Ultracold molecules have attracted great research interests owing to potential applications in chemical physics, quantum information processing and precision measurements. Recently, remarkable progress has been achieved in preparing and studying ultracold diatomic molecules. Direct laser cooling has been successfully applied to the molecules that have nearly closed cycling transitions, and a temperature of a few microkelvins has been achieved. Various alkali–metal diatomic molecules have been created from ultracold atoms in bulk gases or in optical tweezers. Studies of ultracold collisions involving molecules have enabled the demonstration of quantum-state-controlled chemical reactions, the observation of atom–molecule Feshbach resonances and the collisional cooling of ultracold molecules. By suppressing the ultracold reaction, quantum-degenerate diatomic molecular gases have been produced in bulk gases and in two-dimensional layers.

Extending the study of ultracold molecules to triatomic molecules or even more complex polyatomic molecules will open up many new research frontiers in physics and chemistry. For example, ultracold triatomic molecules represent three-body systems under the most stringent quantum constraints. Such a quantum-mechanical three-body problem is notoriously difficult and therefore poses great challenges to the theory of few-body physics. The molecular potential felt by the nuclei in a triatomic molecule is usually described by an anisotropic three-body potential energy surface, which is extremely difficult to calculate with high accuracy, as it requires solving a many-electron Schrödinger equation. The ultracold triatomic molecule provides an ideal platform to investigate the three-body potential energy surface, as the energy level of the ultracold molecule can be measured with exceptional resolution. Moreover, ultracold triatomic molecules have more symmetric properties and more degrees of freedom that can be controlled by external fields. Precise control of these degrees of freedom offers new opportunities in tests of fundamental physics and quantum simulation of exotic Hamiltonians. Recently, laser cooling and optoelectrical cooling have been used to cool linear triatomic molecules and other polyatomic molecules, and the temperatures have been reduced to the sub-millikelvin regime.

Besides direct cooling, another possible approach to prepare ultracold triatomic molecules is to associate pairs composed of an ultracold atom and a diatomic molecule into ultracold triatomic molecules. The major difficulty of the ultracold association is that the coupling strength between the triatomic bound state and the atom–diatomic-molecule scattering state is usually very weak. This problem may be solved by extending the ultracold association to triatomic molecules in a mixture of ultracold atoms and diatomic molecules by using a Feshbach resonance between them. Although ultracold atom–diatomic-molecule Feshbach resonances have been observed recently, using these resonances to form triatomic molecules remains challenging. Here we report on evidence of the association of triatomic molecules near the Feshbach resonance between 23Na40K molecules in the rovibrational ground state and 40K atoms. We apply a radio-frequency pulse to drive the free-bound transition in ultracold mixtures of 23Na40K and 40K and monitor the loss of 23Na40K molecules. The association of triatomic molecules manifests itself as an additional loss feature in the radio-frequency spectra, which can be distinguished from the atomic loss feature. The observation that the distance between the association feature and the atomic transition changes with the magnetic field provides strong evidence for the formation of triatomic molecules. The binding energy of the triatomic molecules is estimated from the measurements. Our work contributes to the understanding of the complex ultracold atom–molecule Feshbach resonances and may open up an avenue towards the preparation and control of ultracold triatomic molecules.
using an atom–diatomic-molecule Feshbach resonance, which occurs if the energy of the triatomic bound state coincides with the energy of the scattering state\(^6,31–34\). Therefore, close to the resonance, the coupling strength between the triatomic bound state and the atom–diatomic-molecule scattering state is resonantly enhanced. Moreover, at ultracold temperatures, Feshbach resonances can be tuned by external electromagnetic fields\(^{45}\). This kind of controllability provides an essential tool to convert pairs of atoms and diatomic molecules into the triatomic molecules close to the atom–diatomic-molecule Feshbach resonance. This technique has been widely used in the association of weakly bound diatomic molecules\(^{30–36}\) and the association of universal Efimov trimers\(^{37–41}\).

