er, our calculations predict that opening of the French door gate lowers the barrier from 26 to 20 kcal/mol. Both French door and sliding door gating are evident in **9**, which shows the highest energy point in the estimated escape trajectory of ethyl acetate. The portal diameters are 3.5 Å in **8** and 7.6 Å in **9**. Both DMA and 2-butanone are intermediate cases showing small effects from French door gating of about 1.5 and 2.5 kcal/mol, respectively.

Gating is a general phenomenon that contributes to the stabilities and rates of complexation of hemicarcerands. In the absence of gating, only guests of nearly exactly the size of the portal can enter the host under normal conditions and still form stable complexes due to constrictive binding. The container molecules recently reported by Meissner *et al.* (*17*) must partially disunite the complementary halves either by sliding door gating or full dissociation to allow the passage of molecules into or out of the cavity. Gating makes it possible for a single host to form stable complexes with guests with a range of sizes. This concept provides a new design criterion for complexes and catalysts.

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Photoinduced Chemical Dynamics of High-Spin Alkali Trimers

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Nanometer-sized helium droplets, each containing about 10^4 helium atoms, were used as an inert substrate on which to form previously unobserved, spin-3/2 (quartet state) alkali trimers. Dispersed fluorescence measurements reveal that, upon electronic excitation, the quartet trimers undergo intersystem crossing to the doublet manifold, followed by dissociation of the doublet trimer into an atom and a covalently bound singlet dimer. As shown by this work, aggregates of spin-polarized alkali metals represent ideal species for the optical study of fundamental chemical dynamics processes including nonadiabatic spin conversion, change of bonding nature, and unimolecular dissociation.

Spectroscopic studies of unimolecular reactions provide detailed insight into the mechanism of formation and decay of reaction complexes (*1*). For example, electronic excitation of a van der Waals complex followed by unimolecular dissociation allows the observation of different decay channels. These channels yield information on both the weakly bound complex and the dissociation process. This dissociation can be particularly interesting if it is accompanied by a change in the bonding nature of the products. Small alkali clusters are good candidates for this kind of study because they can exhibit multiple bonding configurations that are dependent on the alignment of the spins of the valence electrons in the molecule. In the absence of spin polarization, the unpaired valence electron of the group IA alkali atoms can participate in the formation of chemical bonds in the dimer, trimer, and larger clusters of these atoms. Aggregates of atoms with parallel electron spins exhibit instead only van der Waals bonding, resulting from the balance between the attractive dispersion (correlation) forces and the Pauli repulsion between the highly deformable valence electron distributions. With the exception of the noble gas trimers, spin-3/2 alkali trimers are the simplest three-atom van der Waals aggregates. In addition to shedding light on the chemical dynamics experiments reported below, these systems are likely to be useful for the investigation of three-body intermolecular forces.

Numerous experimental (*2–10*) and computational (*11–13*) studies have been conducted on the structure and spectroscopy of the doublet states of the Na trimer (Na_3), but the quartet electronic states of Na_3 have not yet been probed. Using He nanodroplets as an inert substrate, we prepared Na_3 aggregates in their lowest quartet state and used them to investigate one of the simplest three-body nonadiabatic dynamic processes available in nature. We found by dispersed fluorescence measurements that laser excitation to an excited quartet electronic state of an alkali trimer may lead to a curve-crossing into the doublet manifold. This is followed by a dissociation of the doublet trimer into an atom and a covalently bound singlet dimer. After the intersystem crossing into the doublet manifold, the molecule will be in an excited state that is expected to dissociate (*3*).

A beam of large He nanodroplets, each droplet containing $\sim 10^4$ He atoms, was

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produced in a free jet expansion of He gas at a stagnation pressure of 5.4 MPa and a nozzle temperature of 17.5 K. We produced alkali trimers (Na_3 and K_3) by the pickup doping technique (*14*) by passing the beam of He droplets through a small chamber into which a vapor (~10^{-2} Pa) of the alkali of interest had been introduced. We then probed the alkali molecules by laser-induced fluorescence (LIF), using a continuous wave dye laser. If a He droplet becomes doped with three separate alkali atoms that have parallel electron spins, a quartet alkali trimer will form. All alkali molecules reside on the cluster surface (*15*) because of the weak alkali-He interaction energy (*16*). In the absence of electronic excitation, no mechanism is available for inducing electron spin transitions on the surface of the droplets because there are no time-dependent magnetic interactions. Therefore, the high-spin states of the alkali trimers cannot relax to the doublet ground state and so remain relatively unperturbed.

