The business of chemical physics is to understand the transformation of reactant molecules into product molecules during a chemical reaction. On the theory side, this is a daunting task, requiring the construction of elaborate multidimensional potential energy surfaces, complemented by classical, semiclassical, or even fully quantum mechanical scattering calculations on these surfaces. For experiments, the goal is to provide as complete a picture as possible via the complete determination of all initial and final states. For initial states, the use of molecular beam techniques provides excellent selection of internal degrees of freedom in the reactant molecules, and control over their relative state of motion. For final states, spectroscopic methods can select the relative abundance of the different rotational and vibrational states of the products, providing a wealth of information from which reaction dynamics can be inferred [1].

Recently, the experimental attainment of ultracold molecules has pushed molecular beam technology to its ultimate limit. It is now possible to prepare a molecule in a single quantum state in all degrees of freedom, down to the nuclear spin state [2, 3]. The molecules are moreover characterized by an extremely narrow range of velocities, as set by gaseous temperatures on the order of \( \mu \text{K} \). This circumstance has enabled orders-of-magnitude control over chemical reaction rates, by simply altering the nuclear spin state of the reactant molecules [4] or else by applying an electric field [5]. To probe reactions further, one could imagine transferring the molecules from the prepared ground state to any ro-vibrational excited state. These advances suggest what is possible when one prepares and manipulates the initial states of the chemical reaction.

In this Letter, we suggest that manipulation of the final states may also be possible in certain circumstances. Specifically, exit channels can become either energetically allowed, or else energetically disallowed, as a function of electric field \( \mathcal{E} \). This idea was advanced previously, in the context of the \( \text{H} + \text{LiF} \rightarrow \text{Li} + \text{HF} \) reaction, where it was argued that the exothermicity of the reaction could be shifted via electric fields [6]. Here we point out that, for alkali dimers at ultralow temperature, it is conceivable that a previously exothermic reaction can be completely turned off. This possibility is afforded by the fact that, for alkali dimers, the final states of reaction are not terribly different in energy from the reactants. Specifically, we consider collisions of a pair of KRb molecules, prepared in particular rotational states \( n_1 \) and \( n_2 \). These molecules are in general subject to two kinds of reactions: the formation of trimers via

\[
\text{KRb}(n_1) + \text{KRb}(n_2) \rightarrow \text{K}_2\text{Rb} + \text{Rb} + \Delta E_{\text{trimer}} \quad (1a)
\]

\[
\text{KRb}(n_1) + \text{KRb}(n_2) \rightarrow \text{Rb}_2\text{K} + \text{K} + \Delta E_{\text{trimer}} \quad (1b)
\]

and the bond-swapping reaction

\[
\text{KRb}(n_1) + \text{KRb}(n_2) \rightarrow \text{K}_2(n'_1) + \text{Rb}_2(n'_2) + \Delta E_{\text{bs}}. \quad (2)
\]

We report here two circumstances: 1) The reactions (1) that form trimers are energetically disallowed at ultracold temperatures, as the energy released, \( \Delta E_{\text{trimer}} \), is negative and large – several thousand wave numbers, nine orders of magnitude larger than translational kinetic energies in the gas. 2) By contrast, the bond-rearrangement reactions in (2) produce very small energy differences, since the bonds are all covalent and very similar. In zero field the reaction (2) with \( n_1 = n_2 = 0 \) is exothermic by \( \Delta E_{\text{dimer}} = 10.4 \text{ cm}^{-1} \). Moreover, the reactants KRb are polar whereas the products K2 and Rb2 are not, thus the products can only be polarized at comparatively high fields. Therefore, the relative energy \( \Delta E_{\text{dimer}}(\mathcal{E}) \) between reactants and products is, in principle, a function of the applied electric field \( \mathcal{E} \). Indeed, at fields on the order of several \( \times 10^5 \text{ V/cm} \), \( \Delta E_{\text{bs}} \) vanishes and the reaction can be turned off altogether. At fields smaller than this, high-lying rotational final states can be disallowed, thereby changing the possible distribution of product states.

We begin with the first point, that trimer formation (1) is energetically forbidden. As the trimer binding energies have not been measured, we must calculate them from \( \text{ab initio} \) methods. In general, three spin-1/2 alkali atoms can combine to form a trimer with total spin \( S = 1/2 \) (doublet state) or an excited state with \( S = 3/2 \) (quartet state). Several calculations of doublet states have been achieved, for the homonuclear trimers K3 [7] and Li3 [8],
TABLE I: Molecular properties of the diatomic molecules K$_2$, KRb, and Rb$_2$. Equilibrium bond lengths $R_e$ are in Å and dissociation energies $D_e$ are in cm$^{-1}$, (1) denotes a calculation performed at the MCSCF+MRCI level while (2) denotes a geometry optimization at the RHF-CCSD(T) level accounting for BSSE.

| Molecule | R$_e$ (1) | D$_e$ (1) | R$_e$ (2) | D$_e$ (2) | R$_e$ Expt. | D$_e$ Expt. |
|----------|----------|----------|----------|----------|------------|------------|
| K$_2$    | 4.16     | -4293    | 3.92     | -4328    | 3.92       | -4450.78(15) |
| KRb      | 4.33     | -4039    | 4.05     | -4062    | 4.05       | -4217.30(15) |
| Rb$_2$   | 4.50     | -3729    | 4.18     | -3741    | 4.17       | -3993.53(6)  |

and for certain molecular Li$_2$X systems, where X is an alkali-metal atom [9]. Soldán and co-workers have examined the two doublet surfaces of K$_3$ at C$_{2v}$ geometries as well as the conical intersection at the equilateral triangle geometry described by the $D_3h$ group [7].