Here we explore the association of triatomic molecules in mixtures of ultracold ground-state \(^{23}\)Na\(^{40}\)K molecules and \(^{40}\)K atoms. Although a number of Feshbach resonances between \(^{23}\)Na\(^{40}\)K and \(^{40}\)K have been observed\(^7\), understanding these resonances remains challenging, owing to the complexity of the ultracold atom–diatomic-molecule collisions. A detailed experimental and theoretical study of the resonance patterns suggests that the triatomic bound state may be assigned as the long-range bound states that have similar character to the incoming scattering states\(^7\). However, little is known about the free-bound coupling mechanism and the coupling strength. Owing to the predissociation, collisions with atoms and diatomic molecules and excitations by the trap lasers\(^{42}\), the triatomic molecule lifetime may be short. In this case, we use radio-frequency (rf) fields to form the triatomic molecules. We apply an rf pulse to drive the free-bound transition in the vicinity of a Feshbach resonance between \(^{23}\)Na\(^{40}\)K molecules and \(^{40}\)K atoms and monitor the loss of \(^{23}\)Na\(^{40}\)K molecules. The advantage of this method is that, even if the lifetime of the triatomic molecule is short, the association signal can still be observed from the loss of \(^{23}\)Na\(^{40}\)K molecules. We present clear evidence of the formation of triatomic molecules by observing additional loss features that are distinct from atomic loss features in the rf spectra. Moreover, we have observed that the distance between the association feature and the bare atomic transition varies with the magnetic field. The binding energy of the triatomic molecule is extracted from the rf loss spectrum.

Our experiment starts from an ultracold mixture of \(^{23}\)Na\(^{40}\)K molecules in the rovibrational ground state and \(^{40}\)K atoms confined in a three-beam optical dipole trap. The experimental setup has been described previously\(^9\) and the experimental procedures for preparing the ultracold mixture are described in Methods. In brief, we first prepare an atomic mixture of \(^{23}\)Na and \(^{40}\)K at a temperature of about 250 nK and create weakly bound \(^{23}\)Na\(^{40}\)K Feshbach molecules near an atomic Feshbach resonance between \(^{23}\)Na and \(^{40}\)K. The \(^{23}\)Na\(^{40}\)K molecules are then transferred to the rovibrational ground state by stimulated Raman adiabatic passage (STIRAP) and the \(^{23}\)Na atoms are removed by resonant light pulses (see Methods). By selecting an appropriate hyperfine excited state and a proper laser polarization, we prepare \(^{23}\)Na\(^{40}\)K molecules in a specific hyperfine state labelled by \(I = 0, n = 0, m_{\text{nuc}} = -3/2, m_{\text{rot}} = -3\), where \(n\) and \(n\) are the vibrational and rotational quantum numbers and \(m_{\text{nuc}}\) and \(m_{\text{rot}}\) represent the projections of the nuclear spins along the direction of the magnetic field. The \(^{40}\)K atoms are transferred to the \(f = 0, m_{\text{rot}} = -9/2\) state. As illustrated in Fig. 1, we use the Feshbach resonance between the \(0, 0, -3/2, -3\) and \(9/2, -7/2\) states to form the triatomic molecules, by driving the atomic transition \(9/2, -9/2\) to \(9/2, -7/2\) through rf fields.

In the vicinity of the magnetic Feshbach resonance between \(^{23}\)Na\(^{40}\)K and \(^{40}\)K, if the frequency of the rf field is on resonance with the bare atomic transition, then the \(^{40}\)K atoms will be quickly lost owing to inelastic collisions with the \(9/2, -7/2\) atoms, which are resonantly enhanced near the Feshbach resonance. This occurs regardless of the magnetic field being above or below the resonance position. However, on the molecular side of the resonance, the triatomic bound state exists because its energy is below the scattering threshold. At these magnetic fields, if the frequency of the rf field is on resonance with the free-bound transition, triatomic molecules may be formed in the \(^{23}\)Na\(^{40}\)K and \(^{40}\)K mixture. The triatomic molecules are in an unstable excited vibrational state and will decay quickly owing to the predissociation or because of collisions with the atoms and molecules or excitations by the trap lasers. Consequently, the association of triatomic molecules will also lead to the loss of \(^{23}\)Na\(^{40}\)K molecules. The association of triatomic molecules will manifest itself as an additional loss feature in the rf loss spectrum, whose frequency is below the atomic loss feature. The distance between the association feature and the bare atomic transition gives the binding energy of the triatomic molecule, which varies as a function of the magnetic field.

