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Formation of slow molecules in chemical reactions in crossed molecular beams

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We demonstrate that chemical reactions in collisions of molecular beams can generally produce low-velocity molecules in the laboratory-fixed frame. Our analysis shows that collisions of beams may simultaneously yield slow reactant molecules and slow products. The reaction products are formed in selected rovibrational states and scattered in a specific direction, which can be controlled by tuning the kinetic energies of the incident beams and the angle between the beams. Our calculations indicate that chemical reactions of polar alkali-metal dimers are barrierless and we suggest that chemical reactions involving alkali-metal dimers may be particularly suitable for producing slow molecules in crossed beams.

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I. INTRODUCTION

The creation of ultracold molecules is predicted to have a significant impact on atomic and molecular physics [1], condensed-matter physics [2], quantum-information science [3], physics of elementary particles [4], and chemistry [5]. A major goal of current research in molecular physics is therefore to produce ensembles of ultracold molecules with a wide range of properties. This goal stimulated the development of experimental techniques based on Stark deceleration of molecular beams [6], photoassociation of ultracold atoms [7], and cryogenic cooling using He buffer gas [5,8]. Chandler and co-workers have recently demonstrated the possibility of slowing molecules by colliding two molecular beams [9,10]. Their experiment showed that certain configurations of crossed molecular beams allow for inelastic scattering that cancels out the translational energy of molecules in the laboratory fixed (LF) frame. Liu and Loesch proposed an alternative method based on chemical reactions in molecular beams producing heavy molecules and light atoms [11]. They showed that the chemical reaction K+HBr→KBr+H may produce slow KBr molecules, as most of the product recoil energy is carried away by light hydrogen atoms. Here, we generalize the method of Chandler and co-workers [9,10] and Liu and Loesch [11] to show that molecules with zero velocity in the LF frame can be produced in reactive collisions of molecular beams with arbitrary mass compositions of the reactants and products.

While the technique of producing slow molecules based on collisions of thermal beams is very general, it is limited by the velocity spread of colliding beams which broadens the energy distribution of scattered molecules. Recent experimental work on Stark [6] and Zeeman [12–14] deceleration of molecular beams, buffer gas cooling of molecules [15], and electromagnetic guiding of atoms and molecules [16] has lead to the development of new technologies that allow for the production of molecular beams with extremely narrow energy distributions and relatively low forward velocities. For example, molecules cooled in a He buffer gas to temperatures of a few Kelvin can be guided out of the buffer gas cell, yielding a low-temperature beam of molecules in the rovibrationally ground state [17]. Decelerated molecular beams can be injected in a molecular synchrotron to produce packets of molecules with well defined and tunable kinetic energies [18]. External electric fields can be used to bunch the molecular packets together or spread them apart. Electrostatic guiding can be used to deflect slow molecular beams and collide them at a particular angle. Low-energy molecular beams can also be collided with trapped atoms or molecules [19]. Chemical reactions in collisions of molecular beams thus produced may potentially yield a great variety of molecular species for studies of low temperature physics and chemistry. It is therefore important to extend the method of Chandler and co-workers [9,10] to reactive collisions.

A major thrust of recent experimental work has been to create ultracold polar molecules, as ultracold dipolar gases offer exciting opportunities for new fundamental discoveries [4]. Many research groups demonstrated the possibility of creating ultracold polar molecules by photoassociation of ultracold alkali-metal atoms [7]. Alkali-metal dimers have thus become paradigm systems for studies of molecular physics at ultracold temperatures [20]. Although photoassociation usually yields ultracold molecules in vibrationally excited states, Sage and co-workers have recently reported the creation of ultracold RbCs molecules in the vibronic ground state [21]. The stability of ultracold molecules in dense gases is determined by their collision properties. For example, vibrationally inelastic collisions limit the lifetime of vibrationally excited ultracold dimers [20]. Collisions of polar molecules in the rovibrational ground state may lead to chemical reactions resulting in exchange of atoms. Chemical reactions at ultracold temperatures should be suppressed by reaction activation barriers [22]. However, many chemical reactions of alkali metal dimers do not require activation energy. For example, the reactions of K atoms with K_2 molecules, Na atoms with Na_2 molecules, and Li atoms with Li_2 molecules have been found to be barrierless and very efficient at ultracold temperatures [23]. In this work, we examine the interaction energies of two RbCs molecules and the RbCs-Rb reaction complex. Our calculation demonstrates that chemical reactions of alkali-metal dimers in molecule-molecule collisions are barrierless. Based on this calculation, we suggest that chemical reactions of the type Rb_2+Cs→RbCs