A fraction of the binding energy of any molecule formed on the He droplet is dissipated into it, causing evaporation of He atoms to reequilibrate the internal cluster temperature at 0.37 ± 0.05 K (*17*). The dissipation of this binding energy may cause sufficient evaporation to destroy a small He droplet or may cause direct desorption of the alkali molecule. We have calculated the binding energy of the quartet state of Na_3 at the coupled cluster level of theory with single, double, and noniterative triple excitations [CCSD(T)] and found that it is ~850 cm^{-1} (*18*) relative to three free ground-state Na atoms. Hence, the binding energy is significantly less than that of the doublet state [8200 cm^{-1} (*9*)]. By adding the trimer binding energy to the accommodation of the impact energy of three atoms, the formation of the quartet state of Na_3 would cause ~600 He atoms to evaporate from the He droplet; 2200 He atoms would evaporate if a doublet trimer were formed (*19*). Therefore, He droplets doped with quartet trimers are expected to outnumber those carrying chemically bound doublets in the beam emerging from the pickup cell.

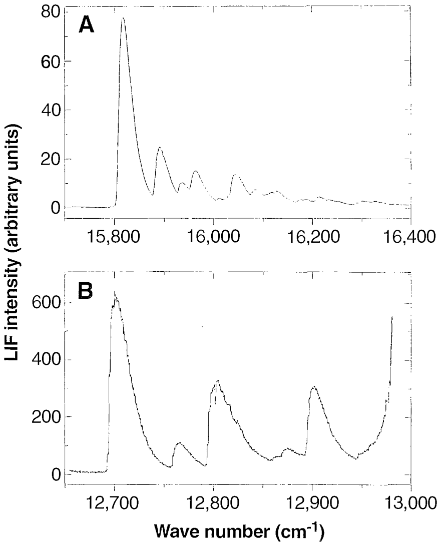

Fig. 1. (**A**) Excitation spectrum of the $2^4E' \leftarrow 1^4A_2'$ transition of Na_3 obtained by collecting total fluorescence. (**B**) Excitation spectrum of a quartet transition of K_3. Both spectra were obtained while the alkali molecule was on the surface of a He nanodroplet.

The LIF excitation spectrum (Fig. 1A), which had escaped assignment in our earlier work (*20*), can now be assigned for the following reasons. Multireference configuration interaction calculations on the quartet states of Na_3 predict an electronic transition from the lowest $1^4A_2'$ quartet state to an excited $2^4E'$ state with a vertical excitation energy of 15,500 ± 1000 cm^{-1} and an oscillator strength of 0.5, in agreement with the observed transition. The assignment to a sodium trimer is further supported by the observed cubic dependence of the LIF signal as a function of alkali vapor pressure in the pickup cell. The $2^4E' \leftarrow 1^4A_2'$ transition lies in the same region of the spectrum as the $B^2A_1' \leftarrow X^2B_2$ transition of Na_3 (*10*). However, because of the selective production of the quartet Na_3 on the He clusters, the quartet spectrum masks the presence of the doublet transition. The corresponding excitation spectrum of K_3 is shown in Fig. 1B.

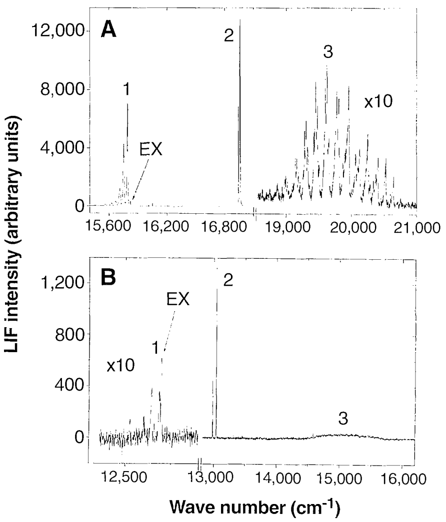

Fig. 2. Emission spectra obtained by dispersing the fluorescence resulting from the quartet transitions displayed in Fig. 1. The position of the excitation laser is marked by EX. The feature at point 1 is the direct fluorescence to the vibrational levels of the lowest quartet state. The fluorescence at points 2 and 3 result from the products of the dissociation of the doublet trimer. (**A**) Emission spectrum obtained by exciting the transition of Na_3 at 15,827 cm^{-1}. (**B**) Emission spectrum of K_3 with excitation at 12,702 cm^{-1}. In the regions around 20,000 cm^{-1} in (A) and 12,500 cm^{-1} in (B), the *y* scale has been expanded by a factor of 10.

