Adiabatic theory for anisotropic cold molecule collisions

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We developed an adiabatic theory for cold anisotropic collisions between slow atoms and cold molecules. It enables us to investigate the importance of the couplings between the projection states of the rotational motion of the atom about the molecular axis of the diatom. We tested our theory using the recent results from the Penning ionization reaction experiment $^4\mathrm{He}(1s2s\,^3S)$ + $\mathrm{HD}(1s^2) \rightarrow\,^4\mathrm{He}(1s^2)$ + $\mathrm{HD}^+(1s)$ + e^- [Lavert-Ofir *et al.*, Nat. Chem. **6**, 332 (2014)] and demonstrated that the couplings have strong effect on positions of shape resonances. The theory we derived provides cross sections which are in a very good agreement with the experimental findings. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4928690]

I. INTRODUCTION AND MOTIVATION

The quantum effects appearing in the translational motion of reactants, such as tunnelling though a potential barrier induced by a weak centrifugal force, are usually negligible at room temperature. As was shown recently, they can dominate reaction dynamics in cold collision experiments.[1–3] In Ref. 1, a strong kinetic isotope effect was observed by measuring the Penning ionization reaction rates between metastable helium and hydrogen isotopologues in the collision temperature ranging from several Kelvin down to 10 mK. The experimental results were compared with the theory, where the zero-order perturbational approach with only the leading isotropic term in the Legendre polynomial expansion of the interaction potential between the reactants was taken into consideration. In order to understand reactive collisions in an atom-molecule system that has very weak long-range anisotropy, one can perform rigorous and sophisticated quantum mechanical scattering calculations as have been done by a number of authors (see, for example, Refs. 4–10).

There has been increasing interest in theoretical works on the applications of adiabatic theories (primarily adiabatic capture theories[11] and their generalizations[12–15]) to atom-molecule and molecule-molecule chemical reactions. Recently, Quéméner and Bohn combined the classical capture theory with the quantum threshold laws to calculate the reaction rates of two colliding bodies as a function of collision energy at low temperatures.[12] Idziaszek and Julienne proposed a general model with a complex potential for threshold molecular collision rates based on multichannel quantum defect theory (MQDT).[13] Gao derived from MQDT a universal model of exoergic bimolecular reactions for a wide range of temperatures.[14] In turn, Tscherbul and Buchachenko used the adiabatic channel capture theory to investigate the dynamics of low-temperature chemical reactions.[15] These capture studies were conducted in the universal limit, where reactions depend only on the long range interactions that do not support resonances.

However, most recently, the reaction rates for the Penning ionization were calculated using QDT by Jachymski and his co-workers.[3,16,17] The theory we developed and are going to present here is different than QDT. It is based on an adiabatic theory that in principle can be extended in a systematic way to provide the exact cross sections and the exact resonance poles of the scattering matrix which are associated with the metastable complex (formed during the atom-molecule collision). A comparison between QDT and our findings is beyond the scope of the present work.

We develop a relatively simple conventional adiabatic theory for cold reactions applying techniques that are well-known and widely used by chemical physicists. Previously, this kind of adiabatic theory has been successfully used by Holmgren *et al.*[18] to reproduce spectroscopic studies of van der Waals complexes. In this approach, the coupling between angular momentum projection states could be neglected. Similar approximations have been successful in reducing the dynamics in $\mathrm{H_2O}$–$\mathrm{H_2}$ collisions from a 5D problem to a 3D model.[19,20] The conventional adiabatic theory[18] assumes that in the case where anisotropy is much smaller as compared to the rotational constant of the colliding molecule, spherically symmetric interaction potentials can be used to describe the collision process. In this paper, we show that the couplings between the projection states of the rotational motion of the atom about the molecular axis of the diatom are enough to introduce the effect of anisotropy and play a crucial role in reproducing the shape and positions of scattering resonances in low-energy collisions.