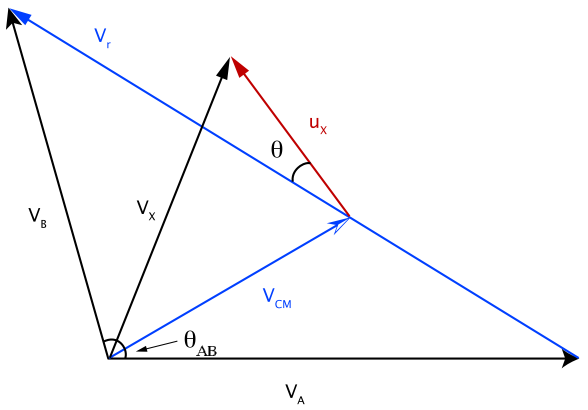

FIG. 1. (Color online) Vector diagram illustrating the kinematics of a molecular beam reactive scattering experiment.

+Rb may be used to produce cold polar molecules and suggest optimal conditions for molecular beam collisions that maximize the yield of cold RbCs molecules.

II. THEORY

A. Slowing molecules by reactive collisions

Consider a chemical reaction

$$A + B \to X + Y, \tag{1}$$

where A and B can be molecules, atoms or ions. We assume that reaction (18) occurs in a crossed molecular beam apparatus so that the velocities of the reactants A and B ($\boldsymbol{v}_A$ and $\boldsymbol{v}_B$) are well defined in the laboratory frame. The velocity of the center of mass (c.m.) of the collision complex is given by $\boldsymbol{v}_{\text{c.m.}} = (m_A\boldsymbol{v}_A + m_B\boldsymbol{v}_B)/(m_A+m_B)$, where m_i is the mass of species i. The relative velocities of the reactants (unprimed) and products (primed) are defined by $\boldsymbol{v}_r = \boldsymbol{v}_A - \boldsymbol{v}_B$ and $\boldsymbol{v}_r' = \boldsymbol{v}_X - \boldsymbol{v}_Y$, and the energy conservation requirement yields [24]

$$\tfrac{1}{2}\mu_{AB}v_r^2 = \tfrac{1}{2}\mu_{XY}v_r'^2 + E'_{\text{int}} - \Delta E_0, \tag{2}$$

where μ_{AB} and μ_{XY} denote the reduced masses of the reactants and products, E'_{int} is the energy deposited into internal modes of the products (vibration and rotation), and ΔE_0 is the difference between the total (electronic+rovibrational) internal energy of the reactants and the electronic energy of the products.

In the c.m. frame, the velocities $\boldsymbol{u}_i$ are defined as

$$\boldsymbol{u}_i = \boldsymbol{v}_i - \boldsymbol{v}_{\text{c.m.}}. \tag{3}$$

Figure 1 shows the vectors for a particular configuration of two beams intersecting at the angle θ_{AB}. The reaction products depart with the velocities $\boldsymbol{v}_X$ and $\boldsymbol{v}_Y$. Using Eq. (3), we find that if

$$\boldsymbol{u}_X = -\boldsymbol{v}_{\text{c.m.}}, \tag{4}$$

the product X has zero velocity in the LF coordinate system.