Dispersed fluorescence spectra (Fig. 2, A and B) reveal three channels of fluorescence, two of which are at a higher energy than the excitation photons. The fluorescence channel near point 1 of Fig. 2 is the direct deexcitation to the lowest quartet state of the trimers, as revealed by a comparison of the measured vibronic structure with theoretical calculations (*21*). The channel at point 2 is atomic $n^2P_{3/2,1/2} \rightarrow n^2S_{1/2}$ fluorescence, and that at point 3 is the $(B)1^1\Pi_u \rightarrow (X)1^1\Sigma_g^+$ fluorescence of the singlet alkali dimers. Direct deexcitation to the lowest quartet state of Na_3 or K_3 competes with the nonadiabatic intersystem crossing and produces the fluorescence to the red of 15,800 cm^{-1} for Na_3 and to the red of 12,700 cm^{-1} for K_3.

The fluorescence channels near points 2 and 3 are at a higher energy than the exciting transition. Hence, either a multiphoton process is occurring or the molecule is converting potential energy into electronic energy upon excitation. As the LIF intensity grows linearly with laser power, multiphoton absorption can be ruled out. The presence of

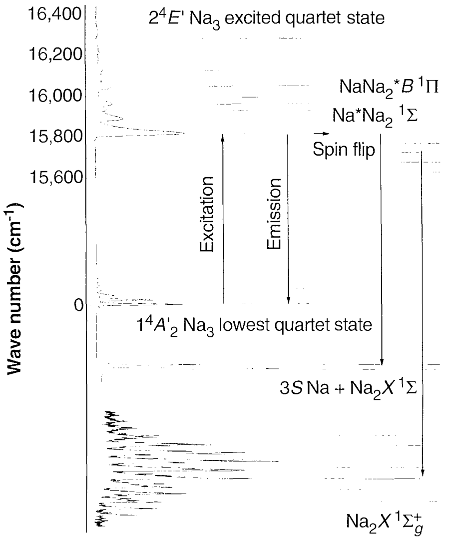

Fig. 3. Schematic of the energy levels involved in the electronic excitation of the $2^4E' \leftarrow 1^4A_2'$ transition of Na_3. The Na_3 is formed in the $1^4A_2'$ state on the surface of the He nanodroplet. The vibronic levels of the $2^4E'$ can be probed in the LIF excitation spectrum. If the strong band at 15,827 cm^{-1} is excited, emission from this level terminates in the lowest $1^4A_2'$ state if electron spin flip does not occur. If intersystem crossing occurs, dissociation of the doublet trimer produces a Na atom and a chemically bound dimer. Electronic excitation can be located on either product (denoted by an asterisk), and emission produces the atomic sodium D lines and the $Na_2(B)1^1\Pi_u \rightarrow (X)1^1\Sigma_g^+$ fluorescence.

the singlet dimer among the products of the excitation shows that the quartet Na_3 is undergoing a nonadiabatic spin flip process to cross into the doublet manifold of Na_3, followed by dissociation. Dissociation leads to atomic and singlet dimer fragments, where electronic excitation can be localized on either product (Fig. 3).

One can assign the fluorescence resulting from the $(B)1^1\Pi_u \rightarrow (X)1^1\Sigma_g^+$ transition by calculating the emission spectrum (*22*), using the Rydberg-Klein-Rees potential curves of these two states (*23*). The spectrum is consistent with an excited state population in the vibrational levels $\nu' = 0$ to 4. Initially, up to 20,988 cm^{-1} of energy is present in the excited quartet state of Na_3 (*24*). Spin flip is induced by a quartet state–doublet state interaction. Dissociation of the excited doublet state with this energy will produce vibrationally excited singlet Na dimers up to $\nu' \approx 5$ in the $(B)1^1\Pi_u$ state in agreement with the observed populations (*25*). The appearance of fluorescence from $\nu' = 0$ to 4 in the emission spectrum can be attributed to either vibrational cooling of the singlet dimer dissociation product into the He cluster or to distribution of energy into rotational and translational degrees of freedom.

