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Reactive scattering calculations for $^{87}\text{Rb} + ^{87}\text{RbHe} \rightarrow \text{Rb}_2(^3\Sigma_u^+, v) + \text{He}$ from ultralow to intermediate energies

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We investigate atom-diatom reactive collisions, as a preliminary step, in order to assess the possibility of forming Rb_2 molecules in their lowest triplet electronic state by cold collisions of rubidium atoms on the surface of helium nanodroplets. A simple model related to the well-known Rosen treatment of linear triatomic molecules [N. Rosen, *J. Chem. Phys.* **1**, 319 (1933)] in relative coordinates is used, allowing to estimate reactive probabilities for different values of the total angular momentum. The best available full dimensional potential energy surface [Guillon *et al.*, *J. Chem. Phys.* **136**, 174307 (2012)] is employed through the calculations. Noticeable values of the probabilities in the ultracold regime, which numerically fulfill the Wigner threshold law, support the feasibility of the process. The rubidium dimer is mainly produced at high vibrational states, and the reactivity is more efficient for a bosonic helium partner than when the fermion species is considered. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919062>]

I. INTRODUCTION

During the last decade, high-spin alkali dimers have attracted considerable attention by both experiment and theory, mainly due to their role in producing samples of cold molecules.¹ Translationally, cold alkali-metal molecules have been produced by indirect techniques, such as photoassociation^{2,3} or association via magnetically tuned Feshbach resonances.^{4,5} The molecules are usually produced in weakly bound states corresponding to high vibrational excitations, and various schemes are proposed to obtain rovibrational ground state molecules.^{6,7} Among alkali metals, earlier studies have focused on heteronuclear and homonuclear mixtures of the lighter species, Li, Na, and K, more recently on the heavier Rb and Cs molecules,⁸ while currently have extended to ultracold polar alkali-alkali earth molecules.^{9,10}

Helium nanodroplets constitute an ideal environment for spectroscopic studies at low temperature and have been extensively exploited in spectroscopical characterizations of dopant molecules.^{11–15} In particular, the helium nanodroplet isolation (HENDI) technique,¹⁶ in which the species to study are captured by a beam of helium clusters in a low-pressure pick-up cell, is an alternative way to spectroscopically investigate cold alkali-metal dimers. Indeed, rubidium dimers in their lowest triplet state have been formed on the surface of cold helium droplets,¹⁷ as it is expected due to the very weak high-spin alkali dimers and helium atoms interaction, and since then their dynamics have been extensively studied (see Refs. 18–20). As it has been observed earlier on, in experiments with alkali doped clusters,²¹ the alkali metal

atoms remain on the helium surface, where they can *skate*, forming cold molecules through collisions.^{17,22} In general, such collisions lead preferentially to high spin (triplet) state alkali dimers,^{17,23} as the binding energy that is released during the collision is larger for the low spin (singlet) state for which the subsequent evaporation of the droplet could be significant. In fact, singlet states, with a stronger bond, may cause either the desorption of the alkali molecule or the complete evaporation of small helium clusters, and thus, triplet-state alkali dimers were selectively produced.¹⁶

In spite of the plausibility of the whole mechanism suggested for the formation of cold alkali dimers on the surface of helium droplets, it is interesting to assess the extent to which different stages are actually met.

In this paper, we address the collisional formation of rubidium dimers in the presence of just one helium atom as a preliminary step for analyzing the feasibility of the *skating* mechanism mentioned above. To this end, we estimate reactive probabilities for the collisional process $^{87}\text{Rb} + ^{87}\text{Rb}^n\text{He} \rightarrow \text{Rb}_2(^3\Sigma_u^+, v) + ^n\text{He}$, $n = 3, 4$, by means of a simplified model which rests on the Rosen treatment to determine the lifetime of a linear triatomic molecule.²⁴ Although a full scattering treatment would be desirable, e.g., solving close-coupling equations in the energy domain, the combination of extremely low collision energies and moderate well-depths, as is the case of the Rb_2 potential, leads to consider a long spatial range of integration and small steps, which means a very large number of integration points. In addition, one has to account for different total angular momentum values, which make the problem computationally challenging.

The best available three-dimensional (3D) potential energy surface (PES) of the trimer²⁵ was used to describe the full interaction. Recently, accurate studies have been reported

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on vibrational relaxation of Rb₂ molecules by collisions with He for a total angular momentum $J = 0$ at low vibrational states of the rubidium dimer²⁵ and extended later on to higher ($J \leq 20$) angular momenta.²⁶ In this work, as in the previous complementary quantum scattering calculations,²⁶ the coupling of final vibrational states of rubidium dimer is neglected, as well as the hyperfine, spin-spin, and spin-rotation terms in the Rb₂ molecule. The paper is organized as follows: Sec. II describes the intermolecular force employed in the present work, while Sec. III provides details on the proposed theoretical model. Section IV presents and discusses the main approximations involved in our calculations and the results we have obtained. Finally, Sec. V summarizes our conclusions and points out some perspectives of this study.