Equation (3) can be rewritten for the reaction products as

$$\boldsymbol{u}_X = \left(1 + \frac{m_X}{m_Y}\right)^{-1}\boldsymbol{v}_r'. \tag{5}$$

Squaring the vectors in Eqs. (3) and (4) and using Eq. (5) to transform the vectors $\boldsymbol{u}_X$ and $\boldsymbol{u}_A$, we obtain the scalar part of the cancellation relation

$$\left(1 + \frac{m_A}{m_B}\right)^{-2} v_r^2 - v_A^2 + 2(\boldsymbol{v}_A \cdot \boldsymbol{v}_{\text{c.m.}}) = \left(1 + \frac{m_X}{m_Y}\right)^{-2} v_r'^2. \tag{6}$$

The scalar product of vectors $\boldsymbol{v}_A$ and $\boldsymbol{v}_{\text{c.m.}}$ can be evaluated using the vector diagram in Fig. 1 to give $(\boldsymbol{v}_A \cdot \boldsymbol{v}_{\text{c.m.}}) = (m_A v_A^2 + m_B v_A v_B \cos\theta_{AB})/(m_A+m_B)$, where the angle θ_{AB} is shown in Fig. 1. Substituting this into Eq. (6) allows us to use the energy balance (2) to obtain after some algebra

$$\begin{aligned} E'_{\text{int}} - \Delta E_0 = {} & \left(1 - \frac{m_A}{m_Y}\right)E_A + \left(1 - \frac{m_B}{m_Y}\right)E_B \\ & - 2\cos\theta_{AB}\left(\frac{m_A m_B}{m_Y^2}\right)^{1/2}\sqrt{E_A E_B}, \end{aligned} \tag{7}$$

where E_A and E_B are the kinetic energies of the reactant beams in the LF frame. When the reactants and products are identical and the beams are perpendicular ($\theta_{AB} = \pi/2$), this result reduces to the expression of Chandler and co-workers for inelastic scattering of molecules [9,10]. Unlike their result, however, the cancellation relation for reactive scattering (7) depends on both E_A and E_B.

To obtain the angular part of the cancellation relation (4), we project it onto the vector $\boldsymbol{v}_r$ and use Eq. (5). This gives

$$\left(1 + \frac{m_X}{m_Y}\right)^{-1} v_r' v_r \cos\theta = (\boldsymbol{v}_B \cdot \boldsymbol{v}_{\text{c.m.}}) - (\boldsymbol{v}_A \cdot \boldsymbol{v}_{\text{c.m.}}), \tag{8}$$

where θ is the c.m. scattering angle. Evaluating the right-hand side of Eq. (8) using Fig. 1 and using Eq. (7), we obtain the angular part of the cancellation relation (4),

$$\cos\theta = \frac{E_A - E_B + \dfrac{m_B - m_A}{\sqrt{m_A m_B}}\sqrt{E_A E_B}\cos\theta_{AB}}{\sqrt{\left[E_A + \dfrac{m_A}{m_B}E_B - 2\left(\dfrac{m_A}{m_B}\right)^{1/2}\sqrt{E_A E_B}\cos\theta_{AB}\right]\left[E_A + \dfrac{m_B}{m_A}E_B + 2\left(\dfrac{m_B}{m_A}\right)^{1/2}\sqrt{E_A E_B}\cos\theta_{AB}\right]}}. \tag{9}$$

For the particular case of perpendicular beams ($\theta_{AB}=\pi/2$), this result reduces to Eq. (2) of Chandler and co-workers [9]. Our derivation thus shows that the angular kinematic constraints (9) are the same for inelastic and reactive scattering while the energy constraints (7) are different.

Equations (7) and (9) show that chemical reactions may produce molecules with zero velocity in the LF frame. In addition, Eq. (9) shows that collisions of beams may simultaneously yield slow reactant molecules (due to inelastic scattering) and slow products (due to chemical reactions), provided their c.m. angular distributions are similar. Equation (7) shows that slow molecules can be produced in both exothermic ($\Delta E_0 - E'_{\text{int}} > 0$) and endothermic ($\Delta E_0 - E'_{\text{int}} < 0$) reactions. The kinematic conditions to produce slow reaction products depend on the type of reactions. For example, the scalar cancellation relation (7) for exothermic reactions can be most easily satisfied when the mass of species Y is smaller than that of A and B. Exothermic reactions may thus be used as a source of slow heavy molecules X. Endothermic reactions with the mass combination $m_Y > m_A$, m_B may be used as a source of slow light molecules. Equation (7) shows that it may be possible to produce slow molecules not only by varying the energies of the incident beams but also by changing the angle θ_{AB} between the beams. This may be used to produce slow reaction products with specific internal energy E'_{int}. Unlike inelastic collisions [9,10], chemical reactions may produce several different products, all of which should be amenable to kinematic slowing. The vector part of the cancellation relation (9) is a constraint on the c.m. scattering angle indicating that almost all of the slow molecules are scattered along a well-defined direction, which can be controlled by varying the reactant beam energies E_A and E_B. This may be useful for manipulating the velocity of slow product molecules in order to use them as reactants for another chemical reaction.

