Laser and Fourier transform spectroscopy of KCa

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KCa was produced in a heatpipe oven and its thermal emission spectrum around 8900 cm\(^{-1}\) was recorded by a high resolution Fourier transform spectrometer. In addition, many selected transitions of this spectrum between deeply bound vibrational levels of the \(X(1)^2\Sigma^+\) and \(2)^2\Sigma^+\) states were studied using laser excitation to facilitate the assignment of the lines. The ground state is described for \(v' = 0 \text{–} 5\) and the \(2)^2\Sigma^+\) state for \(v' = 0 \text{–} 8\) with rotational levels up to 175. For both states, Dunham coefficients, spin-rotation parameters and potential energy curves are derived.

INTRODUCTION

Molecules consisting of one alkali-metal atom and one alkaline-earth atom receive rising interest for their prospective application in the field of ultracold quantum gases because their ground state \(X(1)^2\Sigma^+\) with its electric and magnetic dipole moments offers advantageous properties (see e.g. references [1–3]) for testing and/or demonstrating fundamental properties of quantum gases. After investigating LiCa\(^[4]\) and LiSr\(^[5]\), we proceeded to the heavier KCa for opening perspectives for spectroscopic studies of even heavier species like RbSr for which already ultracold ensembles of Rb and Sr were prepared\(^[2]\). Compared to LiCa and LiSr, however, the experimental study becomes more difficult because of the higher density of spectral lines of KCa and the always accompanying molecule K\(_2\). We present a spectroscopic observation of KCa and its first rovibrational analysis from which the bottoms of the potential energy curves of the ground state \(X(1)^2\Sigma^+\) and the first excited state \(2)^2\Sigma^+\) are derived.

Ab initio calculations for KCa have been performed by other groups\(^[6, 7]\). FIG. 1 shows a part of the potential energy scheme of KCa for the lowest atom pair asymptote K(4s\(^2\)S) + Ca(4s\(^2\)1S) and the excited asymptote K(4p\(^2\)P) + Ca(4s\(^2\)1S) and K(4s\(^2\)S) + Ca(4s4p\(^3\)P). We started with recording the thermal emission spectrum of KCa in a heatpipe to locate the general position of the spectrum and to discriminate it from the K\(_2\) spectrum. The observed spectrum was found in the near infrared region, expected from the ab initio results shown in FIG. 1. Laser excitations of the molecule were performed and were essential for an unambiguous assignment of the dense and overlapping spectral structure. Methods to interpret the results of such experiments for gathering structural information about the molecule are described. For the observed \((2)^2\Sigma^+ - X(1)^2\Sigma^+\) system, molecular parameters are derived. A comparison of results from ab initio studies with experimental findings of this work is presented.

I. EXPERIMENT

The spectroscopic setup consists of a heatpipe oven for the molecular gas and an optical system for imaging the thermal emission spectrum into a Fourier Transform Spectrometer (FTS). The heatpipe is shown in FIG. 2. It is a 88 cm long steel tube with a diameter of 3 cm. The middle section of the heatpipe is enclosed by an oven. The ends of the heatpipe are cooled to room temperature via water-cooling so that no metal vapour can reach the BK7 windows. The windows are tilted to avoid back reflections. The outer regions of the heatpipe are
Internally covered with a steel mesh of approximately 30 cm in length, so that the condensed metal can flow back into the heated middle section. Additionally, shells cooled with forced airflow are installed at these regions (see FIG. 2) to create lower temperature areas and an appropriate temperature gradient for the very different vapour pressures of Ca and K. During the experimental run, crystals grow inside the heatpipe, producing laser stray light and finally blocking the optical path. That significantly reduces the measuring time to about five hours. Therefore, they must be melted intermittently by changing the heatpipe position in the oven. The use of cooling shells slows crystal growth.