II. THE INTERACTION POTENTIAL

In previously published studies on He-Rb₂(³Σ_u⁺) two-dimensional surfaces,^{27,28} the rubidium dimer is considered as a rigid rotor, and thus they cannot be used to describe neither vibrational relaxation nor reactive processes. However, more recently, Guillon *et al.*²⁵ performed accurate *ab initio* 3D calculations on this system. They decompose the full PES describing the interaction of helium with rubidium in its ³Σ_u⁺ state as the sum of two-body (2B) potentials plus a three-body (3B) interaction,

$$V_{\text{TOT}}(R_1, R_2, R_3) = V_{\text{Rb-Rb}}^{2\text{B}}(R_1) + V_{\text{Rb-He}}^{2\text{B}}(R_2) + V_{\text{Rb-He}}^{2\text{B}}(R_3) + V^{3\text{B}}(R_1, R_2, R_3), \quad (1)$$

where R_1 and R_3 are the distances from the incoming Rb atom to the Rb and He atoms in the RbHe complex, respectively, while R_2 is the intramolecular Rb-He distance. In Ref. 25, each term of Eq. (1) is fitted using a reproducing kernel Hilbert space (RKHS) method.²⁹ Albeit, this method is highly accurate, in order to speed up the present calculations, we have resorted to represent the 2B terms analytically via

$$V^{2\text{B}}(R) = V_M(R) \times f(R; R_m, \beta) + [f(R; R_m, \beta) - 1] \times \left(\frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} \right), \quad (2)$$

while keeping the original RKHS fit for the 3B portion. In Eq. (2), $V_M(R) = D[e^{-\alpha(R-R_e)} - 1]^2 - D$ is a Morse potential describing the inner part and the well region, C_n , $n = 6, 8, 10$, are the long-range coefficients given in Table I of Ref. 25, and

$$f(R; R_m, \beta) = \{1 - \tanh[\beta(R - R_m)]\}/2$$

is a matching function that connects smoothly the two ranges.

The parameters of the Morse interactions and the matching function were adjusted through non-linear least-square fittings and are listed in Table I together with the C_n coefficients. A brief analysis of the corresponding errors of the PES is reported below.

III. THEORETICAL APPROACH

In 1933, Rosen introduced a perturbation method to calculate lifetimes of unstable linear triatomic molecules. The basic idea behind the Rosen approach²⁴ is to choose a set of coordinates which render the problem nearly separable, i.e., make it separable if one neglects some of the smaller terms in the Hamiltonian, which are furtherly introduced as perturbations to estimate the couplings among zero-order states. He found that using the distances from the central atom to the outside ones as coordinates, the Hamiltonian, apart from the interaction between the outside atoms which is eventually neglected, corresponds to the sum of two diatomic molecules plus a kinetic crossing term of the type

$$T_{12} = -\frac{\hbar^2}{M} \frac{\partial^2}{\partial r_1 \partial r_2},$$

where M is the mass of the central atom and r_1 and r_2 are the distances mentioned above. In the frame of first order perturbation theory, and keeping constant the energy, T_{12} couples an initial unstable state, product of a vibrational state of one diatomic molecule by a vibrational state of the second molecule, and a final one in which the first diatomic is in a lower vibrational level, while the other diatomics is in the continuum. This coupling is then used to calculate the discrete-continuum transition rate via a Golden Rule expression. Basically, the approach becomes accurate as long as the perturbation is small, i.e., when the central atom is heavy. Here, we extend the Rosen treatment in a three-fold way: (a) the collinear arrangement is generalized to a 3D configuration, (b) a full-collision process is considered instead a half-collision (dissociation) one, and (c) in addition to a kinetic crossing term, potential terms coming from the interaction between outside atoms as well as from the 3B contribution to the PES are included in the calculations.

The Hamiltonian describing the Rb-Rb-He triatomic system can be written in relative (or satellite) coordinates $\{\mathbf{R}_k\}$, after separation of the center of mass motion, as³⁰

$$H = -\frac{\hbar^2}{2\mu_1} \left(\frac{\partial^2}{\partial R_1^2} + \frac{2}{R_1} \frac{\partial}{\partial R_1} \right) + \frac{\ell_1^2}{2\mu_1 R_1^2} + V_{\text{Rb}_2}^{2\text{B}}(R_1) - \frac{\hbar^2}{2\mu_2} \left(\frac{\partial^2}{\partial R_2^2} + \frac{2}{R_2} \frac{\partial}{\partial R_2} \right) + \frac{\ell_2^2}{2\mu_2 R_2^2} + V_{\text{RbHe}}^{2\text{B}}(R_2) + V_{\text{RbHe}}^{2\text{B}}(R_3) + V^{3\text{B}}(R_1, R_2, R_3) + T_{12}, \quad (3)$$

where $T_{12} = -(\hbar^2/m_{\text{Rb}})\nabla_{\mathbf{R}_1} \cdot \nabla_{\mathbf{R}_2}$.³¹ In Eq. (3), μ_1 and μ_2 are the reduced masses of the Rb₂ and RbHe systems, respectively, $\mathbf{R}_k$ are the vectors going from the central Rb atom to the other Rb atom ($k = 1$) or to the He atom ($k = 2$), and ℓ_k are the angular momenta associated with $\mathbf{R}_k$. Denoting the angle formed by $\mathbf{R}_1$ and $\mathbf{R}_2$ as γ , we have $\cos \gamma = \mathbf{R}_1 \cdot \mathbf{R}_2 / R_1 R_2$, the R_3 distance is related with R_1 , R_2 , and $\cos \gamma$ through

TABLE I. Parameters for the analytical description of the 2B interactions, see text.