B. Velocity spreads

In experiments, the reactant beams are often produced in supersonic expansions [9,10] and characterized by the velocity spreads Δv_A and Δv_B defined as the widths of the corresponding velocity distribution functions. These uncertainties bring about the velocity spread of the reaction products Δv_X which is a fundamental factor limiting the efficiency of kinematic cooling. Δv_X must be determined for detecting and trapping of the reaction products. The velocity spread of molecules X can be written as

$$\Delta v_X^2 = \left(\frac{\partial v_X}{\partial v_A}\right)^2 \Delta v_A^2 + \left(\frac{\partial v_X}{\partial v_B}\right)^2 \Delta v_B^2 + \left(\frac{\partial v_X}{\partial \theta_{AB}}\right)^2 \Delta \theta_{AB}^2. \quad (10)$$

The three terms on the right-hand side account for the variation of the product velocity spread due to the uncorrelated uncertainties in reactants' velocities (Δv_A and Δv_B) and the angular spread of the beams ($\Delta \theta_{AB}$). In order to evaluate the derivatives in Eq. (10), we rewrite the kinetic energy of the reactants (2) in the form

$$\tfrac{1}{2}\mu_{AB} v_r^2 = \tfrac{1}{2}\mu_{AB}(v_A^2 + v_B^2 - 2v_A v_B \cos\theta_{AB}). \quad (11)$$

Using Eq. (5), we obtain the c.m. velocity of product X,

$$u_X^2 = \frac{2m_Y\mu_{AB}}{Mm_X}(v_A^2 + v_B^2 - 2v_A v_B \cos\theta_{AB}) - \frac{2m_Y}{Mm_X}(E'_{\text{int}} - \Delta E_0), \quad (12)$$

where $M=m_A+m_B=m_X+m_Y$ is the total mass. For a particular case of backward scattering of the reaction product X, Eq. (4) can be used to write the LF product velocity in the form $v_X = u_X - v_{\text{c.m.}}$ [10]. From Eq. (12) we obtain the derivative of the product velocity spread with respect to that of beam A,

$$\frac{\partial v_X}{\partial v_A} = \frac{1}{v_{\text{c.m.}}}\left(\frac{m_A(m_B - m_X)}{Mm_X} v_A - \frac{m_A m_B}{Mm_X} v_B \cos\theta_{AB}\right), \quad (13)$$

and likewise for beam B,

$$\frac{\partial v_X}{\partial v_B} = \frac{1}{v_{\text{c.m.}}}\left(\frac{m_B(m_A - m_X)}{Mm_X} v_B - \frac{m_A m_B}{Mm_X} v_A \cos\theta_{AB}\right). \quad (14)$$

Finally, the derivative with respect to θ_{AB} can be written as

$$\frac{\partial v_X}{\partial \theta_{AB}} = \sin\theta_{AB} \frac{v_A v_B}{v_{\text{c.m.}}} \frac{m_A m_B}{Mm_X}. \quad (15)$$

To derive Eqs. (13) and (14), we assumed that $v_{\text{c.m.}} \approx u_X$, which follows from the scalar cancellation relation (4). These expressions show that the velocity spread of the reaction products depends on both Δv_A and Δv_B. In contrast, for inelastic collisions $\partial v_X/\partial v_B = 0$, that is, the velocity spread of X is independent of Δv_B [10]. As discussed in Sec. II A, for nonreactive collisions we have $m_A = m_X$ and $m_B = m_Y$. Assuming further that $\cos\theta_{AB}=0$ and transforming Eqs. (13) and (14), we find

$$\frac{\partial v_X}{\partial v_A} = \frac{v_A}{v_{\text{c.m.}}}\frac{m_B^2 - m_A^2}{(m_B + m_A)^2}, \qquad \frac{\partial v_X}{\partial v_B} = 0, \quad (16)$$

which is identical to Eqs. (17) and (15) of Ref. [10]. The expressions for the velocity spread for chemical reactions (13) and (14) are thus more complicated because of the mass asymmetry in the reactant and product channels.