We prepare \(^{23}\)Na\(^{40}\)K molecules in the \(0, 0, -3/2, -3\) state at 77.6 G (see Methods). The Feshbach resonance between the \(0, 0, -3/2, -3\) and \(9/2, -7/2\) states located at about 57.6 G with a width of about 5.3 G (ref. \(^9\)) is used to study the rf association. After preparing the \(^{23}\)Na\(^{40}\)K and \(^{40}\)K mixture, we ramp the magnetic field to a target value \(B\), close to the Feshbach resonance in 3 ms and wait 18 ms for the magnetic field to stabilize. We then apply a 20–30 ms rf pulse with a frequency close to the atomic transition \(9/2, -9/2\) to \(9/2, -7/2\) to form the triatomic molecules. The Rabi frequency of the rf pulse is about 2\(\pi\) \(\times\) 30 kHz. The rf association will be affected by the decay of the triatomic molecules due to the quantum Zeno effect\(^9\). Among the three dominant decay mechanisms, photoexcitation by trap laser photons may be suppressed by modulating the intensity of the trap lasers\(^{43–46}\). Therefore, when applying the rf pulse, we modulate the intensity of the trap laser by a square wave with a frequency of 2.5 kHz and a duty cycle of about 25%, so that the rf association is not affected by the trap light during the 75% dark time (see Methods). After applying the rf association pulse, the \(^{40}\)K atoms are removed by a resonant light pulse. We then ramp the magnetic field back to 77.6 G and transfer the remaining \(^{23}\)Na\(^{40}\)K molecules to the Feshbach state by a reverse STIRAP for detection. The numbers of remaining \(^{23}\)Na\(^{40}\)K molecules as a function of the rf frequency are shown in Fig. 2 for different magnetic fields. The rf spectra are displayed relative to the atomic transition. At the magnetic field \(B = 57.603\) G, the loss due to the atomic transfer is observed. The atomic loss feature can be well fitted to a Gaussian function being above or below the resonance position. However, on the molecular side of the resonance, the triatomic bound state exists because its energy is below the scattering threshold. At these magnetic fields, if the frequency of the rf field is on resonance with the free-bound transition, triatomic molecules may be formed in the \(^{23}\)Na\(^{40}\)K and \(^{40}\)K mixture. The triatomic molecules are in an unstable excited vibrational state and will decay quickly owing to the predissociation or because of collisions with the atoms and molecules or excitations by the trap lasers. Consequently, the association of triatomic molecules will also lead to the loss of \(^{23}\)Na\(^{40}\)K molecules. The association of triatomic molecules will manifest itself as an additional loss feature in the rf loss spectrum, whose frequency is below the atomic loss feature. The distance between the association feature and the bare atomic transition gives the binding energy of the triatomic molecule, which varies as a function of the magnetic field.