The fluorescence resulting from the atomic Na and singlet dimer dissociation products reveals that the emission is occurring in the gas phase after desorption from the He cluster. We have observed the emission spectrum that results from the $3^2P_{3/2,1/2} \leftarrow 3^2S_{1/2}$ transition of Na on He clusters and found a broad fluorescence extending from 16,960 to 13,000 cm^{-1} for the orbital orientations that produce an excited state that remains bound to the He cluster (*26*). This red fluorescence is not present in the emission spectrum of the atomic Na produced in the dissociation of the doublet Na_3. The structure seen in the transitions we have observed for singlet Na_2 on the surface of He nanodroplets (*20*) is also not present in the singlet dimer product. This implies that desorption occurs on a time scale shorter than ~7 ns, the approximate lifetime of bound excited states of the alkali clusters (*27*).

A striking feature of the emission spectra is the complete lack of Na_2 or K_2 $(A)1^1\Sigma_u^+ \rightarrow (X)1^1\Sigma_g^+$ fluorescence. The failure to observe this feature suggests that this channel may close for a symmetry reason. If we assume that the dissociating doublet state is antisymmetric with respect to the plane (x, y) formed by the three atoms, then by symmetry this state can dissociate to both $Na_2(1^1\Pi_{uz})$ + $Na(3^2S)$ and $Na_2(1^1\Sigma_g^+)$ + $Na(3^2P)$, which are symmetry-allowed, whereas dissociation to both $Na_2(1^1\Sigma_u^+)$ + $Na(3^2S)$ and $Na_2(1^1\Sigma_g^+)$ + $Na(3^2S)$ are forbidden. Ab initio calculations (as well as standard molecular orbital diagrams) predict that the excited quartet state contains one electron in a molecular orbital formed from in-plane $3p$ atomic orbitals. Atomic spin-orbit coupling would couple this state only to states with one electron in the out-of-plane p_z orbital, leading to a state of exactly the symmetry that explains the selectivity observed in the emission spectrum.

The intersystem crossing from the quartet to the doublet surface is favored by the presence of spin-orbit coupling and soft vibrational motion as given by the Landau-Zener treatment (*28*). Because the trimer is expected to undergo many vibrational periods in the excited state before fluorescence decay, the overall probability for intersystem crossing can become large as the crossing region is traversed many times through the nuclear motion. The effect of spin-orbit coupling on the probability of intersystem crossing can be demonstrated by comparing the dynamics of Na_3 and K_3. The rate of intersystem crossing will be proportional to the square of the matrix element

$$|\langle\Psi_{\text{doublet}}|\hat{H}_{\text{S.O.}}|\Psi_{\text{quartet}}\rangle|^2 \qquad (1)$$

where $\hat{H}_{\text{S.O.}}$ is the spin-orbit operator and Ψ_{doublet} and Ψ_{quartet} are, respectively, the wave functions of the excited doublet and quartet electronic states. The larger spin-orbit coupling in the quartet state of K_3 (as compared with Na_3) leads to an emission spectrum such that the direct fluorescence to the lowest quartet state decreases and most fluorescence is observed in the photodissociation channels. Whereas 20.2% of the excited Na_3 trimers fluoresce to the lowest quartet state, only 7.9% of K_3 molecules remain unreacted (Fig. 2). Because the fluorescence lifetime of the excited quartet state is not expected to change significantly, the larger matrix element of $\hat{H}_{\text{S.O.}}$ coupling the two excited states in K_3 will more strongly allow the quartet states to undergo the spin-flip process than is the case for Na_3.

The surfaces of He nanodroplets appear to be ideal substrates on which to form these trimer species. The spectral perturbations are limited, and the efficiency of formation of the weakly bound species is high. Further study should provide deeper insight into the nonadditivity of intermolecular forces and the dynamics of bond formation in this simple triatomic system.

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19. This estimate is made under the assumption that each Na atom imparts ~700 cm^{-1} of kinetic energy to the cluster after pickup, which is dissipated in addition to the recombination energy. The number of He atoms evaporated is calculated under the assumption that the binding energy of a He atom in a cluster of 10^4 monomers is ~4.7 cm^{-1}.
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25. The equilibrium bond distance of the $^4A_2'$ state of Na_3 is calculated to be 4.4 Å at the CCSD(T) level of theory. A vertical electronic transition produces a quartet trimer with a similar configuration in the excited $^2E'$ state. Dissociation at this configuration would produce Na_2 in $\nu' = 25$ in the excited $(B)1^1\Pi_u$ electronic state. Because there is insufficient energy to reach this level, this exit channel should be closed. Fluorescence is observed from $\nu' = 0$ to 4 in the $(B)1^1\Pi_u$ state of Na_2, and this fluorescence implies that the bond distance in the excited $^4E'$ quartet state has contracted by ~0.9 to 3.5 Å before intersystem crossing into the doublet manifold.
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