Equations (13)–(15) show that if the reactant and product molecules have similar masses, the colliding beams are well collimated and the angle θ_{AB} is close to $\pi/2$, the velocity spread of product X is much smaller than that of A and B. This remarkable kinematic compression of the velocity spread was observed for inelastic collisions of NO molecules with Ar atoms by Chandler and co-workers [9,10]. Equations (13) and (14) demonstrate that the velocity spreads of cold reaction products can be much smaller than those of the reactants. It also follows from Eqs. (13) and (14) that the derivatives $\partial v_X/\partial v_A$ and $\partial v_X/\partial v_B$ can be minimized by varying the angle θ_{AB} between the beams. By setting $\cos\theta = (m_B - m_X)v_A/m_B v_B$, for example, it may be possible to completely eliminate the velocity spread Δv_X due to the velocity spread of the beam A. This may be taken into account in experiments to produce slow molecules in collisions of a slow, velocity-compressed beam with a thermal ensemble or beam of molecules.

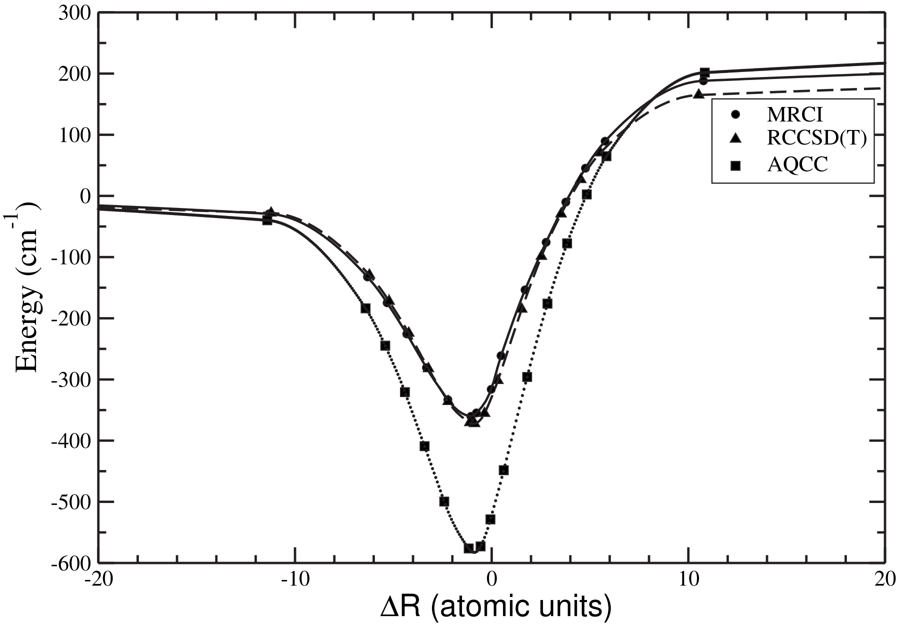

FIG. 2. Potential energy of the Rb-RbCs reaction complex along the minimum energy path. $\Delta R = R_{\text{Rb-Rb}} - R_{\text{Rb-Cs}}$, where $R_{A\text{-}B}$ is the separation between the atoms A and B.

C. Chemical reaction Rb+RbCs

Chemical reactions involving alkali-metal atoms and dimers appear to be particularly suitable for producing slow molecules as described above. For example, Grice and coworkers showed that the reaction

$$Rb_2 + Na \rightarrow NaRb + Rb, \tag{17}$$

in crossed molecular beams is very efficient [25]. It is characterized by forward-backward symmetric c.m. angular distributions and efficient energy transfer of the initial collision energy into the vibrational energy of the products. These observations indicate that the reaction (17) proceeds via a long-lived complex [25]. Chemical reactions of alkali-metal dimers with each other might also provide a rich source of slow molecules, as different combinations of alkali-metal atoms lead to both exothermic and endothermic reactions yielding molecules with a wide range of dipole moments [26]. However, little is known about chemical reactivity in molecule-molecule collisions involving alkali-metal dimers. In order to understand the reaction properties of alkali-metal dimers in molecule-molecule collisions, we calculated the interaction energies of two RbCs molecules and two LiCs molecules using an optimized geometry computation.