Two alternative theoretical approaches are presented here. Within the framework of the first-order adiabatic perturbation theory (APT), the angular momentum of the atom moving about the center of mass of the diatom is a constant of motion. However, all possible transitions among the states characterized by the projection of the angular momentum on the z-axis are included. In turn, within the framework of the adiabatic variational theory (AVT), the transitions between all possible different angular momentum states are also taken into

consideration. A comparison between the measured cross sections and the theoretical results obtained from first-order perturbational and variational calculations enlightens the dominant mechanism of the reaction which takes place during the collision experiments at sub-Kelvin temperatures. The simple theory presented in this work can give physical insight into reaction dynamics as well as intuitively explain many phenomena that otherwise would require a full quantum mechanical treatment. As an illustrative numerical example, we have applied our theory to calculate the Penning ionization reaction rate of the excited metastable helium atom and the HD molecule and compared it with the experimental findings.[1]

II. THEORY

We consider the effective Hamiltonian for the cold collision of an atom (A) with a diatomic molecule (M). For the sake of simplicity and without loss of generality in our approach, we assume that the interaction potential is given by[9,18]

$$V(R,\theta) = \sum_j V_j(R)P_j(\cos\theta) \cong V_0(R) + V_1(R)\cos\theta$$
$$+ V_2(R)\frac{1}{2}\left(3\cos^2\theta - 1\right), \quad (1)$$

where R is the distance between the atom and the center of mass of the diatom, while θ is the angle between $\vec{R}$ and the molecular axis. We do not assume here one electronic configuration surface since in the electronic structure calculations, the possibility of ionization due to the electronic correlation is taken into consideration. See, for example, Ref. 21 for different methods for calculating complex electronic potential energy surfaces. Therefore, $\Gamma(R,\theta) = -2\text{Im}V(R,\theta)$ provides the ionization decay rate as a function of the geometrical structure of the three atoms where the distance between the two creating a molecule is held fixed or is varied adiabatically to follow the same resonance state.

The Hamiltonian under study is

$$\hat{H} = -\frac{\hbar^2}{2\mu_{A/M}}\frac{\partial^2}{\partial R^2} + \frac{\hat{L}^2(\theta_1,\phi_1)}{2\mu_{A/M}R^2} + \frac{\hat{L}^2(\theta_2,\phi_2)}{2\mu_M r^2}$$
$$+ V_0(R) + V_1(R)\cos\theta + V_2(R)\frac{1}{2}\left(3\cos^2\theta - 1\right), \quad (2)$$

where R, θ_1, ϕ_1 are coordinates of the position of the atom (e.g., the helium atom in its first excited triplet state in the experiment described in Ref. 1) with respect to the center of mass of the two-nuclear molecule (e.g., HD in the experiment mentioned above), $d\vec{R} = \sin\theta_1 dR d\theta_1 d\phi_1$, whereas θ_2 and ϕ_2 are the angles of the molecular axis in the same laboratory coordinate frame. Due to the assumption about the stiffness of the molecule, the internuclear distance r is held fixed. The angle θ is the angle between the two vectors $\vec{R}$ and $\vec{r}$ which as usual can be expressed in terms of the angles θ_1, ϕ_1, θ_2, ϕ_2,

$$\cos\theta(\theta_1,\phi_1,\theta_2,\phi_2) = \frac{\vec{r}\cdot\vec{R}}{rR}$$
$$= \cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\phi_2 - \phi_1). \quad (3)$$

When the three atoms move on a two-dimensional plane, then $\phi_2 = \phi_1$ and the above equation is reduced to $\cos\theta = \cos(\theta_2 - \theta_1)$.

A. Adiabatic perturbational approach

Let us first use the adiabatic perturbation theory where the distance between the atom and the diatomic molecule in the cold collision experiment is taken as a parameter (and not as a dynamical variable). In this adiabatic perturbational approach, the zero-order Hamiltonian consists of two uncoupled rigid rotors,

$$\hat{H}^{(0)} = \frac{\hat{L}^2(\theta_1,\phi_1)}{2\mu_{A/M}R^2} + \frac{\hat{L}^2(\theta_2,\phi_2)}{2\mu_M r^2}. \quad (4)$$

In turn, the perturbation is given by

$$\hat{H}^{(1)} = V_0(R) + V_1(R)\cos\theta + V_2(R)\frac{1}{2}\left(3\cos^2\theta - 1\right). \quad (5)$$

Here, r is fixed for the sake of simplicity of our derivation and R, as we mentioned above, is taken as an adiabatic parameter. Therefore, we assume that the distance between the atom and the center of mass of the diatom is varied much more slowly than the rotational motion of the atom about the center of mass of the diatom.