To prepare the heatpipe, 10 g of calcium are placed in the middle of the heatpipe and melted under an atmosphere of 200-300 mbar of argon at an oven temperature of up to 1000°C. After the heatpipe is cooled down, 5 g of potassium are placed on the mesh at a distance of about 25 cm from calcium on the outer region of the heatpipe not facing the spectrometer. Potassium is melted at 8900°C on the side of the potassium and an oven temperature of 400°C. Afterwards, the cooling shells are installed.

The light emerging from the heatpipe is imaged into the FTS (IFS 120HR, Bruker) via a mirror and a lens system and finally detected by an IR-enhanced silicon avalanche photodiode (S11519-30, Hamamatsu). The laser light is introduced counter-propagating the imaging path of the thermal emission to avoid direct laser radiation into the FTS. For this purpose, the mirror is slitted and the laser beam propagates along the optical axis within the heatpipe, indicated in FIG. 2.

To produce the KCa molecules, the region of the heatpipe at the calcium position is heated to approximately 820°C. By varying the air flow, the cooling shells create an region with 260-340°C on the side of the potassium and an region with 450-650°C on the other side. During the measurements, the pressure of the buffer gas, argon, is about 50 mbar.

In addition to KCa, K$_2$ molecules are forming in the heatpipe even at low temperatures and dominate the gas spectrum. Since the observed emission lines of both molecules lie in different spectral ranges, this does not affect the observation of KCa. We use K$_2$ to align the imaging of the fluorescence region by exciting K$_2$ molecules with a HeNe-laser and adjusting the mirror so that only the fluorescence, but no stray light from the walls, is recorded.

The thermal emission is observed in the range from 8000 cm$^{-1}$ to 9700 cm$^{-1}$. FIG. 3 shows the spectrum recorded with a resolution of 0.03 cm$^{-1}$ and represents an average of 290 scans. On the left, one can clearly see lines at 8491.8 cm$^{-1}$ and 8551.8 cm$^{-1}$, which correspond to the transitions $^2P_{3/2} - ^2D_{5/2}$ and $^2P_{1/2} - ^2D_{3/2}$ of atomic potassium. The KCa spectrum of the (2)$^2$$\Sigma^+$-X(1)$^2$$\Sigma^+$ band is located between 8800 cm$^{-1}$ and 9400 cm$^{-1}$, as expected from the ab initio calculations [7]. The shape of the background in this area changes with the temperature in the heatpipe. Since the conditions in the heatpipe change over time, the recordings have different background shapes but this does not influence the position of the lines.

One can well recognize band heads, the largest of which is at 8900.3 cm$^{-1}$ and is assigned to the (0–0) band on the basis of Franck-Condon factors (FCFs) derived from the ab initio potentials. The inset in FIG. 3 is a zoomed part showing clearly the rotational structure.

Due to the atomic masses of about 40 u and the fairly shallow ground state potential, the rotational and vibrational constants of KCa are rather small. Furthermore, the high temperature needed for producing the molecules leads to a wide range of populated vibrational and rotational levels and due to the Franck-Condon factors thermal emission is distributed over many vibrational transitions. The vibrational bands are strongly overlapping which hinders the direct assignment. Therefore, laser induced fluorescence (LIF) is used to identify pairs of lines according to the selection rule $\Delta J = \pm 1$ for the common total angular momentum of the excited state, $J'$, and associate lines of a vibrational progression within the ground state.

To excite the KCa molecules, a tunable diode laser with an antireflection coating (Toptica) is used in a Lit-
trow configuration, and it is stabilized by a wavemeter (WS-U, HighFiness GmbH), leading to an uncertainty of the exciting laser frequency of less than 20 MHz. The frequency range of the diode is about 8730 – 9350 cm\(^{-1}\). The laser light with a power of 10-20 mW and a beam diameter of approximately 2 mm is precisely adjusted along the optical axis, which was fixed before by the fluorescence observation of K\(_2\) induced by a HeNe-laser. Lines selected from the emission spectrum are excited and the fluorescence spectra were recorded with a resolution of 0.05 cm\(^{-1}\). The fluorescence progression appears as enhanced lines in the thermal emission. An overview of the fluorescence studies is given in TABLE [1](a).