The numbers of remaining \(^{23}\)Na\(^{40}\)K molecules as a function of the rf frequency are shown in Fig. 2 for different magnetic fields. The rf spectra are displayed relative to the atomic transition. At the magnetic field \(B = 57.603\) G, the loss due to the atomic transfer is observed. The atomic loss feature can be well fitted to a Gaussian function being above or below the resonance position. However, on the molecular side of the resonance, the triatomic bound state exists because its energy is below the scattering threshold. At these magnetic fields, if the frequency of the rf field is on resonance with the free-bound transition, triatomic molecules may be formed in the \(^{23}\)Na\(^{40}\)K and \(^{40}\)K mixture.
feature emerges on the left shoulder of the atomic loss feature. Owing to the presence of this additional loss feature, the overall loss feature becomes asymmetric and broad. It can be clearly seen that the distance between the additional loss feature and the atomic transition changes with the magnetic field. At the magnetic fields $55.691 \leq B_t \leq 55.890$ G, the additional loss feature moves farther away from the atomic loss feature and therefore can be clearly resolved. The movement of the additional loss feature provides strong evidence for the association of triatomic molecules. We have checked that the additional loss features cannot be explained by the change of the magnetic field. During the application of rf pulses, the uncertainty of the magnetic field is less than about 20 mG (see Methods) and therefore the change of the magnetic field will induce an uncertainty of the atomic transition of a few kHz. This loss feature cannot be caused by the mean field shift either, as the density of $^{23}\text{Na}^{40}\text{K}$ molecules is about one order of magnitude smaller than the density of $^{40}\text{K}$ atoms and therefore the mean field shift is

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**Fig. 2** Rf spectra measured at different magnetic fields near the Feshbach resonance between $|0, 0, -3/2, -3\rangle$ and $|9/2, -7/2\rangle$. The numbers of remaining $^{23}\text{Na}^{40}\text{K}$ molecules are plotted as a function of the rf frequency. The rf frequency is referenced to the atomic transition $|9/2, -9/2\rangle \rightarrow |9/2, -7/2\rangle$. a, At $B_t = 57.603$ G, the loss due to the atomic transfer is observed. The solid line is a Gaussian fit to the data. b–f, At $55.691 \leq B_t \leq 56.134$ G, an additional loss feature due to the formation of triatomic molecules appears on the left shoulder of the atomic loss feature. We use two overlapping Gaussian functions to fit the data (red solid line), where the Gaussian function for the atomic loss feature is centred at the atomic transition. The red dashed line is a Gaussian fit to the data points with positive frequency. The association feature can be clearly seen from the difference between the data and this fit. Each point represents the average of 8–14 measurements and error bars represent the standard error of the mean. The vertical blue dashed lines indicate the position of the association feature obtained from the fit.
The measurement of the rf spectra allows us to extract the binding energies of the triatomic molecules. To this end, we use two overlapping Gaussian functions to fit the data, where the Gaussian function for the atomic loss feature is centred at the atomic transition. The binding energy $E_b$ is given by the central position of the other Gaussian function and is determined by the fit. The binding energies between $B_1 = 56.134$ G and $B_2 = 55.691$ G are shown in Fig. 3. The resonance position of $57.6$ G obtained in our previous work is shown as a reference. It can be clearly seen that the triatomic molecule is located at the low-field side of the resonance. This is consistent with the theoretical model in ref. 7, which suggests that the triatomic molecule states are probably the long-range bound states with the spin character similar to the incoming scattering states. So far, there is still no theoretical model that can quantitatively describe the binding energy of the triatomic molecule. However, close to the resonance point, the magnetic-field-dependent binding energy $E_b$ is given by the universal relation $E_b = (B - B_0)^2$. We fit the data points using the universal relation, with $B_0$ being a fit parameter. We obtain the resonance position $B_0 = 57.58(16)$ G, which is consistent with the resonance position $57.6$ G obtained in ref. 7. As a comparison, a linear fit to the data gives $B_0 = 56.74(7)$ G, which is smaller than the resonance position by about 1 G. The difference between the two fits indicates the bending of the molecular state due to the strong coupling between the scattering state and the bound state.

