Laser cooling and electronic structure studies of CaK and its ions CaK$^\pm$

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Keywords: laser cooling, Franck–Condon factor, dipole moment, potential energy curves, spectroscopic constants, electronic structure, ab initio calculation

Abstract

Aiming at a laser cooling investigation, we have used ab initio complete active space self consistent field (CASSCF)/(MRCI +Q) calculations to study the electronic structure of the diatomic molecule CaK and its molecular ions CaK$^+$ and CaK$^-$. The potential energy curves and the static dipole moment curves have been investigated for the considered molecules along with the spectroscopic constants $T_e$, $\omega_e$, $B_e$, and $R_e$, in addition to the values of dipole moment $\mu_e$ and dissociation energy $D_e$. Overall, 19 and 14 electronic states have been studied respectively for CaK, CaK$^+$, from which 12 for CaK and six for CaK$^+$ have been investigated here for the first time. Our obtained results agree well with data related to states that have been previously examined. Nineteen electronic states have been explored for CaK$^-$, which up to our knowledge have not been previously calculated. The transition dipole moments have been calculated for the lowest $\Sigma^+ - \Sigma^+$ and $\Sigma^+ - \Pi$ transitions along with the Franck–Condon factor, Einstein coefficient, the spontaneous radiative lifetime, and the emission oscillator strength corresponding to the investigated transitions. A ro-vibrational analysis has been done via the canonical function approach, where the vibrational parameters $E_v$, $B_v$, $D_v$, and the turning points $R_{\text{min}}$ and $R_{\text{max}}$ have been determined. These calculations showed that the molecule CaK is a suitable candidate for Doppler laser cooling, and we propose a laser cooling scheme to this end. The Doppler limit temperature $T_D$ and recoil temperature $T_r$ have values as low as $T_D = 51 \, \mu\text{K}$ and $T_r = 156 \, \text{nK}$. The results should provide a useful reference for experimental spectroscopic and ultra-cold molecular physics studies.

1. Introduction

A growing interest toward polar molecules that are composed of one alkali–metal and alkaline–earth atom has emerged in recent years [1–11]. These molecules possess permanent electric dipole moments and magnetic dipole moments, which allow them to be used in many applications ranging from the realization of quantum simulations [12] and lattice spin models [1] to precise measurements of fundamental physical constants [13]. Ultra-cold polar molecules resulting from the combination of alkali–metal (AM) atoms have been recently produced, as their electronic structure proved to be suitable for use in photo association techniques [14]. The ultra-cold polar molecules resulting from the combination of an AM and an alkaline–earth–metal atoms also seem to be promising candidates because their elements can also be cooled efficiently [15, 16]. In this view, accurate theoretical calculation of the diatomic molecules’ electronic structure in their gaseous states seems very necessary to understand the mechanisms of production, collisional cooling, and types of lasers required for the cooling experiments. While the molecule CaK has...
been the subject of few studies that included few of its excited states [17–19], an extensive study about its molecular ions CaK± is still missing up to date.

In the present work, we use the ab initio method (CASSCF/MRCI + Q) to investigate the potential energy (PECs) and the static dipole moment curves of the low lying electronic states of the molecule CaK and its molecular ions CaK±. The spectroscopic constants \( T_v, \omega_v, B_v, R_v \), the permanent dipole moment (PDM) \( \mu_e \), and the dissociation energy \( D_b \) have also been computed. The transition dipole moments, the Einstein coefficients, the spontaneous radiative lifetime, the emission oscillator strength, and the Franck–Condon factors (FCFs) have also been determined along with these constants. A rovibrational study has been performed to determine the vibrational energy \( E_v \), the rotational constant \( B_v \), the centrifugal distortion constants \( D_v \), and the abscessas of turning points \( R_{\min} \) and \( R_{\max} \) for the bound states of the three considered molecules. We find that the CaK molecule is a suitable candidate for Doppler laser cooling, and we propose a plausible laser cooling scheme.