Our calculations were carried out with the MOLPRO package of programs [27]. In order to test the methodology and the convergence of our calculation, we initially carried out an analysis of the triatomic system Rb+RbCs. Figure 2 presents a comparison of two results obtained using the restricted coupled cluster with single, double, and perturbative triple excitations [RCCSD(T)] method and the configuration interaction (CI) calculation. Scalar-relativistic nine-valence-electron pseudopotentials were used for Rb and Cs [28] with accompanying $(7s,6p)/[5s,4p]$ contracted basis sets [29]. The geometry of the complex is fully optimized at every point so Fig. 2 presents the interaction energy of the Rb-RbCs reaction complex along the minimum energy path. The results demonstrate that the $Rb+RbCs \rightarrow Rb_2+Cs$ reaction is barrierless and that both methods provide similar estimation of the interaction energy. We also repeated the calculations using a more accurate approach, multireference-averaged quadratic coupled cluster (MR-AQCC), and found that the multireference-AQCC method consistently yields lower interaction energies.

D. Chemical reaction RbCs+RbCs

In order to calculate the interaction energy of two RbCs molecules, we define the intermolecular coordinates R_1 and R_2 that specify the separation between the geometric centers of two RbCs molecules and the separation between the centers of Rb_2 and Cs_2 molecules, respectively. The geometry of the complex is then optimized at every value of R_1 and R_2 extending to infinity. The initial calculation was based on the RCCSD(T) method. The basis set superposition error (BSSE) for the four-atom complex was calculated as $\Delta E_{ABCD}^{CP} = E_{AB} - E_{AB}^{ABCD} + E_{CD} - E_{CD}^{ABCD}$ [30]. We found that the BSSE was less than 250 cm^{-1} for all the geometries considered. We note that the BSSE always decreases the interaction energy of the complex with respect to the isolated molecules so the calculations with the BSSE removed represent the upper limit of the interaction energy for the particular method employed. Finally, we repeated the calculations at the molecular geometries from the optimized RCCSD(T) calculation using the complete active space with second-order perturbation theory (CASPT2) method. Figure 3 presents the results of these calculations.

While the potential energy of the RbCs-RbCs complex appears to be sensitive to the level of approximation, all calculations indicate that the reaction $2RbCs \rightarrow Rb_2+Cs_2$ is barrierless. The CASPT2 and RCCSD(T) calculations yield a significant maximum at the bottom of the potential well, leading to double-well structure of the minimum energy reaction path. The maximum is apparently an artifact of the restricted basis set and the single-reference character of the RCCSD(T) wave function. To verify this, we repeated the