We employ similar computational techniques as in Refs. [7, 9] to compute doublet ground states, within the MOLPRO suite of molecular structure codes [10]. We use the effective core potentials and basis sets of the Stuttgart group for the K (ECP10MDF) and Rb (ECP28MDF) atoms [11]. In addition, to adequately model three-body forces, we augment these basis functions with a diffuse group [7].

In the second approach, we perform a coupled Hartree-Fock (RHF) calculation on the singlet configuration. The first approach uses the RHF wave function as the foundation for a multi-configuration self consistent field (MCSCF) calculation [12, 13] with an active space that includes the first excited $p$ orbital of each atom. In addition, we include all states resulting from the $ns^0 np^1$ configurations of each atom. All remaining orbitals are closed, meaning they are energy optimized with the restriction that they remain doubly occupied. After each MCSCF calculation, we perform an internally contracted multi-reference configuration interaction (MRCI) [14, 15] calculation with the same active space as in the MCSCF. The minimum energy is then compared to the dissociation energy evaluated in the separated-atom limit.

In the second approach, we perform a coupled clusters with single, double and non-iterative triples (CCSD(T)) [16] on the $X^2\Sigma$ state at the minimum $R_e$ value obtained from the MCSCF+MRCI calculation. We then perform a geometry optimization followed by a basis set superposition error correction (BSSE) [17] to extract the bond length and dissociation energy of the systems at the RHF-CCSD(T)+BSSE level of theory. To check the adequacy of these computational methods, we compare their results with the known binding energies of alkali-metal dimers [18, 22], as shown in Table I. These results show that approach 1 gets close to the dissociation energy of each diatomic species, but noticeably overestimates the bond length, especially for the heavier alkali-metal systems. By contrast, approach 2 does just as well at predicting dissociation energies, but provides far better bond lengths. In either method, binding energies are clearly reproduced to within several hundred cm$^{-1}$. We take this as an empirical measure of the calculations’ accuracy.

We next apply the same methods to determine the minima of the three-body potential energy surfaces. The minimum of the potential energy surface should lie in the $C_{2v}$ point group i.e., the odd-atom-out is expected to lie on the perpendicular bisector of the line joining the two like atoms. Thus we initially restrict ourselves to this geometry. As a case study, we will look in detail at the K$_2$Rb surfaces, but the Rb$_2$K surfaces are similar.

As a first approach we used the RHF-MCSCF+MRCI method due to its time efficiency To be consistent with the method employed for dimers, we keep the same active space, which included the first excited $p$-orbital of each atom. We included 4 states each of $^2B_2$ and $^2A_1$ symmetries, 2 $^2B_1$, 1 $^2A_2$, and 1 $^4B_2$ states in the MCSCF. In each MRCI calculation of the $^2B_2$ and $^2A_1$ surfaces, we included 4 states as well as the reference symmetries of the other doublets.

The results of the RHF-MCSCF+MRCI calculations are presented in Fig. 1 as contour plots of the potential energy surface (PES) in the two independent bond lengths $R_{RB}$ and $R_{RK}$, for the isosceles triangle geometry. These surfaces show that the $^2B_2$ surface (upper
panel) possesses the global minimum, hence represents the ground state of the trimer. The minimum energy occurs near the singlet bond length of the KRb dimer (denoted by a horizontal red arrow), but is intermediate between the singlet and triplet bond lengths of the K₂ dimer (red and green vertical arrows, respectively). In C₂ᵥ symmetries, B₂ corresponds to an odd reflection about the bisector of the isosceles triangle. This means that along the K₂ bond the electronic wave function should roughly resemble the K₂ triplet wave function, and so should the bond length. There is then diminished electron density at the center between the two K atoms, and this allows the Rb atom to fill this space, bringing the two K atoms slightly closer together than they would be in the K₂ triplet state alone.

Similarly, the minimum of the 3A₁ surface in the lower panel of Fig. 1 is located near the K₂ singlet bond length (vertical red arrow), but in between the singlet and triplet bonds of the KRb system (horizontal red and green arrows). The 3A₁ surface requires an even reflection in the electronic wave function across the bisector of the isosceles triangle, therefore preferring a singlet-like bond in Rb₂. Therefore, the Rb atom does not quite know which spin to take since it can form a triplet or singlet with one or the other K atoms, but not both. This frustration manifests itself with a bond somewhere intermediate between singlet and triplet bonds in this coordinate.