	D (cm ⁻¹)	α (Å ⁻¹)	R_e (Å)	β (Å ⁻¹)	R_m (Å)	C_6 (E _h a ₀ ⁶)	C_8 (E _h a ₀ ⁸)	C_{10} (E _h a ₀ ¹⁰)
Rb-Rb	223.6471	0.6928	6.1067	1.3280	10.8116	4.707×10^3	5.730×10^5	7.665×10^7
Rb-He	0.9363	0.8130	7.4497	1.6820	9.5921	4.469×10^1	3.145×10^3	3.038×10^5

the cosine theorem $R_3 = \sqrt{R_1^2 + R_2^2 - 2R_1R_2 \cos \gamma}$. In a space-fixed coordinate system, we consider the following zero-order states describing the reactants (*in*) and the products (*out*):

$$\begin{aligned}\Psi^{(in)}(\mathbf{R}_1, \mathbf{R}_2) &= \frac{\phi_{\epsilon_1}(R_1)\varphi_{v_0}(R_2)\mathcal{Y}_{\ell_1\ell_2}^{JM}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2)}{R_1R_2}, \\ \Psi^{(out)}(\mathbf{R}_1, \mathbf{R}_2) &= \frac{\phi_v(R_1)\varphi_{\epsilon_2}(R_2)\mathcal{Y}_{\ell'_1\ell'_2}^{JM}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2)}{R_1R_2},\end{aligned}\quad (4)$$

where the ϕ_{ϵ_1} and ϕ_v radial functions correspond to the Rb₂ molecule in a continuum (incoming) or a discrete (outgoing) state, respectively, while the φ radial functions describe (reversed) similar states of the HeRb subunit. They will be specified later on. In Eq. (4), the $\mathcal{Y}_{\ell_1\ell_2}^{JM}$ are angular functions in the coupled representation,

$$\begin{aligned}\mathcal{Y}_{\ell_1\ell_2}^{JM}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2) &= (-1)^J \sqrt{2J+1} \sum_{\omega} \begin{pmatrix} \ell_1 & \ell_2 & J \\ -\omega & \omega & -M \end{pmatrix} \\ &\times Y_{\ell_1\omega}(\theta_1, \phi_1) Y_{\ell_2 M-\omega}(\theta_2, \phi_2),\end{aligned}\quad (5)$$

where $\hat{\mathbf{R}}_k = \mathbf{R}_k/R_k = (\theta_k, \phi_k)$ are unit vectors, $\begin{pmatrix} \ell_1 & \ell_2 & J \\ -\omega & \omega & -M \end{pmatrix}$ are 3-*j* symbols, and $Y_{\ell k\omega}$ are spherical harmonics. J is the quantum number associated with the total angular momentum $\mathbf{J} = \mathbf{\ell}_1 + \mathbf{\ell}_2$ with third component M .

Denoting by $W(R_1, R_2, \cos \gamma) = V_{\text{RbHe}}^{2B}(R_3) + V_{\text{RbHe}}^{3B}(R_1, R_2, R_3)$, the two last potential terms in Eq. (3) and taking into account that average values of $\cos \gamma$ become zero,^{31,32} $\langle \mathcal{Y}_{\ell_1\ell_2}^{LM} | \cos \gamma | \mathcal{Y}_{\ell_1\ell_2}^{LM} \rangle = 0$, we consider a Taylor expansion around $\cos \gamma = 0$ up to the first order,

$$W(R_1, R_2, \cos \gamma) \approx W_0(R_1, R_2) + \cos \gamma \Delta W(R_1, R_2), \quad (6)$$

where $W_0 = W(R_1, R_2, \cos \gamma = 0)$ and $\Delta W = \partial W / \partial \cos \gamma|_{\cos \gamma=0}$. For this later contribution, the portion coming from the 2B interaction is readily obtained by multiplying the analytic derivative of Eq. (2) with $\partial R_3 / \partial \cos \gamma = -R_1R_2/R_3$. Regarding the 3B contribution, according with the RKHS fitting method followed in Ref. 25, one obtains

$$\begin{aligned}\frac{\partial V^{3B}}{\partial \cos \gamma} \Big|_{\cos \gamma=0} &= \sum_i \alpha_i \min[e^{-0.4R_1}, x_2^{(i)}] \\ &\times \left\{ (1 + \min[R_2/R, x_3^{(i)}]) t_i \right. \\ &\left. + \min[e^{-0.4R}, x_1^{(i)}] t'_i \right\},\end{aligned}\quad (7)$$

where $R = \sqrt{R_1^2/4 + R_2^2}$ is the Jacobi distance between He and the center of mass of Rb₂; t_i and t'_i are

$$\begin{aligned}t_i &= \begin{cases} e^{-0.4R} R_1 R_2 / 5R & \text{if } e^{-0.4R} < x_1^{(i)} \\ 0 & \text{otherwise} \end{cases}, \\ t'_i &= \begin{cases} R_1 R_2^2 / 2R^3 & \text{if } R_2/R < x_3^{(i)} \\ 0 & \text{otherwise} \end{cases}\end{aligned}$$

and the coefficients α_i , as well as the grid points $x_k^{(i)}$, see Eq. (3) in Ref. 25, are provided in the supplementary material in that reference.