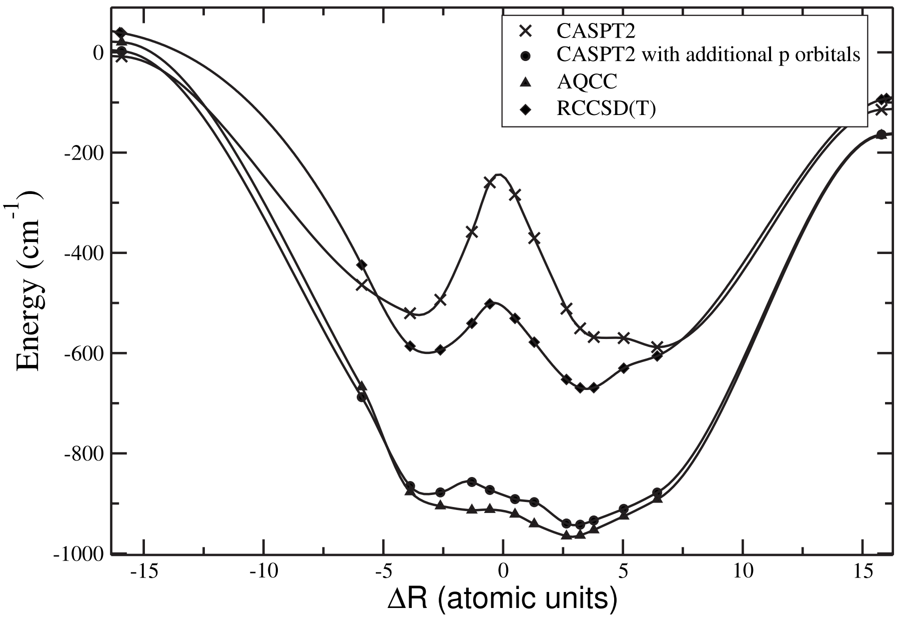

FIG. 3. Potential energy of the RbCs-RbCs reaction complex from an optimized geometry calculation. $\Delta R = (R_{\text{Rb-Rb}} + R_{\text{Cs-Cs}})/2 - (R_{\text{Rb-Cs}} + R_{\text{Rb-Cs}})/2$, where $R_{A\text{-}B}$ is the separation between the atoms A and B.

calculation with a larger set of active orbitals including three *p* orbitals for each of the four atoms and with the MR-AQCC method. The inclusion of higher order excitations removes the maximum (see Fig. 3). The results obtained with the MR-AQCC method should be regarded as most accurate, as this calculation accounts for higher excitations and multireference interactions.

The RbCs molecule is the most extended and least polar of heteronuclear alkali-metal dimers [26]. The long-range attractive dipole-dipole interaction is therefore less significant and the repulsive exchange interaction is more significant in collisions of RbCs molecules than in reactions of other polar alkali-metal dimers. To verify this, we have computed the interaction potential between two LiCs molecules using the same procedure as described above. The interaction potential between two LiCs molecules was found to be much more attractive leading to a minimum of the potential energy at <5000 cm^{-1} with respect to the limit of the separated LiCs molecules.

III. DISCUSSION AND SUMMARY

Our calculations show that chemical reactions of alkali-metal dimers in molecule-molecule collisions are barrierless, similarly to chemical reactions of alkali-metal atoms with molecules [23,25]. This has two consequences for kinematic slowing. First, molecules formed in such reactions have broad distributions over rovibrational energy levels [25]. The scalar cancellation relation (7) should therefore apply to a broad range of initial beam energies E_A and E_B, which makes reactive scattering experiments simpler. Second, the c.m. angular distributions of the reaction products are peaked near $\theta=0$ and $\theta=\pi$ [24,25]. In order to maximize the yield of cold molecules, the kinetic energies of molecular beams E_A and E_B should be adjusted to ensure that $E_A \gg E_B$ so that the fraction on the right-hand side of Eq. (9) is close to unity. This can be achieved in two ways: (i) increasing the speed of the beam A (or decreasing that of B) and (ii) decreasing the mass of the second reactant B. The method (ii) is similar to that used by Liu and Loesch for generating slow KBr products in the K+HBr chemical reaction [11]. However, the method of Ref. [11] relies on the mass asymmetry of the reaction products, while the present discussion is based on the difference of kinetic energies of the reactants.

As an illustrative example, consider the reaction

$$\mathrm{Rb}_2 + \mathrm{Cs} \rightarrow \mathrm{RbCs} + \mathrm{Rb}. \tag{18}$$

In Sec. II C, we demonstrated that this reaction proceeds without a barrier, and is likely to occur at a substantial rate in collisions of molecular beams. For simplicity of the example, we assume that the molecular beams are perpendicular and well collimated so that the third term in Eq. (11) can be omitted. If the reactant beams have equal velocities, the derivatives (14) and (15) take the values $\partial v_X/\partial v_A = -0.082$ and $\partial v_X/\partial v_B = -0.232$. Inserting this into Eq. (11), we find

$$\Delta v_X = (0.0067\Delta v_A^2 + 0.0538\Delta v_B^2)^{1/2}. \tag{19}$$

This equation shows that the velocity spread of molecules X is smaller than that of the parent beams A and B. Under typical experimental conditions ($v_A = v_B = 500$ m/s, $\Delta v_A = \Delta v_B = 50$ m/s), we obtain $\Delta v_X = 12.3$ m/s for the velocity spread of the RbCs products, corresponding to the temperature 1.9 K. The RbCs molecules formed can be loaded into an electrostatic trap [31] for subsequent use in evaporative cooling and scattering experiments.