We note that the exact resonance position may be different from the value determined using the universal relation. Besides the uncertainty of the fit, there are also systematic errors in determining the resonance position. The binding energy determined in our work has systematic errors caused by the fitting model, power broadening and finite temperature effects. The universal relation is only approximately correct and the resonance position is extrapolated from the data. Further improvement may be achieved with the help of a theoretical model that can explain the resonance. In ref. 7, it is suggested that the Feshbach resonance between $^{23}$Na$^{40}$K and $^{40}$K is caused by long-range bound states with the character of a separated atom and a molecule. This opens up the possibility to construct a collision model to quantitatively describe the resonance based on the long-range interaction. The long-range atom–molecule interactions have been intensively discussed in theory. Multichannel quantum-defect theory (MQDT) may be used to build such a collision model. For the atomic collision, MQDT with two scattering lengths accounting for the short-range interaction and one van der Waals coefficient for the long-range interaction can describe the atomic Feshbach resonances well. For the atom–molecule Feshbach resonance, however, the highly anisotropic interaction makes the problem extremely difficult. In ref. 14, a general formalism of MQDT for anisotropic interactions has been developed. The atom–molecule resonance may be quantitatively explained by the MQDT for anisotropic interactions with a small number of short-range and long-range parameters, which can be determined by experiments.

In conclusion, we have observed evidence for rf association of triatomic molecules in ultracold mixtures of $^{23}$Na$^{40}$K and $^{40}$K. The rf association provides a spectroscopic probe of the triatomic molecule close to the Feshbach resonance between $^{23}$Na$^{40}$K and $^{40}$K. These observations may help to understand the complex ultracold atom–molecule Feshbach resonances, which are much more challenging to understand than atomic Feshbach resonances. Our work represents one of the first steps towards preparing an ensemble of ultracold triatomic molecules. The rf association method can be applied to other ultracold atom–diatomic-molecule systems in which magnetic Feshbach resonances can be observed. For example, the magnetic Feshbach resonance between NaLi and Na has been observed very recently. Besides systems consisting of an alkali-metal atom and a molecule, Feshbach resonances have also been predicted in other atom–diatomic-molecule systems. Compared with the direct cooling of triatomic molecules, the advantage of the association of triatomic molecules is that the difficulty in achieving ultracold temperatures through direct cooling is bypassed. We only need to prepare an ultracold mixture of atoms and diatomic molecules and form the triatomic molecules in the mixture by using the Feshbach resonance. The temperature of triatomic molecules will then be similar to the temperature of the ultracold mixture. The triatomic molecules formed close to the Feshbach resonance are unstable, weakly bound molecules near the atom–diatomic-molecule scattering threshold, and they may be transferred to deeply bound states by STIRAP. To this end, the potential energy surface of the electronic excited states has yet to be carefully studied. Recently, ab initio calculations of excited states of various alkali trimers have been carried out. Triatomic molecular spectra may be studied by the photoassociation of long-range polyatomic molecules in atom–diatomic-molecule mixtures. The association of triatomic molecules in our experiment is performed in bulk gases. The technique can be extended to the creation of a single triatomic molecule from a pair comprising a single diatomic molecule and a single atom using the optical tweezer technique. In optical tweezers, the decay due to collisions is suppressed and therefore the lifetime of the triatomic molecule may be improved.

Online content

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Preparation of $^{23}\text{Na}^{40}\text{K}$ molecules

We use a Zeeman slower for $^{23}$Na atoms and a 2D magneto-optical trap (MOT) for $^{40}$K atoms to produce cold atom fluxes. The atoms are captured by a double-species dark-spot MOT. After the MOT loading stage, the $^{23}\text{Na}$ and $^{40}\text{K}$ atoms are optically pumped to the maximally polarized states $| f, m_f=−2, 2 \rangle$ and $| f, m_f=−9/2, 9/2 \rangle$ and are then loaded into a cloverleaf-type magnetic trap to perform evaporative cooling. The atoms are then loaded into a large-volume crossed horizontal optical dipole trap formed by two elliptical laser beams ($\lambda=1,064\text{ nm}$ with beam waists of about $39\mu\text{m} \times 160\mu\text{m}$ crossed at an angle of about $5^\circ$). After being loaded into the dipole trap, the Na atoms are transferred to the $|1, 1\rangle$ state to suppress the three-body losses. A vertical laser beam with a waist of about $235\mu\text{m}$ is then adiabatically applied to provide confinement along the axial direction of the horizontal dipole trap. The atoms are further cooled in the three-beam optical dipole trap. At the end of optical evaporative cooling, we create an ultracold mixture containing about $3.0 \times 10^{12} 23\text{Na}$ atoms and $2.3 \times 10^{18} 40\text{K}$ atoms at a temperature of about $250\text{ nK}$. The trap frequencies for $^{40}\text{K}$ atoms are $2\pi \times (251, 67, 24)\text{ Hz}$.