Moreover, the T_{12} term in Eq. (3) also fulfills³¹

$$\langle \Psi^{in} | T_{12} | \Psi^{in} \rangle = \langle \Psi^{out} | T_{12} | \Psi^{out} \rangle = 0,$$

in such a way that the ϕ and φ functions in Eq. (4) are solutions of the following Schrödinger equations:

$$\left[-\frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial R_2^2} + V_{\text{RbHe}}^{2B}(R_2) - E_0 \right] \varphi_{v_0}(R_2) = 0, \quad (8)$$

$$\left[\frac{\hbar^2}{2\mu_1} \left(-\frac{\partial^2}{\partial R_1^2} + \frac{\ell_1(\ell_1+1)}{R_1^2} \right) + V_{\text{Rb}_2}^{2B}(R_1) + \langle \varphi_{v_0}(R_2) | W_0 | \varphi_{v_0}(R_2) \rangle - \epsilon_1 \right] \phi_{\epsilon_1}(R_1) = 0, \quad (9)$$

$$\left[\frac{\hbar^2}{2\mu_1} \left(-\frac{\partial^2}{\partial R_1^2} + \frac{\ell'_1(\ell'_1+1)}{R_1^2} \right) + V_{\text{Rb}_2}^{2B}(R_1) - \varepsilon_v^{(\ell'_1)} \right] \phi_v^{(\ell'_1)}(R_1) = 0, \quad (10)$$

$$\left[\frac{\hbar^2}{2\mu_2} \left(-\frac{\partial^2}{\partial R_2^2} + \frac{\ell'_2(\ell'_2+1)}{R_2^2} \right) + V_{\text{RbHe}}^{2B}(R_2) + \langle \phi_v^{(\ell'_1)}(R_1) | W_0 | \phi_v^{(\ell'_1)}(R_1) \rangle - \epsilon_2 \right] \varphi_{\epsilon_2}^{(\ell'_2)}(R_2) = 0. \quad (11)$$

The first equation corresponds to the unique existing eigenstate $\varphi_{v_0=0}$ for $v_0 = \ell_2 = 0$ of the HeRb diatomics, with eigenvalue E_0 , and the second equation to a continuum function ϕ_{ϵ_1} of the incoming Rb atom with kinetic energy ϵ_1 , respectively. In turn, the two last equations describe an exiting Rb₂ molecule in a ro-vibrational (ℓ'_1, v) state, Eq. (10), and an ejected He atom with kinetic energy ϵ_2 , Eq. (11). All the calculations are performed *on shell* energy, that is, $\epsilon_1 + E_0 = \varepsilon_v^{(\ell'_1)} + \epsilon_2$.

Extending now the Rosen calculation of discrete-continuum transition rates for unstable linear triatomic molecules²⁴

towards the present full-collision process, for a given total angular momentum J , one estimates the reaction probability of a rubidium atom colliding at an energy ϵ_1 with a HeRb dimer to produce Rb₂(³ Σ_u^+, ℓ'_1, v) while ejecting the He atom with an energy ϵ_2 and an orbital angular momentum ℓ'_2 as

$$P_{\ell'_1, v}^J(\epsilon_1) = \left| \langle \Psi^{in} | (\cos \gamma \Delta W + T_{12}) | \Psi^{out} \rangle \right|^2. \quad (12)$$

Summing over the vibrational states of Rb₂ gives a total probability of $P_{\ell'_1}^J(\epsilon_1) = \sum_v P_{\ell'_1, v}^J(\epsilon_1)$. The two terms in Eq. (12) are small enough to apply first order perturbation theory.

Moreover, they allow for a partially analytical evaluation as described in the following. The first term, involving a double quadrature, is^{31,32}

$$\begin{aligned} \langle \Psi^{(in)} | \cos \gamma \Delta W | \Psi^{(out)} \rangle \\ = (-1)^{\ell_1 - \ell'_1 + J} A(\ell_1, \ell_2, \ell'_1, \ell'_2) \\ \times \begin{Bmatrix} \ell_1 & 1 & \ell'_1 \\ \ell'_2 & J & \ell_2 \end{Bmatrix} \begin{Bmatrix} \ell_1 & 1 & \ell'_1 \\ 0 & 0 & 0 \end{Bmatrix} \begin{Bmatrix} \ell_2 & 1 & \ell'_2 \\ 0 & 0 & 0 \end{Bmatrix} \\ \times \int dR_2 \varphi_{v_0} \varphi_{\epsilon_2} \left[\int dR_1 \phi_{\epsilon_1} \Delta W(R_1, R_2) \phi_v \right], \end{aligned} \quad (13)$$

where $A(\ell_1, \ell_2, \ell'_1, \ell'_2) = \sqrt{(2\ell_1 + 1)(2\ell_2 + 1)(2\ell'_1 + 1)(2\ell'_2 + 1)}$ and $\left\{ \begin{smallmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{smallmatrix} \right\}$ are 6- j symbols. In turn, the second contribution, involving single quadratures, becomes³¹