The zero-order energy and corresponding wave function within the adiabatic approximation are as follows:

$$E_{l_1,l_2}^{(0)}(R) = \frac{\hbar^2 l_1(l_1 + 1)}{2\mu_{A/M}R^2} + \frac{\hbar^2 l_2(l_2 + 1)}{2\mu_M r^2}, \quad (6)$$

$$\psi_{l_1,m_1,l_2,m_2}^{(0)}(\theta_1,\phi_1,\theta_2,\phi_2) = Y_{l_1,m_1}(\theta_1,\phi_1)Y_{l_2,m_2}(\theta_2,\phi_2), \quad (7)$$

where $\{Y_{l,m}\}$ are spherical harmonic functions. Note that the zero-order energy does not depend on the quantum numbers m_1 and m_2. We assume that for all internuclear distances, the anisotropy is smaller compared to the rotational constant of a molecule. In such a case, the conventional adiabatic theory given in Ref. 18, where only one relative atom-molecule angular momentum projection state was considered, predicts that anisotropic effects are negligible. In our case, this condition corresponds to the following choice of quantum states $l_2 = 0$, $m_2 = 0$ and $l_1 > 0$, $m_1 = -l_1, -l_1 + 1, \ldots, l_1 - 1, l_1$. The value of l_1 depends on the experimental parameters such as collision energy. Taking the above into account, the zero-order energy for the atom-diatom collision is

$$E_{l_1,l_2=0}^{(0)}(R) = \frac{\hbar^2 l_1(l_1 + 1)}{2\mu_{A/M}R^2}. \quad (8)$$

The total degeneracy is equal to $2l_1 + 1$.

The adiabatic perturbation operator $\hat{H}^{(1)}$ couples the two rotational vectors $\vec{R}$ and $\vec{r}$. Thus, we use functions $\psi^{(0)}$ [Eq. (7)], as usual, as basis functions[5,7,9] to construct the potential matrix whose elements are as follows:

$$\langle\psi_{l_1,m_1',0,0}^{(0)}|\hat{H}^{(1)}|\psi_{l_1,m_1,0,0}^{(0)}\rangle = V_0(R)\delta_{m_1',m_1} + V_2(R)\mathcal{M}_{m_1',m_1}^{(l_1)}, \quad (9)$$

where

$$\mathcal{M}_{m_1',m_1}^{(l_1)} = -\frac{1}{2}\delta_{m_1',m_1}$$
$$+ \frac{3}{2}\langle\psi_{l_1,m_1',0,0}^{(0)}|\cos^2\theta(\theta_1,\phi_1,\theta_2,\phi_2 = 0)|\psi_{l_1,m_1,0,0}^{(0)}\rangle$$

$$= -\frac{\delta_{m'_1, m_1 \pm 2}}{2(2l_1 - 1)(2l_1 + 3)}$$

$$\times \sqrt{\frac{(l_1 + m_{\min}^{(1)} + 2)!(l_1 - m_{\min}^{(1)})!}{(l_1 - m_{\min}^{(1)} - 2)!(l_1 + m_{\min}^{(1)})!}} \quad (10)$$

and $m_{\min}^{(1)} = \min\{m'_1, m_1\}$. According to the perturbation theory, the first-order correction to the energy contains two terms. One term is $V_0(R)$ as expected. The other term is proportional to $V_2(R)$. In turn, $V_1(R)$ contributes only to the second-order correction. Therefore, the first-order correction energy (including the m_1-degeneracy) to the zero-order energy is given by

$$E_{l_1, l_2=0}^{(1)}(R) = V_0(R) + \lambda_j^{(l_1)} V_2(R), \quad (11)$$

where $\lambda_j^{(l_1)}$, $j = 1, \ldots, 2l_1 + 1$, is one of the $2l_1 + 1$ eigenvalues of matrix (10). The eigenfunctions corresponding to the eigenvalues $\{\lambda_j^{(l_1)}\}$ are $\{\Psi_j^{(l_1)}\}$. Note that $\bar{m}_1 = \langle \Psi_j^{(l_1)} | -i\hbar \frac{\partial}{\partial \phi_1} | \Psi_j^{(l_1)} \rangle = 0$ for every j and l_1. The derivation details of the first-order perturbational correction to the adiabatic energy are given in the supplementary material.[22] Eqs. (9) and (10) in general form in terms of Wigner 3-j symbols can be found in many works, e.g., in Refs. 5, 7, 9, and 23.