Because a recorded spectral line consists of several overlapping Doppler-broadened transitions, we assign an uncertainty of 0.02 cm\(^{-1}\) to most transition frequencies. For broad lines, a higher uncertainty is assumed. The measured frequency differences have been generally given an uncertainty of 0.01 cm\(^{-1}\) if the fluorescence lines are sufficiently enhanced compared to the thermal emission spectrum because of the significantly reduced Doppler shift due to a mismatch of the laser excitation.

II. ANALYSIS

A. Overview

Laser excitations in the band heads yield easily recognizable fluorescence (by the enhanced intensity compared to primary thermal emission) in other band heads which can be used to order the vibrational structure of the X(1)\(^2\Sigma^+\) and (2)\(^2\Sigma^+\) states. FIG. [1](a) to (c) shows eight vibrational bands which are associated in three systems of almost equal vibrational spacing, representing the vibration of the ground state. The laser excitation is at the overshooting line. The short progressions also allowed for a preliminary assignment of vibrational quantum numbers starting with \(v'' = 0\), since no fluorescence could be observed beyond this labeled line. This assignment is consistent with the later calculated FCFs (see section [IV]). In FIG. [2] the three progressions are shown above each other on the same absolute scale. The vibrational ladder for the excited state becomes visible by differences between two of such recordings as indicated at the bottom of the figure. The obtained vibrational spacings allowed for extrapolating the vibrational ladders. The band heads predicted in this way coincide with other band heads observed up to (7–4) in the thermal emission spectrum, even if they showed no or hardly recognizable fluorescence, as indicated in FIG. [3].

The bands are blue shaded, thus the band head is given by the P branch. Excitations in the band heads could yield fluorescence of a group of rotational lines in the R branch as seen in trace (a) of FIG. [4] above the band head (0–0). These rotational fluorescences form two distinct systems, later identified as transitions between spin-up states or spin-down states, labeled F\(_1\) and F\(_2\) (see section [V]). FIG. [5] depicts these fluorescences in detail, explaining the appearance of the group of rotational lines and the possibility to observe the energy difference between F\(_1\) and F\(_2\) lines by only slightly shifting the excitation frequency in the band head. We should point out that the experiment does not give information which line system is F\(_1\) or F\(_2\). Similar groups of fluorescence lines were also observed for the (0–1) band. The lines of such a group correspond to consecutive rotational quantum numbers \(N\). (We use \(N\) as rotational quantum number, see later Hund’s coupling case(b)). For relatively small ranges of \(N\), the changes in the effective rotational constant \(B\) are negligible, thus the frequency differences \(\Delta\nu\) of the PR pairs for \(N'\) follow the formula

\[
\Delta\nu = B''(4N' + 2),
\]

Requiring that \(N'\) is integer, a discrete set of values for the rotational constant is derived from each observed \(\Delta\nu\). For several observed PR differences, we construct the sum over the weighted quadratic distances to the closest integer for each observation with index \(i\)

\[
\frac{1}{\#\text{obs}} \sum_{i} \left( \frac{N'_i(B) - N''_i(B)}{\delta\nu_i} \times 2\delta\nu_{\text{min}} \right)^2,
\]

and the minimum of this function with respect to \(B\) gives the value for \(B''\) of the studied band. Here, \(\#\text{obs}\) is the number of observations, \(N'_i(B)\) is calculated with the observed \(\Delta\nu_i\) from rearranging Eq. [1]. \(N''_i(B)\) is the integer
FIG. 5. (Colour online) The red and blue spectra show LIF from excitations in the P band head of the (0–0) band of KCa and fluorescence lines in the R branch. The thermal emission spectrum (black) is shown for reference. The upper part of the figure shows the Fortrat parabolas corresponding to the P and R branches for $N'$ separating the overlaps in the band head to the wide spread in the R branch. Red and blue circles correspond to $F_1$ and $F_2$ levels, respectively. The two cases of excitations show the differences between $F_1$ and $F_2$: the red spectrum contains only fluorescence of $F_1$ lines, the blue spectrum contains mainly fluorescence of $F_2$ lines with some $F_1$ lines at the edges of the fluorescence region.