In order to estimate the number density of cold molecules consider again the reaction (18). The number of cold RbCs molecules formed in 1 cm^3 per second is given by

$$\frac{dn_{\mathrm{RbCs}}}{dt} = k n_{\mathrm{Rb}_2} n_{\mathrm{Cs}}, \tag{20}$$

where k is the rate of production of RbCs with a particular amount of internal energy as specified by Eq. (7). In Eq. (20), n_{Cs} and n_{Rb_2} are the densities of the reactant beams. Continuous beams of alkali-metal atoms with fluxes of 5

$\times 10^{15}$ at. s^{-1} sr^{-1} and velocities of 500 m/s can be obtained using a candlestick source [32], which corresponds to $n_{Cs} = 10^{11}$ at. cm^{-3} at a distance of 10 cm away from the source. A beam of Rb dimers can be produced by expanding the mixture of alkali-metal atoms and dimers and deflecting the atoms using a Stern-Gerlach magnet [25] or by seeding Rb vapor in Ar carrier gas [33]. Pulsed supersonic beams of Rb dimers similar to those produced in Refs. [33,34] consist mostly of the carrier gas so the molecule densities tend to be rather low. Toennies and co-workers produced a beam of Li dimers with a density of 2×10^{-9} mol cm^{-3} [35]. We estimate $n_{Rb_2} = 10^9$ mol cm^{-3}. The total integral cross section σ_r for reaction (18) is unknown; however, based on the value for a similar reaction Rb_2+Na obtained by Grice and co-workers [25] we can assume $\sigma_r \approx 150$ Å^2, which corresponds to the total reaction rate of 5×10^{-9} cm^3 s^{-1} mol^{-1} at $T = 500$ K. As noted above, reaction (18) leads to the population of many excited rovibrational levels of the products. Assuming that the state-to-state integral cross section for the reaction into the rovibrational state required by Eq. (7) is a factor of 50 smaller than the total reactive cross section, we obtain the accumulation rate of cold reaction products $n_{RbCs} = 10^{10}$ mol cm^{-3} per second. Depending on the detection time, this may lead to cold molecule densities of $10^8 - 10^9$ mol cm^{-3}, which are comparable to those observed in the experiments of Chandler and co-workers. We note that the estimates above were based on the parameters of fast supersonic beams. Using Zeeman slowed beams of atomic Cs [36] and buffer-gas cooled beams of alkali-metal dimers [15], it may be possible to increase the product density by several orders of magnitude.

In summary, we have shown that chemical reactions in crossed molecular beams may produce molecules with zero velocity in the laboratory-fixed frame. Our analysis shows that collisions of beams may simultaneously yield slow reactant molecules and slow products. All reaction products are amenable to kinematic slowing. Our equations establish that slow reaction products are formed in selected rovibrational states. The kinematic slowing technique based on reactive collisions thus contains an inherent and natural state selection mechanism that can be controlled by tuning the kinetic energies of the reactant beams. Similarly, the vector part of the cancellation relation ensures that most of the slow reaction products are scattered in a well-defined direction. This direction can be controlled by changing the reactant beam energies, which can be used for generating slow molecules in order to study stereodynamics of molecular collisions at low temperatures. Chemical reactions involving alkali-metal dimers appear to be particularly suitable for producing slow molecules using the proposed method. We have presented an analysis of the interaction potential describing the chemical reaction of two RbCs molecules. Our calculations demonstrate that the reaction of Rb atoms with RbCs molecules and the reaction of two RbCs molecules are barrierless. This indicates that chemical reactions in molecule-molecule collisions involving alkali-metal dimers, if allowed, must be very efficient at ultracold temperatures.

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