In the next step of the APT for the cold collision experiment, we define a set of uncoupled $2l_1 + 1$ effective 1D Hamiltonians where R is now a dynamical variable and $E_{l_1, l_2=0}^{(1)}(R)$ presented in Eq. (11) serves as a potential. Therefore, within the framework of the first-order APT, we get

$$\hat{H}_{j, l_1, l_2=0}^{\text{APT}} = -\frac{\hbar^2}{2\mu_{A/M}} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2 l_1(l_1 + 1)}{2\mu_{A/M} R^2}$$

$$+ V_0(R) + \lambda_j^{(l_1)} V_2(R), \quad (12)$$

where $j = 1, 2, \ldots, 2l_1 + 1$. Here, we obtain that l_1 referred to as an atom-molecule collisional partial wave is kept as a good quantum number.

B. Adiabatic variational approach

Let us use the zero-order solutions given in Eq. (7) as a basis set. We take the Hamiltonian matrix in the form

$$\hat{H}_{j', j}^{\text{var}} = -\frac{\hbar^2}{2\mu_{A/M}} \frac{\partial^2}{\partial R^2} \delta_{j', j} + V_{j', j}^{\text{var}}(R), \quad (13)$$

where

$$V_{j', j}^{\text{var}}(R) = \left\langle \psi_{j'}^{(0)} \left| \frac{\hat{L}^2(\theta_1, \phi_1)}{2\mu_{A/M} R^2} + \frac{\hat{L}^2(\theta_2, \phi_2)}{2\mu_M r^2} + V(R, \theta) \right| \psi_j^{(0)} \right\rangle \quad (14)$$

and j denotes a superindex containing quantum numbers l_1, m_1, l_2, m_2 ($l_1 = 0, 1, \ldots, l_{\max}^{(1)}$, $m_1 = 0, \pm 1, \pm 2, \ldots, \pm l_1$, $l_2 = 0, 1, \ldots, l_{\max}^{(2)}$, $m_2 = 0, \pm 1, \pm 2, \ldots, \pm l_2$). We first diagonalize the potential matrix $\mathbf{V}^{\text{var}}$ where its elements are as follows:

$$V_{j', j}^{\text{var}}(R) = \left(\frac{\hbar^2 l_1(l_1 + 1)}{2\mu_{A/M} R^2} + \frac{\hbar^2 l_2(l_2 + 1)}{2\mu_M r^2} + V_0(R) \right) \delta_{j', j}$$

$$+ V_1(R) \langle \psi_{l'_1, m'_1, l'_2, m'_2}^{(0)} | \cos\theta | \psi_{l_1, m_1, l_2, m_2}^{(0)} \rangle$$

$$+ V_2(R) \frac{1}{2} \langle \psi_{l'_1, m'_1, l'_2, m'_2}^{(0)} | 3\cos^2\theta - 1 | \psi_{l_1, m_1, l_2, m_2}^{(0)} \rangle, \quad (15)$$

where θ is a function of θ_1, ϕ_1, θ_2, ϕ_2 (see Eq. (3)). The dimension of the matrix is $[(l_{\max}^{(1)} + 1)^2 (l_{\max}^{(2)} + 1)^2] \times [(l_{\max}^{(1)} + 1)^2 (l_{\max}^{(2)} + 1)^2]$. All matrix elements can be calculated based on our analytical expressions given in the supplementary material.[22] Thus,

$$\mathbf{V}^{\text{var}}(R)\mathbf{v}_j(R) = V_j^{\text{ad}}(R)\mathbf{v}_j(R), \quad (16)$$