Closest to $N'_i$, $\Delta \nu_i$ is the experimental uncertainty of $\Delta \nu_i$ and the factor $2 \cdot \delta \nu_{\text{min}}$, with the smallest uncertainty of the series, serves to normalize the expression. FIG. 6 exemplifies such sums in dependence of a given rotational constant $B''$. Trace (a) is the example of a single observation and the zero-positions represent the discrete set of possible $B''$ mentioned above. Adding more and more observations (from (b) to (c)), the desired minimum of the function becomes more pronounced. The value for $B''$ determined with this procedure from FIG. 6 (c) is $0.0470 \text{ cm}^{-1}$ and close to the later determined value of $Y''_{01}$ of the full evaluation (see TABLE II).

Having thus determined $B''$, Eq. (1) could directly be applied to assign rotational quantum numbers to the observed fluorescence lines and fluorescence lines in other vibrational bands from the same LIF spectrum. These assignments together with $B''$ can immediately be used to determine a value for $B'$. Thus LIF experiments with the laser tuned to several band heads provided the starting point for the analysis of the rovibrational spectrum.

B. Assignment and molecular parameters

Hund’s coupling case (b) with the basis vector $|\Lambda, (N, S), J\rangle$ is used to describe both $2 \Sigma^+$ states, where $\Lambda$ is the quantum number associated with the projection of the orbital angular momentum to the molecular axis (here $\Lambda = 0$), $N$ is the total angular momentum without spins, $S$ is the total spin of the electrons and $J = N + S$ is the total angular momentum of the molecule excluding the nuclear spins. The rovibrational energies can be expressed by the Dunham expansion

$$E(v, N) = \sum_{m,n} Y_{mn} (v + \frac{1}{2})^m |N(N+1)|^n,$$

for each electronic state with the so-called Dunham parameters $Y_{mn}$. The parameter $Y_{00}$ is used in this analysis.
to approximate the electronic term energy $T_e$ and thus has a different meaning than the conventional Dunham correction $Y_{00}$.

The energy levels with $J = N + 1/2$ and $J = N - 1/2$ of a doublet state ($S = 1/2$) are labeled by $F_1$ and $F_2$, respectively, and are split for the same $N$ because of the spin-rotation coupling given by the Hamiltonian $\hat{\gamma} \hat{S} \cdot \hat{N}$ with a coupling constant $\gamma$. This energy is added to the rovibrational energies since the interaction operator is diagonal in the Hund’s case (b) basis:

$$E = E(v, N) + \frac{\gamma}{2} \times N$$

for $F_1$  \hspace{1cm} (4a)

$$E = E(v, N) - \frac{\gamma}{2} \times (N + 1)$$

for $F_2$ \hspace{1cm} (4b)

In principle, the spin-rotation contribution will depend on the vibrational and rotational level and thus could be described by a corresponding Dunham-like series with $\gamma_{mn}$ as expansion parameters. Our evaluation program contains this form for both states, but the energy expression being linear in $N$ results for P and R transitions to a function which mainly depends on the differences of the spin-rotation interactions of the two electronic states. Thus we choose $\gamma_{00}$ of the excited state as non-zero and this value actually represents the difference of the two interactions. Because we have sets of fluorescence progressions, each with a common excited level, we found that the data contain a slight $\gamma$ dependence of the vibrational level of the ground state, thus we introduced for this fact the parameter $\gamma_{10}$ for the ground state. All other expansion parameters $\gamma_{mn}$ were set to zero.

The parameters $Y_{00}$, $Y_{01}$ for both states and $\gamma_{00}$ of the excited state can be fitted using the fluorescence spectra of the $(0–0)$ band head excitations. Starting with these initial parameters, more fluorescence lines with assigned quantum numbers are subsequently included in the fit based on their PR differences. Similarly, fluorescence lines from other vibrational bands are included.