Knowing that the the RHF-CCSD(T)+BSSE results in the dimer case are markedly better when compared to experimental values, we choose to characterize the minimum of the PES’s at RHF-UCCSD(T)+BSSE level of theory, including a basis set superposition correction. The U in UCCSD(T) refers to the spin-unrestricted formalism due to the open-shell nature of the trimer systems. Starting near the parameters obtained above for the 3B₂ surface, we find the optimum geometry by the method of steepest descents. Binding energies are determined at the RHF-UCCSD(T) level of theory, accounting for basis set overlap errors. The results are presented in Table II for all the alkali-metal trimers containing K and Rb. In the case of K₃, where results have previously been computed, we find excellent agreement with the reported values of the isosceles bond length r₁₂₃ = 4.10 Å and apex angle θₚₑₓₚ = 77.13° [1]. Based on these results, we conclude that the formation of the K₂Rb trimer would require ΔEₘᵢₜᵣₐᵣ = 2(4217) − 5982 = 2452 cm⁻¹ of energy, certainly rendering this reaction impossible at ultralow temperatures.

While a minimum of the surface appears to be in the B₂ symmetry of the C₂ᵥ point group, an examination of the trimers K₂Rb and Rb₂K away from this symmetry is needed in order to determine whether this is a global minimum. We looked at the systems in the C₃ point group and found minima which correspond to bent geometries using similar optimization procedures. In both trimers the bent geometry minimum is found to be the global minimum making the B₂ minimum a saddle point. The parameters are given in Table II. rₘᵢₜᵣᵣₐᵣ refers to the shorter of the two bonds between heteronuclear pairs when in C₃ symmetry. θ is the angle made by A-q-B, where A and B are differing atoms and q is the midpoint between the homonuclear bond.

We therefore now consider the bond-swapping reaction [2], and in particular the variation of ΔEᵣₛₑ with electric field. To do so, we look at the energy eigenvalues of the reactant and product molecules, as given by the Hamiltonian

\[ H = B_e \vec{N}^2 - D \vec{N}^4 - \vec{d} \cdot \vec{E} \]  \hspace{1cm} (3)

where \( B_e \) is the molecule’s rotational constant, \( D \) is centrifugal distortion constant, \( \vec{d} \) is the body-fixed molecular
dipole moment (which is zero for the products), and $\mathbf{E}$ is the applied electric field. In addition, both kinds of molecules also experience a shift due to their electronic polarizability $\alpha$. Using the known KRb dipole moment \[\mathbf{d}\] and computed molecular polarizabilities \[\alpha\], we can compute the relative energies of the reactants and products.

In Fig.2a) we plot the energy of the ground state (red) and several rotationally excited states of KRb+KRb as a function of electric field. Also shown (black) is the ground state energy of the products, $K_2(n = 0) + RB_2(n = 0)$. In zero field, the reactants are their natural 10.4 cm\(^{-1}\) above the products. As the field increases, the energy of the polar reactant states decreases rapidly, but that of the non-polar product states decreases far more slowly. Therefore, at a field beyond $\sim 625\ \text{kV/cm}$, the reactants are actually lower in energy than the products, $\Delta E_{\text{bs}}$ becomes negative, and the reaction is completely shut off. While a static electric field this large is probably impractical to implement, it may be possible to achieve the required energy shifts in a suitably designed microwave cavity, such as those proposed for trapping polar species \[24\]. Theory would then naturally have to account for collisions of the field-dressed states \[25\ [26]\]. As a point of reference, Fig. 2b) shows the 235 energetically allowed states of the products in zero electric field, indexed by their rotational quantum numbers $n'_1$ and $n'_2$. It is clear that, before the electric field shuts off all reactions completely, it shuts off first higher-$n'$, then successively lower-$n'$ states. Recall that the $n'$-distribution of the products is one of the key observables of physical chemistry. The ability to allow only certain values of $n'$ into this distribution will likely provide an even greater wealth of information from such experiments. The detailed effect on chemistry of shutting off successively lower rotational exit channels remains to be explored. It may be hoped, for example, that the new information gleaned would shed additional light on the role in these reactions of conical intersections.

So far we have focused on KRb, since it is the molecule for which ultracold chemistry has recently been demonstrated experimentally. However, there are other reasonable candidates for these experiments, notably RbCs \[27\], whose reaction is endothermic by 28.7 cm\(^{-1}\). Such a reaction would proceed only by placing the reactant RbCs molecules into excited states, which could certainly be done. An applied electric field could then still dictate which final channels are available, by moving these rotationally excited states relative to the Rb$_2$ + Cs$_2$ products.

Note added in preparation: New work shows that the timer reactions \[1\] are energetically forbidden for all alkali dimer collisions \[28\].

The authors acknowledge useful discussions with G. Quéméner and C. H. Greene, as well as funding from the NSF.

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