where $V_j^{\text{ad}}(R)$ and $\mathbf{v}_j(R)$ are eigenvalues and eigenvectors, respectively, $j = 1, 2, \ldots, (l_{\max}^{(1)} + 1)^2 (l_{\max}^{(2)} + 1)^2$. Namely, $\mathbf{V}^{\text{var}}(R)\mathbf{v}(R) = \mathbf{v}(R)\mathbf{V}^{\text{ad}}(R)$, where $\mathbf{V}^{\text{ad}}(R)$ is diagonal matrix with $\{V_j^{\text{ad}}\}_{j=1,2,\ldots}$ on diagonal. Consequently,

$$\mathbf{V}^{\text{var}}(R) = \mathbf{v}(R)\mathbf{V}^{\text{ad}}(R)\mathbf{v}^T(R). \quad (17)$$

By carrying out the unitary transformation

$$\mathcal{H}^{\text{var}} = \mathbf{v}^T \mathbf{H}^{\text{var}} \mathbf{v}, \quad (18)$$

one gets the matrix elements of $\mathcal{H}^{\text{var}}$ in the form

$$\hat{\mathcal{H}}_{j', j}^{\text{var}} = -\frac{\hbar^2}{2\mu_{A/M}} \left(\mathbf{v}_{j'}^T \frac{\partial \mathbf{v}_j}{\partial R} \frac{\partial}{\partial R} + \mathbf{v}_{j'}^T \frac{\partial^2 \mathbf{v}_j}{\partial R^2} + \delta_{j', j} \frac{\partial^2}{\partial R^2} \right)$$

$$+ V_j^{\text{ad}}(R)\delta_{j', j}. \quad (19)$$

In the second step, we perform the adiabatic approximation assuming that the non-adiabatic terms in the Hamiltonian matrix $\mathcal{H}^{\text{var}}$ are negligible. That is, we ignore the terms $\mathbf{v}_{j'}^T \frac{\partial}{\partial R} \mathbf{v}_j \frac{\partial}{\partial R}$ and $\mathbf{v}_{j'}^T \frac{\partial^2}{\partial R^2} \mathbf{v}_j$ in Eq. (19). This approximation which is equivalent to the Born-Oppenheimer approximation holds when the adiabatic potential functions are separable and not get too close to one another since

$$\mathbf{v}_{j'}^T \frac{\partial}{\partial R} \mathbf{v}_j = \frac{\mathbf{v}_{j'}^T (\partial \mathbf{V}^{\text{var}} / \partial R) \mathbf{v}_j}{V_j^{\text{ad}}(R) - V_{j'}^{\text{ad}}(R)}. \quad (20)$$

Finally, within the framework of the AVT, we have

$$\hat{\mathcal{H}}_j^{\text{AVT}} = -\frac{\hbar^2}{2\mu_{A/M}} \frac{\partial^2}{\partial R^2} + V_j^{\text{ad}}(R), \quad (21)$$

where $j = 1, 2, \ldots, (l_{\max}^{(1)} + 1)^2 (l_{\max}^{(2)} + 1)^2$. Note that the centrifugal barriers are included inside the effective potentials $\{V_j^{\text{ad}}(R)\}_{j=1,2,\ldots}$. It is important to order these potentials such that for any value of R, $V_{j+1}^{\text{ad}}(R) > V_j^{\text{ad}}(R)$. The fact that the potentials are smooth and do not show an avoided crossing behavior is an indication of the applicability of the AVT approach. In the adiabatic variational calculations, we take into consideration all possible transitions among the different angular momentum states and also the different angular momentum projection states during the cold collision experiment. The maximal values of the angular momentum of the atom and the diatomic molecule, $l_{\max}^{(1)}$ and $l_{\max}^{(2)}$, are determined by the experiment. In the calculations, they should be varied to get converged cross sections.