Since the KCa spectrum is dense, the laser we use in an LIF experiment can affect several transitions from different bands. Examples of such cases of fluorescence are given in FIG. 2. In this figure, two laser excitations are shown on the same absolute scale to illustrate the relation of the different vibrational bands. In both cases, two progressions are excited simultaneously. Trace (b) shows very different $N$ and results in Stokes pairs of the band $(0–1)$ and trace (a) is an excitation of a line in $(0–0)$ and one in $(0–1)$ showing anti-Stokes fluorescence to $(0–0)$. From the fluorescence spectra, lines from bands with $v' = 0 - 2$ and $v'' = 0 - 3$ could initially be identified and assigned. Reviewing the fluorescence spectra with the final molecular parameters yielded the identification of additional fluorescence lines with $v' = 3$ and $v'' = 4 – 5$. The ranges of observed rotational quantum numbers are listed in TABLE I.

Further bands are analyzed using the thermal emission spectrum. For this purpose, the thermal emission spectrum is simulated with the Dunham parameters determined up to the actual intermediate evaluation step with Franck-Condon factors derived from the initial ab initio potentials and a line width estimated from the Doppler width and the selected resolution of the FTS and a population according to the actual temperature. This theoretical spectrum is compared with the recorded spectrum and allows for adding additional lines to the fit and to adjust the parameters and add new ones. Occasionally, the simulated spectrum shows a high intensity line close to lines with similar intensity and width in the experimentally recorded spectrum. If these lines show this behavior for a long series of quantum numbers, they are identified with the lines from the recorded spectrum and a fit will show the consistency with the other assignments done before. The extension in quantum number space was done in small steps, avoiding large extrapolation in quantum numbers $v$ and $N$, because due to the dense spectra it is very probable to assign a wrong line. By doing this carefully, the shape of the simulated spectrum converges to the shape of the experimental spectrum.

In total, 2554 lines and frequency differences could be measured between 878 levels in the ground state up to $v'' = 5$ and 549 levels in the excited state up to $v' = 8$. The resulting Dunham parameters are listed in TABLE I with their estimated standard deviations. The normalized standard deviation $\sigma = 0.95$ of this linear fit validates the choice of the uncertainties described in section I. All assigned lines used in the the final fit of the Dunham parameters are contained in the supplementary material.
TABLE II. Dunham and spin-rotation parameters for the first two $^2\Sigma^+$ states of $^{39}$K$^{40}$Ca. The parameters give an accurate description for levels with quantum numbers as given in TABLE III. All values given in cm$^{-1}$.

| n  | $Y_{n0}$          | $Y_{n1}$          | $X(1)^2\Sigma^+$ | $Y_{n2}$          | $Y_{n3}$          | $Y_{n4}$          |
|----|------------------|------------------|------------------|------------------|------------------|------------------|
| 0  | 0.0              | 4.75384(25) $\times 10^{-2}$ | -9.3968(190) $\times 10^{-8}$ | -8.54(88) $\times 10^{-14}$ | -6.57(15) $\times 10^{-18}$ |
| 1  | 67.9826(37)      | -6.4306(84) $\times 10^{-4}$ | -2.062(64) $\times 10^{-9}$ | -7.20(14) $\times 10^{-14}$ | - |
| 2  | -9.3950(45) $\times 10^{-1}$ | -5.87(15) $\times 10^{-6}$ | -1.771(74) $\times 10^{-10}$ | - | |
| 3  | -1.01(15) $\times 10^{-3}$ | - | - | - | |

$^a$ Note that the experimental data only yields the difference, namely $\gamma'_{00} - \gamma''_{00}$.