To this end, we transfer the $^4$K atoms to the hyperfine state $|9/2, −7/2 \rangle$ by a Landau–Zener sweep at $32\text{ G}$ and then ramp the magnetic field to $80\text{ G}$. We transfer the $^{40}\text{K}$ atoms to the $|9/2, −9/2 \rangle$ state by a rf pulse. We then ramp the magnetic field to $77.6\text{ G}$ in $1\text{ ms}$ to create the $^{23}\text{Na}^{40}\text{K}$ Feshbach molecules. We typically produce about $2.8 \times 10^{12} 23\text{Na}^{40}\text{K}$ Feshbach molecules. The $^{1}\text{Na}^{40}\text{K}$ Feshbach molecules are then transferred to the rovibrational ground state by STIRAP. We use the mixture of $B\Pi \left( | f=12, j=1 \rangle \right)$ and $c\Pi \left( | f=35, j=1 \rangle \right)$ molecular electronic excited states $3\text{a}_2$ as the intermediate states. The pump laser ($805\text{ nm}$) that couples to the Feshbach state and the intermediate state and the Stokes laser ($567\text{ nm}$) that couples to the intermediate state and the rovibrational ground state are locked to an ultralow expansion cavity to suppress noise arising from frequency fluctuations. We use the hyperfine level of the excited state $F_1=3/2, m_{F_1}=−3/2, m_F=−3$ as the intermediate state to prepare $^{23}\text{Na}^{40}\text{K}$ molecules in the hyperfine level $|1, 0\rangle$. The $\pi$ polarized Stokes laser propagates perpendicular to the direction of the magnetic field and the $\sigma$ polarized pump laser propagates along the direction of the magnetic field. Rabi frequencies for the Stokes and the pump light are about $2−3\text{ MHz}$ and the efficiency of a round-trip STIRAP is about $40−50\%$. After the ground-state $^{23}\text{Na}^{40}\text{K}$ molecules are created, we remove the remaining $^{23}\text{Na}$ atoms by resonant light pulses. In this way, the ultracold mixture of $^{23}\text{Na}^{40}\text{K}$ and $^{40}\text{K}$ is prepared.

Magnetic field

After the preparation of the mixture of $^{23}\text{Na}^{40}\text{K}$ and $^{40}\text{K}$, we ramp the magnetic field to a target value $B_0$ in $3\text{ ms}$ and then wait $18\text{ ms}$ for the magnetic field to stabilize. We have programmed the profile of the current of the magnetic coils to compensate the eddy currents induced by the stainless steel chamber and the coils. The $^{23}\text{Na}^{40}\text{K}$ and $^{40}\text{K}$ mixture is held at the target magnetic field and we apply a $20−30\text{ ms}$ rf pulse to associate the atom and diatomic molecular pairs into triatomic molecules. The $^{40}\text{K}$ atoms are then removed by resonant light pulses and we ramp the magnetic field back to the initial value in $3\text{ ms}$. We wait about $26\text{ ms}$ for the magnetic field to stabilize and then transfer the ground-state $^{23}\text{Na}^{40}\text{K}$ molecules to the Feshbach state and detect the remaining $^{23}\text{Na}^{40}\text{K}$ molecules by standard absorption imaging. Evidence for the association of triatomic molecules has been shown in Fig. 2.