III. APPLICATION OF THE ADIABATIC THEORY FOR COLD COLLISION EXPERIMENTS

Let us now discuss the illustrative application of our adiabatic theory towards the cold Penning ionization reaction

investigated in Ref. 1,

$$^4\mathrm{He}(1s2s\,^3S) + \mathrm{HD}(1s^2) \rightarrow {}^4\mathrm{He}(1s^2) + \mathrm{HD}^+(1s) + e^-. \quad (22)$$
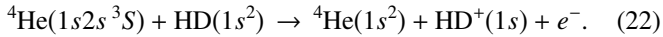
The hydrogen deuteride is in the ground rovibrational state (100% of the HD molecules in the experiment are, using our notation, in $l_2 = 0$). For the sake of notation simplicity, the excited helium atom will be denoted as He*. The phase shift, δ, is defined such that $\exp(i2\delta)$ is the ratio between the amplitudes of the outgoing and incoming waves in the asymptotes of the solution of the time-independent radial Schrödinger equation with the adiabatic Hamiltonian derived above [Eqs. (12) and (21) for the first-order APT and the AVT, respectively]; for more details see, e.g., page 44 in the textbook on non-Hermitian quantum mechanics.[21] The total reaction cross section within the framework of APT is given by

$$\sigma_{\mathrm{tot}}^{\mathrm{APT}}(k) = \frac{\pi}{k^2} \sum_{l_1=0}^{l_{\max}^{(1)}} \sum_{j=1}^{2l_1+1} \left[1 - \exp\left(-4\mathrm{Im}\,\delta_{j,l_1}^{\mathrm{APT}} \right) \right], \quad (23)$$

where $k = \sqrt{2\mu_{A/M}E}/\hbar$ and E is the collision energy, i.e., the relative energy between the colliding atom and the molecule. Eq. (23) is obtained by the generalization of the expression derived by using the optical theorem as shown in Ref. 24 where in our case, the couplings between different m_1 states for a given angular momentum quantum number are included. The calculations have been performed for $l_{\max}^{(1)} = 30$. As a matter of fact, the results are fully converged such that increasing the number of partial waves gives the same result for $\sigma_{\mathrm{tot}}^{\mathrm{APT}}$. The total cross section [as well as the Penning ionization reaction rate: $(\hbar k/\mu_{A/M})\sigma_{\mathrm{tot}}$] of the excited helium atom and the hydrogen deuteride has been computed using the expression for the isotropic radial interaction potential, $V_0(R)$, as used in Ref. 1, the anisotropic radial interaction potentials, $V_1(R)$[25] and $V_2(R)$,[25] as calculated in Ref. 26, and the APT as described above. For this case, the position of the center of mass is shifted along the internuclear axis such that the potential energy surface had to be re-expanded in the shifted coordinate system.[1,27] Note that for the collision of an atom with a homonuclear diatomic molecule, $V_1(R) = 0$ since $V(R,\theta) = V(R,-\theta)$. When the diatom is heteronuclear (as, e.g., in the case of HD), then $V_1(R) \neq 0$ but is expected to have a small effect on the dynamics. The radial interaction potentials, $\{V_j(R)\}_{j=0,1,2}$, are shown in Fig. 1, whereas the reaction rate results are presented in Fig. 2 together with the experimental and zero-order theoretical data discussed in Ref. 1. As one can see, the effect of couplings among the different m_1 states (for a given partial wave) is quite substantial in the He*-HD collisions where it introduces a better agreement with the experimental measurements.

The comparison of the APT results with experiment and previous zero-order theoretical calculations for the He* collisions with HD is performed in order to test the new theory for collision reactions at low temperatures. However, the application of this new theory is not limited to the specific Penning ionization process. This theory can be used to study and design experiments where other types of reactions take place, e.g., where the ionization due to the cold collision process is not the Penning ionization but the interatomic Coulombic decay (ICD) mechanism.[28,29]
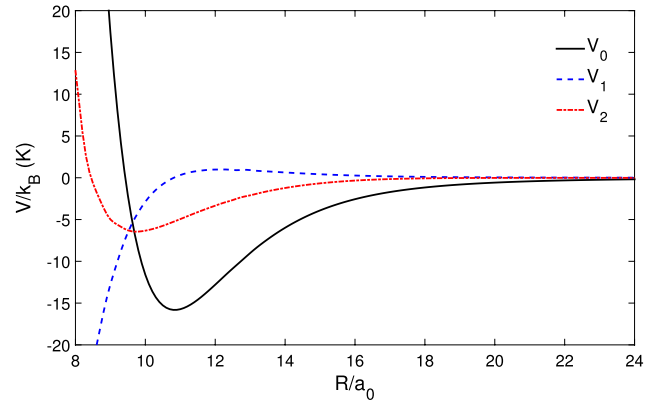

FIG. 1. The expanded radial interaction potential terms of $^4\mathrm{He}(1s2s\,^3S)$ with the hydrogen deuteride, $\{V_j(R)\}_{j=0,1,2}$, calculated[25] using potential energy surface from the work of Hapka *et al.*[26] scaled by a factor of 1.15. The 2D potential energy surface is given by $\sum_j V_j(R)P_j(\cos\theta)$, see Eq. (1).