2. Computational approach

We have performed ab initio calculations for CaK and CaK± molecules in the \( C_{2v} \) point-group symmetry by employing the state averaged complete active space self consistent field (CASSCF), followed by multireference configuration interaction (MRCI) method with Davidson correction (+Q) [20], with the computational program MOLPRO [21] taking advantage of the graphical user interface GABEDIT [22]. The calcium atom, consisting of 20 electrons, has been treated in the following way: using the quasi-relativistic energy consistent pseudo-potential ECP10MWB basis set [23], ten electrons were frozen within the core of Ca. The remaining ten electrons were considered as active electrons within the considered molecular orbitals. The potassium atom K is treated in all electrons schemes by the weighted core valence five zeta basis set (wCV5Z) [24]. For the considered molecules in the \( C_{2v} \) symmetry, the active space is denoted by: \( 7 \sigma \) (Ca: 4s, 4p\(_0\), 3d\(_0\), 3d \( \pm \) 2; K: 4s, 5s, 4p\(_0\)), \( 3 \pi \) (Ca: 4p \( \pm \) 1, 3d \( \pm \) 1; K: 4p \( \pm \) 1), \( 1 \delta \) (Ca: 3d \( \pm \) 2) distributed into the irreducible representation \( a_1, b_1, b_2, \) and \( a_2 \) as \([7, 3, 3, 1]\). We have used this method because of the nature of the basis sets: the wCV5Z basis set is a relatively recent basis set that has been made available in MOLPRO and other databases. We were interested in the high precision quality that was portrayed by this basis set. We chose the ECP basis set for the Ca atom by referring to different papers published in the literature that used this type of basis set successfully for group II atoms [25–27]. Additionally, other groups and we had used a similar combination of basis sets types in previous work related to alkaline–alkali–earth compounds and obtained results that agreed well with the literature [28–30].

Additionally, using the same methods and computing packages, we have calculated the lowest-lying molecular curves for CaK using ECP10MWB basis set for both atoms Ca and K. For the considered molecules in the \( C_{2v} \) symmetry, the active space is denoted by: \( 9 \sigma \) (Ca: 3s, 3p\(_0\), 4s, 3d\(_0\), 4p\(_0\), 5s; K: 5s, 5p\(_0\), 6s); \( 4 \pi \) (Ca: 3p \( \pm \) 1, 3d \( \pm \) 1, 4p \( \pm \) 1, K: 5p \( \pm \) 1), \( 1 \delta \) (Ca: 3d \( \pm \) 2).

3. Results and discussion

3.1. Potential energy curves

The PECs that were obtained using the (wCV5Z) and ECP10MWB basis set of the low-lying electronic states of the molecules CaK and CaK± are investigated and presented as a function of the internuclear separation in figures 1–8. Doublet CaK PECs are represented in figure 1 (\( ^2 \Sigma^+ \) and \( ^2 \Delta \) electronic states) and figure 3 (\( ^2 \Pi \) electronic states), quartet CaK PECs are represented in figure 2 (\( ^4 \Sigma^{(+)−} \) and \( ^4 \Delta \) electronic states) and figure 3 (\( ^4 \Pi \) electronic states). Singlet CaK± PECs are represented in figure 4 (\( ^1 \Sigma^+ \) and \( ^1 \Delta \) electronic states) and figure 6 (\( ^1 \Pi \) electronic states), triplet CaK± PECs are represented in figure 5 (\( ^3 \Sigma^{(+)−} \) and \( ^3 \Delta \) electronic states) and figure 6 (\( ^3 \Pi \) electronic states). Singlet and triplet states of CaK− anion are presented in figures 7 and 8, respectively. We display the lowest dissociation limits of the calculated low-lying electronic states of the CaK and CaK± molecule in table 1, in comparison with the combination of atomic orbitals values obtained from the National Institute of Standards and Technology website (NIST) [31]. Some of the higher excited molecular states are not presented since the dissociation limits have not been obtained for these electronic states due to the undulations in the PECs at the long-range of the internuclear distance \( R \). The undulation in the PECs is explained by the breakdown of the Born–Oppenheimer approximation. The dissociation limits are also displayed on the PECs for more clarity. In the case of CaK, we notice that the dissociation limits of the PECs agree well with those obtained with the NIST database, with a relative error of 8.1% for the first dissociation limit and 12% the second. In the case of CaK±, we also see like values between the values obtained with NIST and those with our calculations, except for the
second dissociation limit. We could not present a similar table for CaK\(^-\) ion as the energy values of negative ions are not available on the NIST web site. However, we could deduce the dissociating species from the behavior of the PDM curves at the asymptotic limit and the atomic orbital of the neutral Ca and K atoms. Avoided crossings and non-adiabatic couplings repeatedly appear between the investigated states of the three considered molecules. Table TS1 of the supplementary material SM1 (https://stacks.iop.org/NJP/23/013017/mmedia) shows the positions of crossing and avoided crossing between the electronic states of CaK, CaK\(^+\), and CaK\(^-\) with their corresponding energy gaps \(\Delta E\).