$$\begin{aligned} \langle \Psi^{(in)} | T_{12} | \Psi^{(out)} \rangle = \frac{-\hbar^2}{m_{\text{Rb}}} (-1)^{J - \ell'_1 + \ell_1} \begin{Bmatrix} \ell'_2 & J & \ell'_1 \\ \ell_1 & 1 & \ell_2 \end{Bmatrix} \\ \times G_1(\epsilon_1, v, \ell_1, \ell'_1) G_2(v_0, \epsilon_2, \ell_2, \ell'_2), \end{aligned} \quad (14)$$

where the G_i factors are

$$\begin{aligned} G_1(\epsilon_1, v, \ell_1, \ell'_1) &= \delta_{\ell_1 \ell'_1 \pm 1} (-1)^{s_1} \sqrt{s_1} \int dR_1 \phi_{\epsilon_1}(R_1) \left[\frac{d\phi_v}{dR_1} \mp s_1 \frac{\phi_v}{R_1} \right], \\ G_2(v_0, \epsilon_2, \ell_2, \ell'_2) &= \delta_{\ell_2 \ell'_2 \pm 1} (-1)^{s_2} \sqrt{s_2} \int dR_2 \varphi_{v_0}(R_2) \left[\frac{d\varphi_{\epsilon_2}}{dR_2} \mp s_2 \frac{\varphi_{\epsilon_2}}{R_2} \right], \end{aligned} \quad (15)$$

with $s_i = \max(\ell_i, \ell'_i)$, $i = 1, 2$. Note that the constraint $\ell_2 = 0$ implies that $\ell_1 = J$. Moreover, the two contributing terms to Eq. (12), Eqs. (13) and (14), vanish unless $\ell'_2 = 1$ and $\ell'_1 = \ell_1 \pm 1$.

Partial reactive cross sections are then obtained as

$$\sigma_r^J(\epsilon_1) = \frac{\pi \hbar^2}{2\mu_1 \epsilon_1} \sum_{\ell'_1, v} P_{\ell'_1, v}^J(\epsilon_1), \quad (16)$$

from which the total cross section becomes

$$\sigma_r(\epsilon_1) = \sum_J (2J + 1) \sigma_r^J(\epsilon_1). \quad (17)$$

IV. RESULTS

The masses used were (amu) 86.909 180 527 (^{87}Rb), 4.0026 (^4He), and 3.016 04 (^3He), with the following conversion factors: $1 \text{ K} = 0.695\,038\,77 \text{ cm}^{-1}$, $1 \text{ cm}^{-1} = 4.556\,335\,38 \times 10^{-6} \text{ E}_h$, and $1 \text{ a}_0 = 0.529\,177\,26 \text{ \AA}$. We have considered 40 000 points of R_1 and R_2 in the interval $[2\text{--}750] \text{ \AA}$. As in some previous works, see, e.g., Ref. 33, the radial discrete equations, Eqs. (8) and (10), were efficiently solved by a mixed Truhlar and Numerov-Cooley procedure,³⁴ while continuum energy normalized solutions of Eqs. (9) and (11) were calculated by outward Numerov propagation of the wave function and by matching it to a sine behavior at large distances to determine the phase-shift.³⁵ For energies below 100 cm^{-1} , the analytical fits of the 2B interactions, given in Sec. II, present root mean squares (rms) errors of 9.8×10^{-4} and $1.2 \times 10^{-3} \text{ cm}^{-1}$ for Rb_2 and HeRb , respectively, when compared with the RKHS values.²⁵ At the minimum configuration, the relative error is less than 0.5% for Rb_2 and 0.2% for HeRb .

The calculations were performed for the reactive channels,

$$(J, \ell_1 = J, \ell_2 = 0) \rightarrow (J, \ell'_1 = J \pm 1, \ell'_2 = 1),$$

with $J \leq 3$, where it has been taken into account that the $^3\text{He}^{87}\text{Rb}$ ($^4\text{He}^{87}\text{Rb}$) dimer only has a rotationless ($\ell_2 = 0$) level at $-5.26 \times 10^{-3} \text{ cm}^{-1}$ ($-3.029 \times 10^{-2} \text{ cm}^{-1}$) in such a way that $\ell_1 = J$ and $\ell'_2 = 1$. Note that previous estimations using a slightly different He-Rb interaction³⁶ did not find any bound level for the $^3\text{He}^{87}\text{Rb}$ dimer, in spite of the value of the long range coefficient (atomic units) C_6 , 46.48, is greater than the present one of 44.69, see Table I (an accurate value of 43.4³⁷ is widely recognized^{25,36}). In turn, the rubidium $^{87}\text{Rb}_2$ dimer in its lowest triplet electronic state presents 39 vibrational levels for angular momenta $1 \leq \ell'_1 \leq 4$ and 40 for $\ell'_1 = 0$ (41 levels are reported for the model potential obtained from high-resolution two-photon dark-state spectroscopy in the presence of a magnetic field³⁸). For the different channels leading to a reaction, Figure 1 displays probabilities and cross sections as functions of the kinetic energy (log scale) of the incident Rb atom colliding with $^4\text{HeRb}$. In the upper panel, at $J = 1$, and for the possible values $\ell'_1 = 0, 2$, a clear peak located at an extremely low energy of $1.69 \times 10^{-5} \text{ cm}^{-1}$ which reaches a value of ≈ 0.22 for $\ell'_1 = 2$ is found. In addition, for all the channels, a secondary peak near $\epsilon_1 = 0.036 \text{ cm}^{-1}$ does appear, reaching a maximum value of $\approx 1.5 \times 10^{-2}$ for $J = 0$. For energies beyond the cold regime, $\epsilon_1 > 1 \text{ cm}^{-1}$, the reaction probabilities decay quickly and become negligible ($\leq 1 \times 10^{-3}$). The first peak corresponds to an $\ell_1 = 1$ orbiting resonance in the entrance channel, i.e., $J = 1$, while the secondary peaks are also orbiting resonances for the exiting value $\ell'_2 = 1$ which is common to all the channels. The values attained by these reaction probabilities are of the order of those corresponding to the vibrational relaxation of Rb_2 by collision with He ²⁵ although within a narrower interval of energy.