III. POTENTIAL FIT

The evaluation with the Dunham expansion shows that the two electronic states are well described by Hund’s coupling case (b) with basis vectors $|A,(N,S)J\rangle$ and the possible coupling to other electronic states for example by spin-orbit coupling is not observed within the present experimental accuracy of 0.02 cm$^{-1}$. Thus we can set up two separate Hamiltonians for the two states. Because the spin-rotation interaction is diagonal in the basis, the corresponding energy contribution adds to the rovibrational eigenenergies $E(v,N)$ as given in Eq. (4). The Schrödinger equation for the rovibrational energies and for the rovibrational wavefunction $\psi_{vN}$ has the conventional form

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + U(R) + \frac{\hbar^2}{2mR^2} N(N+1) \right] \psi_{vN}(R) = E(v,N)\psi_{vN}(R),$$

with the reduced mass $m$ of the molecule and the potential function $U(R)$ for each electronic state. The approach by potential functions gives the advantage to release the constraints by the truncation of the power expansion in quantum numbers $(v,N)$ for the energies in Dunham representation. Such possible effect can be contained in the solution in TABLE III looking at the different centrifugal contributions for the two electronic states, namely the highest term $Y_{02}$ for the excited state and $Y_{04}$ for the ground state.

For solving the Schrödinger equation, we set up the potential in the analytic form as successfully applied in several earlier papers (e.g. [1])

$$U(R) = \sum_{i=0}^{n} a_i \xi(R)^i,$$

$$\xi(R) = \frac{R - R_m}{R + b R_m},$$

where the coefficients $a_i$ are fitted parameters and $b$ and $R_m$ are fixed. $R_m$ is normally set close to the value of the equilibrium separation $R_e$. The potential is extrapolated for $R < R_{\text{inn}}$ with:

$$U(R) = A + B/R^{N_o}$$

by adjusting the parameters $A$, $B$ with $N_o = 6$ to get a continuous transition at $R_{\text{inn}}$. For large internuclear separations ($R > R_{\text{out}}$) we adopted the standard long range form:

$$U_{\text{LR}} = U_{\infty} - C_6/R^6 - C_8/R^8 - C_{10}/R^{10}$$

The dispersion parameters $C_i$ do not play any role in our present case, because we observed only low vibrational levels and did not reach the long range region in $R$, thus these parameters serve for setting up a smooth potential function to the dissociation limit $U_{\infty}$.

A non-linear least squares fit to all assigned transitions and transition differences with common upper levels obtained from the fluorescence study was performed, fitting simultaneously the potential functions for the two electronic states. The spin-rotation contribution was included in exactly the same form as used before, see Eq. (2). The fit describes the experimental data with the same quality, namely the normalized standard deviation $\sigma = 0.94$, as obtained for the Dunham fit. The derived potential parameters are given in TABLES III and IV the number of fit parameters is only 20, thus smaller than.
TABLE III. Parameters of the analytic representation of the potential for state $X(1)^3\Sigma^+$. Parameters with an asterisk * ensure smooth continuous extrapolation of the potential at $R_{\text{in}}$ and $R_{\text{out}}$, with ** for constructing the dissociation asymptote.

\begin{align*}
\text{TABLE IV. Parameters of the analytic representation of the potential for state (2)$^3\Sigma^+$. Parameters with an asterisk * ensure smooth continuous extrapolation of the potential at $R_{\text{in}}$ and $R_{\text{out}}$, with ** for constructing the dissociation asymptote.}

\end{align*}
This is mainly due to the fact that in this region lie lines of bands with $v'' = 6 - 10$ and good FCFs that were not taken into account in the potential fit. Due to the strong overlap of the bands, even small displacements of these lines by incomplete modeling strongly influence the overall intensity profile. The spectrum below 8820 cm$^{-1}$ and beyond 9380 cm$^{-1}$ cannot be analyzed convincingly because the intensity is too low (see FIG. 3). A screenshot from the simulation program is shown in FIG. 8. In the upper part the individual transition positions are indicated by colored vertical bars. Notice that small deviations of the measured and simulated profiles appear throughout the diagram. They can mostly be attributed to result from the sum of many lines, each might deviate within the uncertainty of the model from the “true” transition frequency, see the dense pattern in the upper part of the figure. Lines for the second abundant isotopologue $^{41}\text{K}^{40}\text{Ca}$ are extrapolated since all transitions could be attributed to the main isotopologue $^{39}\text{K}^{40}\text{Ca}$. With the help of the simulation, we revisited the fluorescence studies. The systematic inspection shows relatively long vibrational progressions with fluorescence intensities in agreement with the predicted FCFs. Many such fluorescence lines were not sufficiently pronounced compared to the thermal emission, so that they were overlooked in the former assignment process. This successful extension shows the overall consistency of the whole simulation despite the existence of less well described spectral regions mentioned above.

