J all possible M states are populated. Moreover, for any given collision energy in the calculations of the cross section (e.g., for the Penning ionization reaction), we should take into consideration all possible J states. Thus, there is no need to make the calculations more expensive by construction of the Clebsch–Gordan coefficients, which guarantee that a collision between the atom and the diatom takes place when the two quantum numbers J and M are conserved. The conservation of J and M as two good quantum numbers is embedded in the structure of the potential (i.e., includes the angle θ between \vec{R} and the molecular axis) even when we do not use the Clebsch–Gordan coefficients to construct our basis set. As we will explain below within the framework of the adiabatic approach

rather than solving the Schrödinger equation for large Hamiltonian matrix, we solve many times the Schrödinger equation for relatively small Hamiltonian matrices.

According to AVT that we presented in ref 5, the Hamiltonian in the matrix form is given by

$$\hat{H}_{\alpha', \alpha}^{\text{var}} = -\frac{\hbar^2}{2\mu_{A/M}} \frac{\partial^2}{\partial R^2} \delta_{\alpha', \alpha} + V_{\alpha', \alpha}^{\text{var}}(R) \quad (5)$$

where

$$V_{\alpha', \alpha}^{\text{var}}(R) = \left\langle \psi_{\alpha'} \left| \frac{\hat{L}^2(\theta_1, \phi_1)}{2\mu_{A/M}R^2} + \frac{\hat{L}^2(\theta_2, \phi_2)}{2\mu_M r^2} + V(R, \theta) \right| \psi_\alpha \right\rangle \quad (6)$$

and

$$\hat{L}^2(\theta_1, \phi_1) Y_{j_1, m_1}(\theta_1, \phi_1) = \hbar^2 j_1(j_1 + 1) Y_{j_1, m_1}(\theta_1, \phi_1) \quad (7)$$

$$\hat{L}^2(\theta_2, \phi_2) Y_{j_2, m_2}(\theta_2, \phi_2) = \hbar^2 j_2(j_2 + 1) Y_{j_2, m_2}(\theta_2, \phi_2) \quad (8)$$

Hence, by substituting eqs 2 and 4 into eq 6, one gets

$$\mathbf{V}^{\text{var}} = V_0(R) \mathbf{I} + V_1(R) \mathbf{A} + V_2(R) \frac{1}{2}(3\mathbf{B} - \mathbf{I}) \\ + \frac{1}{2\mu_{A/M}R^2} \mathbf{C} + \frac{1}{2\mu_M r^2} \mathbf{D} \quad (9)$$

where \mathbf{I} stands for a unity matrix and

$$A_{\alpha', \alpha} = \langle \psi_{\alpha'} | \cos \theta | \psi_\alpha \rangle \quad (10)$$

$$B_{\alpha', \alpha} = \langle \psi_{\alpha'} | \cos^2 \theta | \psi_\alpha \rangle \quad (11)$$

$$C_{\alpha', \alpha} = \langle \psi_{\alpha'} | \hat{L}^2(\theta_1, \phi_1) | \psi_\alpha \rangle \quad (12)$$

$$D_{\alpha', \alpha} = \langle \psi_{\alpha'} | \hat{L}^2(\theta_2, \phi_2) | \psi_\alpha \rangle \quad (13)$$

All above matrix elements can be calculated based on our analytical expressions presented in the Supporting Information. Here, the rotation of the molecule is not limited to a plane as it was in ref 5. Because j_1 is varied from 0 to $j_{\max}^{(1)}$ and $m_1 = 0, \pm 1, \dots, \pm j_1$, and similarly for j_2 , the dimension of the matrix \mathbf{V}^{var} is $[(j_{\max}^{(1)} + 1)^2 (j_{\max}^{(2)} + 1)^2] \times [(j_{\max}^{(1)} + 1)^2 (j_{\max}^{(2)} + 1)^2]$.