FIG. 1. Probabilities (upper panel) and cross sections (lower panel) for the $(J, \ell_1 = J, \ell_2 = 0) \rightarrow (J, \ell'_1 = J \pm 1, \ell'_2 = 1)$ reactive channels, depending on the kinetic energy of the incoming Rb atom, ϵ_1 . In the upper panel, the labels denote $(\ell_1 = J, \ell'_1)$. The scales are logarithmic, with the exception of the y-axis in the upper panel which is linear. An enlargement of the main peak is displayed in the inset of the lower panel, where in linear scales the x-axis should be multiplied by 10^{-5} cm^{-1} and the y-axis by 10^{-12} cm^2 .

The total cross section, Eq. (17), and the corresponding J -dependent contributions, Eq. (16), already multiplied by the $(2J + 1)$ factor are shown in a logarithmic scale in the lower panel of Fig. 1. The peaks observed in probabilities appear at almost same energies. For the peak at lower energy (see inset plot in Fig. 1), the width at half-maximum is of $\sim 1.1 \times 10^{-5} \text{ cm}^{-1}$, corresponding to a long lifetime resonance of about $0.48 \mu\text{s}$. In addition, the different partial cross sections numerically follow almost perfectly the expected trend according to the Wigner threshold law³⁹ at energies below 10^{-6} cm^{-1} , $\sigma^J(\epsilon_1) \sim \epsilon_1^{\ell_1-1/2}$. Total reaction cross section is dominated by s -waves in the ultra-cold regime, $\epsilon_1 \leq 10^{-7} \text{ cm}^{-1}$, and is fully converged up to an energy of 10^{-4} cm^{-1} . Hereupon, higher values of the total angular momentum ($J > 3$) should be considered to attain convergence as it occurs in the vibrational relaxation.²⁶ However, we do not expect that the present results would be qualitatively affected by the addition of extra partial waves. In order to estimate the efficiency of the reaction, we can compare the present reactive cross sections for Rb + RbHe with the values recently reported for the case of Li + LiYb collisions at low energies.⁴⁰ In fact, exact quantum mechanical calculations for this latter reaction yielded values of $\sim 10^{-9} \text{ cm}^2$ for cross sections at a collision energy of $\sim 10^{-8} \text{ cm}^{-1}$ and $\sim 10^{-15} \text{ cm}^2$ at $\sim 1 \text{ cm}^{-1}$. That is,

even after accounting for the different masses, see Eq. (16), a difference of 3 orders of magnitude. Nevertheless, for both processes, the contribution of the $J > 0$ partial waves starts to be noticeable at similar energies beyond 10^{-5} – 10^{-4} cm^{-1} .

At the energies of the two peaks in the precedent figure for the $(\ell_1 = 1, \ell'_1 = 2)$ channel at 1.69×10^{-5} and $3.57 \times 10^{-2} \text{ cm}^{-1}$, and also at a higher energy of 1 cm^{-1} , we plot in Figure 2 vibrational populations of the Rb₂ product. As it was mentioned above, for the rotational $\ell'_1 = 2$ state, the diatom exhibits 39 bound levels. For the two lowest collision energies considered, the rubidium dimer is preferably formed at very high vibrational levels. At the highest energy shown, the vibrational population moves towards intermediate excitations, with a maximum at $v = 32 - 33$, and shows a Gaussian-like behavior. At all energies, the population of states below $v \leq 25$ becomes negligible. Accounting for the coupling among vibrational states of rubidium induced by the presence of the helium atom, and in particular for highly excited states, would lead to a redistribution, and therefore to a modification of the individual populations, although the general behavior would remain essentially unchanged. These results resemble the findings reported in the work by Knoop *et al.* on the competition of processes of exchange/relaxation in ultracold mixtures of atom/diatom caesium species in the presence of magnetic fields.⁴¹ Specifically, the predominance of exchange is attributed to the universal regime of halo dimers, indicating that for large scattering lengths, the exchange (reactive) process occurs predominantly when all three atoms are within distances comparable to the scattering lengths and, therefore, none of the atoms feel the short-range details of the interatomic interactions. Indeed, it is hard to classify the molecular states involved in our case as “halo.” In fact, we obtain a scattering length of $\sim 170 a_0$ for the effective $^{87}\text{Rb}_2$ interaction (to be compared with the outer classical turning point for the last $v = 39$ level, placed at $\sim -1.8 \times 10^{-4} \text{ cm}^{-1}$, which becomes $\sim 132 a_0$), while the corresponding values for the $^{87}\text{Rb}-^4\text{He}$ interaction are ~ 39 and $\sim 27 a_0$, respectively. However, if the present reactive process occurred at distances comparable to the scattering lengths, the 3B potential term would not play