Both evaluation approaches, the energy representation by Dunham coefficients or by molecular potentials, fit the measurement data equally well. TABLE VI shows for comparison the molecular parameters determined in this work and those from known ab initio calculations. The agreement of the fitted parameters is very good and differences between $Y_{10}$ defined by the Dunham approach and $\omega_e$ for the potentials are not significant but they are different in definition and this is also true for $Y_{01}$ and $B_e$. The experimentally determined equilibrium separation $R_e$ and vibrational constant $\omega_e$ of the ground state lie between the two ab initio values. In the excited state, these theoretical values deviate from the experimental ones by less than 1%. The potential depth could not be derived because of missing high vibrational states. The experimentally determined electronic term energy of the excited state differs only by 34 cm$^{-1}$ from the calculated value, confirming the good quality of the ab initio calculations.

Compared to the lighter molecule LiCa, the rotational and spin rotational constants of KCa are smaller. KCa does not show any perturbations of the $^2\Sigma^+$ state within the achieved accuracy, in contrast to LiSr where we observed the coupling between $(2)^2\Sigma^+$ and $(1)^2\Pi$ in our previous work.

Because of the high density of the lines in the KCa emission spectrum, the LIF experiments were indispensable for assignment. To extend these results to higher vibrational bands, we will start a new series of laser excitations. We expect to detect lines up to $v'' = 10$ of the ground state because of sufficiently large FCFs. For further investigations of KCa, we will study $(3)^2\Sigma^+ - X(1)^2\Sigma^+$ transitions in the visible spectral range for which a high transition dipole moment is predicted. The relevant spectral region around 14000 cm$^{-1}$ should be sufficiently devoid of $K_2$ spectra, whereas Ca$_2$ lines can be expected, but should not dominate the spectrum. These proposed studies will provide higher vibrational levels of the ground state needed for extrapolating to the atom pair asymptote which is greatly desired for the study of ultracold KCa.

SUPPLEMENTARY MATERIAL

See the supplementary material for the full recorded thermal emission spectrum, a list of the assigned lines, an overview of the deviations of the Dunham and potential model and derived tables of Franck-Condon factors for various $N$.

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TABLE V. Comparison of measured spectroscopic constants of $^{39}$K$^{40}$Ca with results of known ab initio calculations. All values are given in cm$^{-1}$, except $R_e$ which is given in Å.

| Method | $R_e$ | $D_e$ | $\omega_e \approx Y_{10}$ | $\omega_e \chi_e \approx -Y_{20}$ | $B_e \approx Y_{01}$ | $T_e$ | Ref. |
|--------|-------|-------|-----------------|-----------------|----------------|-------|------|
| X(1)$^2\Sigma^+$ | | | | | | | |
| CCSD(T) | 4.32 | 974 | 61 | - | 0.045 | 0 | [6] |
| MRCI | 4.197 | 1474 | 70.8 | 0.85 | - | 0 | [7] |
| Dunham | 4.2377 | - | 67.983 | 0.940 | 0.047538 | 0 | this work |
| potential fit | 4.2395 | - | 67.971 | - | 0.047541 | 0 | this work |
| (2)$^2\Sigma^+$ | | | | | | | |
| MRCI | 4.177 | 5633 | 95.0 | 0.40 | - | 8922$^a$ | [7] |
| Dunham | 4.1811 | - | 94.960 | 0.271 | 0.048831 | 8888.047 | this work |
| potential fit | 4.1825 | - | 94.937 | - | 0.048846 | 8888.019 | this work |

$^a$ derived from potential given in private communications

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