As noted above, the basis set (eq 4) gives all different uncoupled solutions associated with the different values of J and M (the standard Clebsch–Gordan coefficients are used as the coefficients in the linear combination of the primitive basis functions to ensure that the total angular momentum and its projection on the z -axis are conserved). Within the framework of AVT, the Hamiltonian is as follows⁵

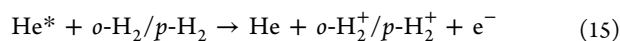
$$\hat{H}_\alpha^{\text{AVT}} = -\frac{\hbar^2}{2\mu_{A/M}} \frac{\partial^2}{\partial R^2} + V_\alpha^{\text{ad}}(R) \quad (14)$$

where $V_\alpha^{\text{ad}}(R)$ are eigenvalues of the matrix \mathbf{V}^{var} (eq 9) and $\alpha = 1, 2, \dots, (j_{\max}^{(1)} + 1)^2 (j_{\max}^{(2)} + 1)^2$. As we pointed out in our earlier paper,⁵ the effective potentials have to be ordered such that for any value of R , $V_\alpha^{\text{ad}}(R) < V_{\alpha+1}^{\text{ad}}(R)$. The AVT is applicable when the potential curves are smooth and no avoided crossings are observed. Moreover, this theory holds when the strength of the anisotropy is smaller as compared with the molecular rotational constant.

In order to find out and explain effects in atom–diatom collision processes occurring during the experiment, one can carry out rigorous quantum calculations over all internal degrees of freedom. By assuming the stiffness of the molecule, there are five independent coordinates θ_1 , ϕ_1 , θ_2 , ϕ_2 , and R . The size of the matrix in the conventional variational approach is extremely large. For example, let us assume 1000 primitive basis functions^{19–21} for R and $j_1 = 0, \dots, 10$; $m_1 = -j_1, \dots, j_1$; $j_2 = 0, \dots, 3$; $m_2 = -j_2, \dots, j_2$; the total matrix size is equal to about $2\,000\,000 \times 2\,000\,000$. Our method reduces the complexity of the considered problem without losing essential physics and greatly enhances the computational efficiency. We have to diagonalize many times (e.g., 500) the matrix \mathbf{V}^{var} , varying R , which is treated as a parameter, and then solve α uncoupled Schrödinger equations of R only (with Hamiltonians given in eq 14). The typical time computational complexity for diagonalizing is $O(n^3)$. It means that our method is roughly $(2 \times 10^6)^3 / [500 \times 2000^3 + 2000 \times 10^9] \approx 1.3$ million times faster with respect to the full variational approach. The gain for $j_1 = 0, \dots, 12$ and $j_2 = 0, 1$ is about 0.4 million.

APPLICATION OF THE AVT FOR THE COLD COLLISION EXPERIMENT

We have applied our theory to calculate the Penning ionization reaction rate of the excited metastable helium atom and the H_2 molecule and compared it with recent experimental measurements⁶



where He^* denotes $^4\text{He}(2^3\text{S}_1)$. Note that the hydrogen molecule comes in two configurations: $p\text{-H}_2$ and $o\text{-H}_2$. Due to symmetry reasons, the $p\text{-H}_2$ possesses only even rotational states, while $o\text{-H}_2$ has only odd ones. In a supersonic expansion, hydrogen is cooled to the lowest rotational state with an ortho/para ratio of 3/1. At low temperatures, $j_2 = 0$ and $j_2 = 1$ states are the only two states that matter.

The total cross section within the framework of AVT is defined as

$$\sigma_{j_2}^{\text{total}}(k) = \frac{1}{2j_2 + 1} \frac{\pi}{k^2} \sum_{\alpha_{j_2}} \sigma_{\alpha_{j_2}}^{\text{AVT}}(k) \quad (16)$$

where

$$\sigma_{\alpha_{j_2}}^{\text{AVT}}(k) = 1 - \exp(-4\text{Im} \delta_{\alpha_{j_2}}^{\text{AVT}}) \quad (17)$$

$k^2 = 2\mu_{\text{A/M}}E/\hbar^2$, E is the relative energy between the colliding atom and the molecule (the collision energy), and $\delta_{\alpha_{j_2}}^{\text{AVT}}$ is the complex phase shift. The superindex α_{j_2} refers to the case where postselected states asymptotically correspond to specific j_2 (rotational state of the molecule). Equation 16 is obtained by generalization of the expression derived by using the optical theorem as shown in ref 22, where in our case the couplings between different angular momentum states and different angular momentum projection states are included.