FIG. 2. Population of the vibrational states, v , of the formed Rb₂ molecule at three energies of the incoming Rb atom for the $(J = \ell_1 = 1, \ell_2 = 0) \rightarrow (J = 1, \ell'_1 = 2, \ell'_2 = 1)$ reactive channel. Red: $\epsilon_1 = 1 \text{ cm}^{-1}$, green: $\epsilon_1 = 3.57 \times 10^{-2} \text{ cm}^{-1}$, and blue: $\epsilon_1 = 1.69 \times 10^{-5} \text{ cm}^{-1}$. Dashed lines are depicted to guide the eye.

FIG. 3. For the leading channels $J=0, 1$, comparison of reaction probabilities for the ^4He (solid lines) or ^3He (dotted lines) partners in terms of the incoming energy of the Rb projectile. The labels denote $(\ell_1=J, \ell'_1=J \pm 1)$ channels. The values at $J=0$ have been enhanced by a factor 10.

a significant role, and the full interaction potential could be effectively described by two-body interactions only.

Figure 3 shows reaction probabilities for channels with $J=0, 1$ as a function of the kinetic energy of the incoming Rb atom, depending on the He isotope considered. Owing to the minor influence on the effective Rb_2 potential added by the $\langle \varphi_0(R_2) | W_0 | \varphi_0(R_2) \rangle$ term in Eq. (9), with φ_0 coming from Eq. (8) for ^3He or ^4He , both isotopes show a main peak ($J=1, \ell'_1=0, 2$) at almost the same energy of $1.69 \times 10^{-5} \text{ cm}^{-1}$ mentioned above, although the probability corresponding to the lightest isotope reaches only 1/2 of the value attained for the heaviest one. In general, the probabilities are lower for ^3He than they are for ^4He . This fact suggests that by increasing the mass of the third body (or by considering the presence of additional helium atoms), the formation of molecular rubidium would be enhanced. The difference is stressed in Fig. 3 where the corresponding profiles for $J=0$ have been multiplied by a factor of ten.

Taking advantage of the energy conservation and the detailed balance principle, one can consider the inverse reaction $\text{He} + \text{Rb}_2(v, \ell'_1) \rightarrow \text{HeRb} + \text{Rb}$ for a given vibrational state of Rb_2 at an energy of the He atom that is its departure energy in the direct reaction. Reaction probabilities $P_{\ell'_1, v}^J$ are thus calculated as in Eq. (12) by replacing ϵ_1 by ϵ_2 . So, for the ^4He isotope, using logarithmic scale in energies and probabilities, we plot in Fig. 4 such reaction probabilities for the different channels for $v=37$ in the upper panel and for $v=38$ in the lower one (as well as $v=39$ for the unique channel in which it exists, that is, $J=\ell_1=1, \ell'_1=0$). In the upper panel, the plots begin at energies $0.03 \leq \epsilon_2 \leq 0.04 \text{ cm}^{-1}$, the threshold value of exiting energy for the He atom in the direct reaction, while in the lower panel they start at 0.001 cm^{-1} . In the latter case, a perfect fulfillment of Wigner threshold law for $\epsilon_2 \leq 0.01 \text{ cm}^{-1}$ can be realized, that is, for reactive probabilities, $P(\epsilon_2) \propto \epsilon_2^{\ell'_2+1/2} = \epsilon_2^{3/2}$. Interestingly, whatever be the channel analyzed and for the two initial vibrational states of rubidium dimer considered, a clear sink in the reactive probabilities at an energy of $\approx 0.165 \text{ cm}^{-1}$ (0.23 K) is obtained, denoting that the reaction is practically forbidden at this energy and non-reactive processes should be enhanced

FIG. 4. Reaction probabilities at different channels for the inverse reaction $\text{He} + \text{Rb}_2(v, \ell'_1) \rightarrow \text{HeRb} + \text{Rb}$ as function of the kinetic energy of the helium atom, ϵ_2 (in cm^{-1} and K). The labels indicate (ℓ_1, ℓ'_1) . Upper panel: $v=37$ and lower panel: $v=38$ and $v=39$ (dashed black line, see text).

there. As a matter of fact, for all initial vibrational states of the rubidium dimer considered, $1 \leq v_i \leq 4$, a clear increase of the vibrational relaxation probability is reported at 0.145 K in Ref. 25. Taking into account the approximations involved in the present study, this is not too far from our prediction.