3.2. Spectroscopic parameters

We have calculated the spectroscopic constants for the molecules CaK and CaK\(^\pm\) by fitting the obtained PEC to a polynomial in terms of the internuclear distance \(R\). These constants include the vibrational harmonic frequency \(\omega_v\), the internuclear distance at equilibrium \(R_e\), the rotational constant \(B_e\), the electronic transition energy \(T_e\) and the dissociation energy \(D_e\).

The spectroscopic constants for 19, 13, and 18 electronic states of the molecule CaK, and its ions CaK\(^+\) and CaK\(^-\), obtained by using mixed type basis sets have been respectively calculated and tabulated in tables 2–4. Comparison with data that has been published in the literature and respective relative differences has been provided for CaK and CaK\(^+\) molecules (a positive/negative sign means respectively an increase/decrease of a value compared to the one calculated in this work).

3.2.1. CaK neutral molecule

(i) Spin-free CaK potential energy curves

CaK molecule data that we have obtained has been mainly compared with three references [17–19]. Extensive spectroscopic and rovibrational experimental data using laser and Fourier transform spectroscopy have been presented by Gerschmann et al [17]. This neutral system has been theoretically studied with three valence electrons in all the compared calculation methods: CCSD(T) [18], CCSD, CASPT2, and MCSCF/MRCI [19]. The CASPT2 and MCSCF/MRCI calculation done in [19] had considered for K atom a combination of the effective core potentials of Lim et al [32, 33] extended with additional K basis set functions. For Ca atom, the basis set used was a combination of the cc-pCV5Z-PP basis set of the Peterson group [34] with that of Lim et al. A similar basis set was recently published by Peterson et al [24].

For the ground state of CaK neutral molecule, the values of \(R_e\), \(T_e\), \(\omega_v\) and \(B_e\) are very close to those already found in the literature, with relative differences: 0.7% < \(|\Delta R_e/R_e|\) < 4.7%, 3.30% < \(|\Delta \omega_v/\omega_v|\) <
Figure 2. PECs of the lowest (a) $^4\Sigma^+(\pm)$ and (b) $^4\Delta$ electronic states of the CaK using CASSCF/MRCI method with three valence electrons. The spin–orbit curves (c) for the parents state $^4\Delta$.

13.3\%, and $|\Delta B_e / B_e| = 2.5\%$. The ground state dissociation energy $D_e$ was equal to $1245$ cm$^{-1}$, while the calculated values obtained with the CCSD(T), MCSCF/MRCI, CASPT2, and CCSD methods are: $974$ cm$^{-1}$, $1474$ cm$^{-1}$, $1438$ cm$^{-1}$, and $875$ cm$^{-1}$. It seems that the MCSCF/MRCI and CASPT2 calculations give closer values to our results as they both use the same multiconfigurational reference method.

The excited states show a recurrent lower value of $T_e$ as calculated in this work, compared to the literature’s values. As expected, the relative differences that we obtained for $T_e$ among all the excited states, in comparison with the MCSCF/MRCI and CASPT2 methods ($4.77\% < |\Delta T_e / T_e| < 11.33\%$) are smaller than those obtained with the CCSD method, where ($6.31\% < |\Delta T_e / T_e| < 20.5\%$). Up to the highly excited level ($^4\Sigma^+$), the equilibrium distances $R_e$ found in this work seem to be slightly higher than those previously calculated. Except for the $^2\Pi$ state, the relative differences between the values that we obtained and those with the various calculation methods vary as $0.7\% < |\Delta R_e / R_e| < 6.55\%$. Likewise, we have obtained values for $\omega_e$ that agree very well with other calculation methods, with relative differences majorly
lower than 8%. State (2)\(^2\Pi\) however, shows a remarkably smaller value of \(\omega_e\) than other calculation methods. Overall, our results agree well with the experiment.