Last but not least, we will show how to apply the adiabatic variational theory for low-energy collisions of the triplet metastable helium atom with the hydrogen deuteride. As we did before, we assume that the diatomic molecule is in its ground rovibrational state during the collision reaction. Within the adiabatic variational calculations, we take into consideration the couplings between all possible different l_1 and m_1 states. The Hamiltonian that is obtained when the AVT is applied is given in Eq. (21). The total cross section in that case is defined as

$$\sigma_{\mathrm{tot}}^{\mathrm{AVT}}(k) = \frac{\pi}{k^2} \sum_{j=1}^{(l_{\max}^{(1)}+1)^2} \left[1 - \exp\left(-4\mathrm{Im}\,\delta_{j,l_{\max}^{(1)}}^{\mathrm{AVT}} \right) \right], \quad (24)$$

where $l_{\max}^{(1)}$ is taken such that the convergence is satisfied. Here, $l_{\max}^{(1)}$ in the calculations equals 30. The computed reaction rate is presented in Fig. 2. It is compared with available experimental and theoretical data[1] as well as with the results obtained based on the APT. Both approaches lead to similar results improving the agreement with the experiment in comparison with previous theoretical studies.[1]
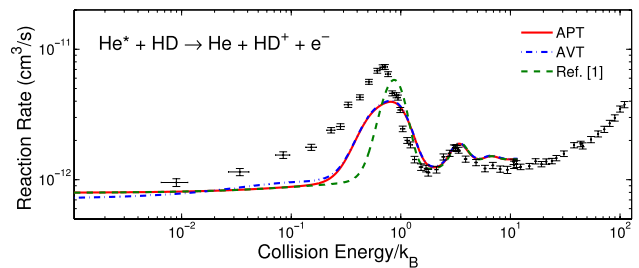

FIG. 2. The reaction rate $[(\hbar k/\mu_{A/M})\sigma_{\mathrm{tot}}]$ of $^4\mathrm{He}(1s2s\,^3S)$, denoted as He*, with the hydrogen deuteride observed in Ref. 1 is depicted by black points. The reaction rate (dashed green curve) has been calculated using the potential energy surface from the work of Hapka *et al.*[26] scaled by a factor of 1.15 to correct the energies of the resonances,[1] such that they fit the experiment. The reaction rates calculated based on the same potential energy surface with the additional correction according to the adiabatic perturbation theory (APT, solid red curve) and with the adiabatic variational theory (AVT, dotted-dashed blue curve) are plotted for comparison. Both corrections produce similar results and make the resonances less symmetric, enhancing the resemblance to the experiment. The calculations [see Eqs. (23) and (24)] have been carried out for $l_{\max}^{(1)} = 30$.

IV. CONCLUDING REMARKS

In summary, the simple theoretical approach that we have developed using well-known techniques enables us to study the role of the couplings among the degenerate angular momentum projection states due to weak anisotropy in cold chemistry experiments. We have demonstrated that these couplings have strong effect on positions of shape resonances. Our adiabatic theory has been applied to the cold Penning ionization reaction as an example to illustrate the insight information on the sub-Kelvin collision experiment. The presented theory can be also used for cases where $l_2 > 0$, but this type of application is beyond the scope of our paper that focuses on the representation of the perturbational and variational adiabatic approaches for cold molecule collisions. Besides helping in understanding the experiment, the theory might be applied as a tool for designing new experiments where different types of mechanisms, which have never been studied before, control the dynamics. No doubt, the development of theory for these kinds of experiments is important for new fields of cold chemistry since it allows investigations of quantum effects in chemical reactions.

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