The interaction potential was scaled, similarly as was done in refs 5 and 23, by a factor to fit the calculated cross section to the experimental results. By taking a factor of 1.205, we increased the potential well depth, obtaining reasonable agreement with the experimental data in terms of the position of the major resonance peak. On the one hand, it is because the ab initio calculations for the potential are not of high enough precision. On the other hand, the cross section is calculated for

the phase shift as done for nondecaying processes, although the potential that we use is complex due to the Penning ionization. This approximation holds only when the decay rate is sufficiently small.

The radial interaction potentials, $\{V_k(R)\}_{k=0,2}$, are taken from refs 23–25, where V_0 is complex and V_2 is real. These were obtained from supermolecular unrestricted coupled cluster singles and doubles with noniterative triples correction computations (UCCSD(T)).^{23–25} The imaginary decay part was calculated using the ab initio Fano algebraic-diagrammatic construction method; see details in ref 24. The potential curves are presented in Figure 1. It should be noted that for the

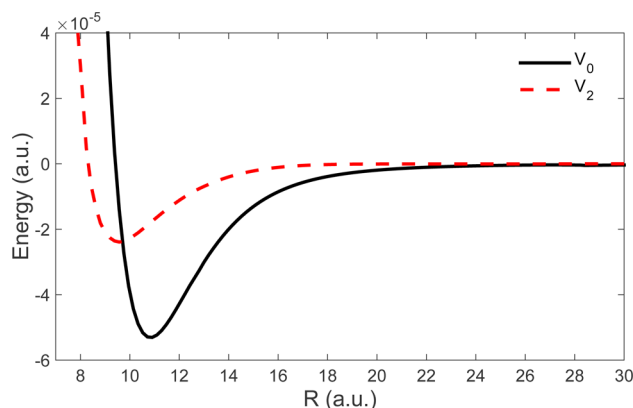


Figure 1. Isotropic and anisotropic radial interaction potential terms of $^4\text{He}(2^3\text{S}_1)$ with molecular hydrogen, V_0 and V_2 , respectively, scaled by a factor of 1.205. The potential energy surface is in the form $V(R, \theta) \cong V_0(R) + V_2(R)(3 \cos^2 \theta - 1)/2$.

collision of an atom with a homonuclear diatomic molecule, $V_1(R) = 0$ because $V(R, \theta) = V(R, -\theta)$. Consequently, there is no coupling between para states and ortho states. In other words, the potential matrix elements do not vanish when $|\Delta j_2|$ is equal to an even number; see the Supporting Information. Figure 2 demonstrates the eigenvalues of the potential matrix $\mathbf{V}^{\text{var}}(R)$ providing two families of effective one-dimensional potentials (adiabats) $V_{\alpha}^{\text{ad}}(R)$ for application for the collision of a metastable helium atom and the H_2 molecule computed for $j_{\text{max}}^{(1)} = 12$ and $j_{\text{max}}^{(2)} = 1$. No avoided crossings are observed.

When the interaction potential is isotropic, j_1 and j_2 are good quantum numbers. In turn, when the anisotropy of the potential starts playing a role, the degeneracy of the (j_1, j_2) levels is lifted—the levels split into sublevels $J = |j_1 - j_2|, \dots, j_1 + j_2$.²⁶ Here, we observe both situations. The former case correlates with $j_2 = 0$ (para), whereas the latter one corresponds to $j_2 = 1$ (ortho); see Figure 2. It clearly shows that the anisotropic effect appears for diatoms in a rotationally excited state. This holds only when the strength of the anisotropy is smaller as compared with the molecular rotational constant. The same conclusions of the role of anisotropy were recently presented based on state-of-the-art ab initio theory and close-coupling quantum scattering calculations.⁶

We performed calculations, as mentioned above, for $j_{\text{max}}^{(1)} = 12$ (i.e., $j_1 = 0, 1, \dots, 12$) and $j_{\text{max}}^{(2)} = 1$ (i.e., $j_2 = 0, 1$). We chose postselected states asymptotically corresponding to $j_2 = 0$ and $j_2 = 1$ in order to calculate the Penning ionization reaction rates $(\hbar k/\mu_{\text{A/M}})\sigma_{j_2}^{\text{total}}$ for $\text{He}^* - p\text{-H}_2$ and $\text{He}^* - o\text{-H}_2$, respectively. It should be pointed out that we considered in this paper the general case (5D problem) and did not assume $\phi_2 = 0$ as we