In Fig. 5, we compare for the two helium isotopes the reaction probabilities for the inverse reaction $\text{He} + \text{Rb}_2(v=39, \ell'_1=0) \rightarrow \text{HeRb} + \text{Rb}$, as function of the

FIG. 5. Reaction probabilities, in units of 10^{-5} , for the $J=1$ inverse reaction $\text{He} + \text{Rb}_2(v=39, \ell'_1=0) \rightarrow \text{HeRb} + \text{Rb}$ as function of the kinetic energy of the incoming helium atom, ϵ_2 (in cm^{-1} and K), depending on the helium isotope.

kinetic energy of the incoming helium atom. They were calculated for the only reactive channel $J = \ell_1 = 1, \ell'_1 = 0$ in which the formation of the rubidium dimer in such an excited vibrational state is possible through the direct reaction. Although reaching small values, the reaction probability for ^4He presents at 0.017 cm^{-1} (24 mK) a maximum of 2.2×10^{-4} , while for ^3He , the peak moves towards a lower energy of 0.0084 cm^{-1} (12 mK) and gets a value $\sim 3 \times 10^{-5}$. A qualitatively similar behaviour has been recently reported²⁶ for the $J = 1$ main peaks in the rate coefficient for vibrational relaxation of $\text{Rb}_2(v = 1, j = 0)$ by collisions with ^4He or ^3He , which occur at 63 mK and 3.2 mK, respectively.

We should note that the potentials employed here have been obtained through accurate *ab initio* calculations; however, there is still a remaining inaccuracy in the PES which will probably give rise to an uncertainty in the results. Previous collision calculations at ultralow kinetic energies have addressed the sensitivity of their results to the underlying PES by introducing a multiplicative λ (scaling) parameter in the potential form. Indeed, the results become very sensitive to details of the potential used in the calculations.^{42,43} In the present case, we can also expect large variations for different λ values around 1. For the channel ($\ell_1 = J = 1, \ell'_1 = 2$) leading to the highest reaction probability, we have performed additional calculations for λ varying in the range [0.95-1.05], and, as expected, large variations of the probability profile were obtained. However, the average profile shows characteristics similar to the original one ($\lambda = 1$): a main peak at an energy of $2.80 \times 10^{-5} \text{ cm}^{-1}$, with a value of around 5×10^{-2} , i.e., ~ 5 times lower than the original one, and a secondary broad structure in the energy range [0.01-0.05] cm^{-1} with probabilities of $\approx 7 \times 10^{-3}$. Moreover, the population of high vibrational states of the formed Rb_2 molecule maintains this trend at all the energies and all the λ values considered. Therefore, within a variation of the full PES of the order of $\pm 5\%$, we may conclude that our semi-quantitative results are reliable.

V. SUMMARY

As a preliminary attempt to investigate the formation of rubidium dimers in their lowest triplet electronic state by atomic collisions on the surface of helium droplets, we studied reactive collisions $^{87}\text{Rb} + ^{87}\text{Rb}^n\text{He} \rightarrow \text{Rb}_2(^3\Sigma_u^+, v) + ^n\text{He}$ ($n = 3, 4$) in a range from ultracold to moderate collision energies, 10^{-8} - 100 cm^{-1} . Using the best PES available,²⁵ we extended a pioneering model of linear triatomic molecules²⁴ to an approximate three-dimensional treatment which accounts for the main features of the process. The model leads to a great simplification of significant reactive channels and it almost reduces to analytic evaluations. The main conclusions of the present work can be summarized as follows:

- (1) The reactive process shows a high efficiency at ultracold energies for $J = 1$ that is similar to what has been recently reported on vibrational relaxation of the rubidium dimer by collisions with atomic helium.²⁶ Reaction probabilities and cross-sections fulfill numerically the

Wigner threshold law and become negligible at collision energies greater than 1 cm^{-1} .

- (2) The rubidium dimer is preferentially produced at highly excited vibrational levels, i.e., $v > 25$ for the collision energies of interest.
- (3) A complementary study of the inverse reaction reveals the presence, for all the reactive channels, of a sinking energy at which non-reactive processes should be dominant, close to the findings in Ref. 25.
- (4) Fermionic and bosonic helium as partners show similar results although with quantitative differences. The two species display clear maxima in the reaction probabilities for $J = 1$ (orbiting resonances in the entrance channel) at the same ultralow energy ($1.69 \times 10^{-5} \text{ cm}^{-1}$), as well as a secondary peak near 0.04 cm^{-1} , corresponding to orbiting resonances in the exiting channel, for all the J values. The efficiency of the reaction is clearly greater for the ^4He than for the ^3He for all the energies and in all the channels.
- (5) For $J = 1$ and $\text{Rb}_2(\ell'_1 = 0, v = 39)$, fermionic as well as bosonic helium gives rise to peaks in probabilities of the inverse reaction. The maximum in the case of the ^3He appears at a lower energy than it does for the boson, as it has also been found in the vibrational relaxation process.²⁶ However, the efficiency of the reactive process is clearly lower for the fermion than that for the boson, in contrast to the findings on the vibrational relaxation results.²⁶

Finally, since the presence and further ejection of just one helium atom enables the formation of the rubidium dimer, we plan to extend the present model to $\text{Rb}_2(\text{He})_N$ systems containing a number $N \geq 2$ of helium atoms by using some spectator model.⁴⁴⁻⁴⁶ According to the present reactive model, which involves the breaking and formation of two bonds, only one helium atom participates in the reaction, while the other $N - 1$ helium atoms will be frozen all along the reactive process. With this approach, mimicking the scenario of rubidium atoms on the surface of helium droplets, we plan to estimate the efficiency of the formation of molecular rubidium in terms of the number of spectators. A similar model will be also employed to investigate vibrational de-excitation mechanisms, as, e.g., sequential vibrational predissociation processes,⁴⁷ reaching the vibrational ground state of the rubidium dimer by the successive ejection of helium atoms.

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