To ensure that the association feature is not caused by the change of the magnetic field, we measure the magnetic field as a function of the hold time by performing rf spectroscopy on the $|9/2, −7/2 \rangle \rightarrow |9/2, −9/2 \rangle$ transition. To include the effects of the association rf pulse on the magnetic field, we use the same time sequence as for the association experiment, except that the loading time of $^{23}\text{Na}$ atoms is shortened so that, after the evaporative cooling, only $^{40}\text{K}$ atoms remain in the optical trap. The frequency of the association pulse is chosen to be about $200\text{ kHz}$ lower than the free atomic transition $|9/2, −7/2 \rangle \rightarrow |9/2, −9/2 \rangle$. The magnetic field at the various hold times is measured immediately after the truncation of the association pulse. The magnetic field as a function of the hold time is shown in Extended Data Fig. 1. We find that the magnetic field drifts and fluctuates during the hold time, with an uncertainty of about $10\text{ mG}$. Besides this uncertainty, there is a long-term fluctuation of the magnetic field, which is estimated to be about $10\text{ mG}$. Therefore, we estimate the overall uncertainty of the magnetic field to be about $20\text{ mG}$.

Modulation of the trap laser intensity

The trap light can excite the short-range collision complex, as demonstrated in molecule–molecule collisions$^{43,44}$ and atom–molecule collisions$^{45}$. This indicates that the trap laser can induce fast decay of the triatomic molecules, which will suppress the rf association due to the quantum Zeno effect$^{39}$. In refs. $^{43−45}$, it has been demonstrated that photoexcitations due to the trap laser can be effectively suppressed by modulating the intensity of the trap light by a square wave. Therefore, in our experiment, when the rf association pulse is applied, we modulate the intensities of the trap laser beams by a square wave with a frequency of $2.5\text{ kHz}$ and a duty cycle of about $25\%$. In the experiment, the intensity of the trap laser is stabilized by using an acousto-optic modulator. The modulation of the optical intensity is achieved by controlling the power of the rf source that drives the acousto-optic modulator. During the dark time, besides reducing the power, the rf source is also turned off by an rf switch to ensure that the trap light is completely switched off. The mean intensity of the modulated trap laser is equal to the continuous wave trap laser, so that the average trap potential is the same. No notable heating or loss of atoms or molecules is observed for these modulation parameters. We have compared the rf loss spectrum in a modulated dipole trap and a continuous-wave dipole trap at $55,798\text{ G}$ and $55,890\text{ G}$. As shown in Extended Data Fig. 2, in both the modulated dipole trap and the continuous-wave dipole trap, the association feature can be clearly observed. However, the association feature can be better resolved in the modulated dipole trap. Therefore, the rf loss spectra measured in the intensity-modulated dipole trap are used in the main text to show evidence of the association of triatomic molecules and to extract the binding energies.

Data availability

All data generated or analysed during this study are included in this published article (and its supplementary information files). Source data are provided with this paper.

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Author contributions

B.Z., C.-L.B. and J.-W.P. conceived the experiments. H.Y., X.-Y.W., Z.S., J.C., P.Z., C.-Y.L. and J.-W.P. performed the experiments. H.Y., Z.S. and J.-W.P. carried out the data analysis and contributed to the writing of the paper. B.Z., C.-L.B. and J.-W.P. supervised the work.

Competing interests

The authors declare no competing interests.

Additional information

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Extended Data Fig. 1 | The magnetic field as a function of the hold time. After preparation of the $^{23}$Na$^{40}$K molecules, the magnetic field is then ramped to the target value $B_t$ in 3 ms, after which we wait 18 ms for the magnetic field to stabilize. The rf association pulse is applied between 21 ms and 51 ms. The magnetic field is measured by rf spectroscopy. The dashed lines represent the target magnetic field $B_t$. 
Extended Data Fig. 2 | Comparison of the rf spectra in the continuous-wave dipole trap and in the intensity-modulated dipole trap. a, b, The rf spectra measured in the continuous-wave dipole trap. We use two overlapping Gaussian functions to fit the data (red solid line), where the Gaussian function for the atomic loss feature is centred at the atomic transition. Each point represents the average of 6–10 measurements and error bars represent the standard error of the mean. As a comparison, the rf spectra measured in the intensity-modulated optical dipole trap are shown in c and d. It can be seen that the association feature is better resolved in the modulated dipole trap.