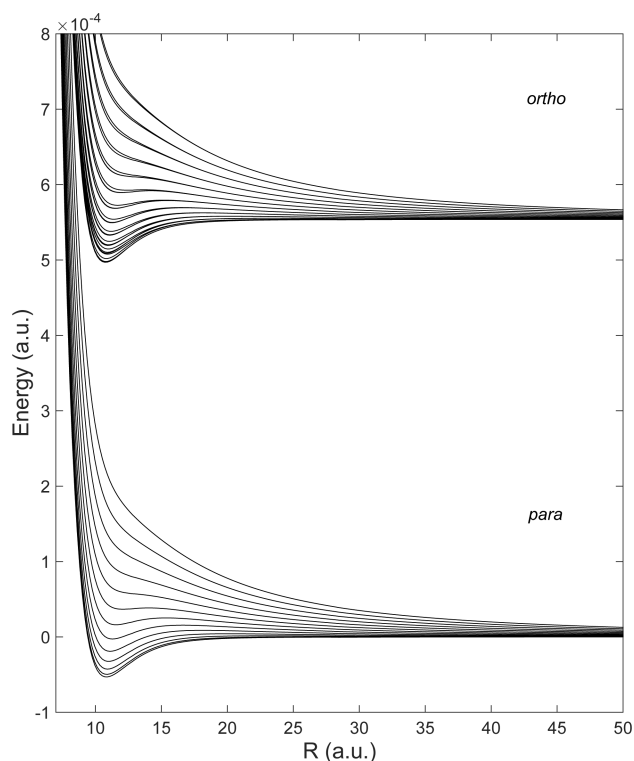


Figure 2. Eigenvalues of the potential matrix V^{var} (eq 9) as a function of R computed for $j_{\text{max}}^{(1)} = 12$ and $j_{\text{max}}^{(2)} = 1$. The adiabats asymptotically coincide with a specific rotational state of the hydrogen molecule. The lowest eigenvalue for para is nondegenerate and corresponds to $J = 0$, $M = 0$ ($j_1 = 0, j_2 = 0$); the second eigenvalue from the bottom is three times degenerate and corresponds to $J = 1, M = -1, 0, 1$ ($j_1 = 1, j_2 = 0$); the next eigenvalue is five times degenerate and corresponds to $J = 2, M = -2, -1, 0, 1, 2$ ($j_1 = 2, j_2 = 0$); and so forth. In the case of ortho, j_1 and j_2 are not good quantum numbers. The degeneracy of the (j_1, j_2) levels is lifted under the influence of the anisotropy of the potential energy surface.

did in the previous application of the AVT for He^*-HD in the rotational ground state in ref 5. The reaction rate results of He^* with $p\text{-H}_2$ ($j_2 = 0$) using our approach are demonstrated in Figure 3 together with the new experimental measurements presented in ref 6. As one can see, we obtained very good agreement with the merged beam experiment. In the calculations, all matrix elements of $(3\mathbf{B} - \mathbf{I})$ in eq 9 corresponding to $j_2 = 0$ when $j_{\text{max}}^{(2)} = 1$ are zero. If we take

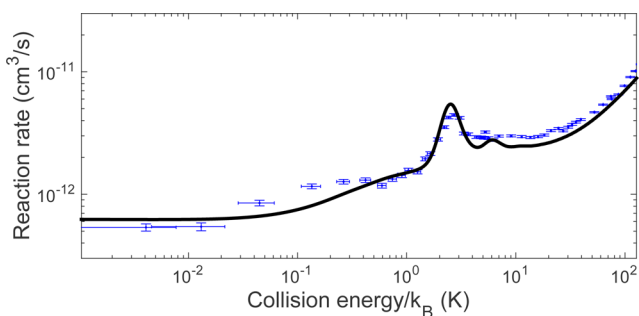


Figure 3. Comparison of theoretical (solid curve) and experimental⁶ (points with error bars) reaction rates $[(\hbar k/\mu_{A/M})\sigma_{j_2=0}^{\text{total}}]$ of ${}^4\text{He}(2^3\text{S}_1)$ with H_2 in the ground rotational state ($j_2 = 0$). The calculations were performed for $j_{\text{max}}^{(1)} = 12$ and $j_{\text{max}}^{(2)} = 1$.

$j_{\text{max}}^{(2)} > 1$, some matrix elements do not vanish; however, the contribution of the anisotropic term with $V_2(R)$ is very small and can be neglected. Thus, the total cross section as well as the reaction rate of the excited helium atom and the hydrogen molecule in the ground rotational state can be computed accurately enough using the expression for the isotropic radial interaction potential $V_0(R)$.

Figure 4 presents the reaction rate between He^* and $o\text{-H}_2$ ($j_2 = 1$) with and without potential term $V_2(R)(3\cos^2\theta - 1)/2$.

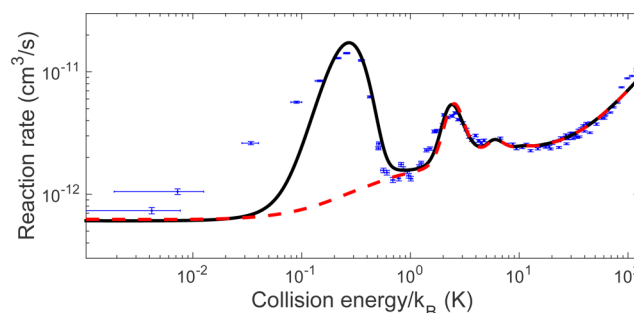


Figure 4. Comparison of theoretical (curves) and experimental⁶ (points with error bars) reaction rates $[(\hbar k/\mu_{A/M})\sigma_{j_2=1}^{\text{total}}]$ of ${}^4\text{He}(2^3\text{S}_1)$ with H_2 in the first excited rotational state ($j_2 = 1$). The calculations were performed for $j_{\text{max}}^{(1)} = 12$ and $j_{\text{max}}^{(2)} = 1$ where the isotropic and anisotropic radial interaction potentials, V_0 and V_2 , respectively, were included (solid black curve) and the isotropic radial interaction potential, V_0 , was only included (dashed red curve).

The low-temperature peak in the reaction rate is missed when the only leading isotropic term in the Legendre polynomial expansion of the interaction potential (eq 2) between the reactants is taken into consideration. Here, there are nonzero matrix elements of $(3\mathbf{B} - \mathbf{I})$ in eq 9 corresponding to $j_2 = 1$ even when $j_{\text{max}}^{(2)} = 1$. Only lower-energy resonance is sensitive toward anisotropy of the potential energy surface. The higher-energy resonance is located at large internuclear separation where anisotropy is negligible. The agreement with experiment is excellent provided that the anisotropic (orientation-dependent) part of the interaction potential is included in calculations.

SUMMARY

We have presented here an application of simple AVT that we recently developed⁵ for cold anisotropic atom–diatom collisions where the anisotropy is small compared with the rotational constant of the molecule. In our approach, the diatom is treated as a rigid rotor and all rotations are included. We have demonstrated how this theory can be applied to investigations of cold Penning ionization reactions of the excited triplet helium atom and molecular hydrogen (ortho/para). Our results are in remarkable agreement with the latest experimental findings.⁶ Moreover, the use of adiabatic theory for cold molecular collisions not only simplifies the calculations by reducing the computational efforts even by several orders of magnitude but also enlightens the reason for the differences and similarities between the measured reaction rates for the collision pairs $\text{He}^*-p\text{-H}_2$ and $\text{He}^*-o\text{-H}_2$ at subkelvin temperatures. One of the peaks (the higher-energy resonance) in the reaction rate results from the isotropic radial interaction term in the potential, whereas the other one (the lower-energy resonance) results from the anisotropic interactions that exist only when a metastable helium atom collides with ortho-hydrogen. In summary, our results clearly show how dramatic

the effect of anisotropy is in cold/ultracold molecular processes. We believe that the AVT for calculating cross sections can be successfully used for studying low-energy collision reactions when other types of ionization take place, such as the Auger effect or interatomic (intermolecular) coulombic decay^{27,28} (and not only the Penning ionization, as in the presented case).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b13038.

(Details of the calculations for cold atom–molecule collisions PDF)

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Notes

The authors declare no competing financial interest.

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