In general, using a given basis set can significantly affect the value of the well depths \(D_e\). For example, Van Mourik et al computed the well depths \(D_e\) of \(H_2\) molecule at several correlated levels of theory, using correlation consistent basis sets that varied from aug-cc-pVDZ to aug-cc-pV6Z, d-aug-cc-pVDZ to d-aug-cc-pV6Z, and t-aug-cc-pVDZ to t-aug-cc-pV6Z [35]. Typical relative differences between \(D_e\) values among different basis sets and computational methods reached values as high as 165% (\(D_e\) obtained using the MP2 method with aug-cc-pVDZ was equal to 12.69\(\mu E_h\), while that obtained with CCSD (T) technique with t-aug-cc-pV6Z was equal to 33.53\(\mu E_h\)). Similarly, relative differences between \(D_e\) values among different basis sets and computational methods for \(Ne_2\) and \(Ar_2\) molecules reached values as high as 250% and 101%, respectively. In our case, the MRCI results we obtained with our chosen basis sets seem to agree relatively well with those cited in the literature. For all the studied states, \(D_e\)'s values are smaller than those obtained with MCSCF/MRCI and CASPT2 methods, with up to about 33% relative difference. Values
Figure 4. PECs of the lowest (a) $^1\Sigma^+$ and (b) $^1\Delta$ electronic states of the CaK$^+$ molecule using CASSCF/MRCI method with two valence electrons.

obtained with the CCSD method appear to be closer to our values, especially for states $(1)^2\Pi$, $(2)^2\Sigma^+$, $(2)^2\Pi$ and $(1)^4\I$. The agreement ensures the accuracy and reliability of our calculations. The curves and the comparison with the literature of the spectroscopic constants obtained with the ECP10MWB basis sets used for both atoms are placed in the supplementary material document SM2. We find that the relative errors for all the spectroscopic constants with respect to data in the literature are rather high, compared to the mixed basis set method. They vary such as: $5.20\% < \Delta R_e/R_e < 8.98\%$ for the ground state and $4.47\% < \Delta R_e/R_e < 5.31\%$ for the first excited state. By comparison, the values obtained with the ECP and wCV5Z basis sets stated above are: $0.70\% < \Delta R_e/R_e < 4.70\%$ for the ground state and $4.00\% < \Delta R_e/R_e < 4.48\%$ for the first excited state. Similarly, the relative errors for $T_e$ obtained using the ECP basis set for both atoms are $4.7\% < \Delta T_e/T_e < 8.48\%$ for $(1)^2\II$, while those obtained with ECP and wCV5Z basis sets are $5.3\%$ for the MCSCF/MRCI method and CASPT2 method. Finally, the degraded values of the relative errors become blatant with the ECP basis set for the values of $\omega_e$, where $35.22\% < \Delta \omega_e/\omega_e < 56.37\%$ for X$^2\Sigma^+$ and $9.52\% < \Delta \omega_e/\omega_e < 10.34\%$ for $(1)^2\II$, while the values obtained with the ECP and wCV5Z basis sets stated in the paper are $3.3\% < \Delta \omega_e/\omega_e < 13.93\%$ for X$^2\Sigma^+$ and $5.9\% < \Delta \omega_e/\omega_e < 6.9\%$ for $(1)^2\II$. Given these values, we estimate that it would be more suitable to use the mixed basis set method for this molecule.

(ii) Spin–orbit CaK potential energy curves

We have calculated the spin–orbit curves for some selected states of CaK, using the same configuration and basis sets described above. We introduced the spin–orbit effects for both atoms through their corresponding spin–orbit pseudopotentials. The energies of the molecular states are computed by diagonalizing the total Hamiltonian ($H_t = H_e + W_{SO}$). We have also calculated the spin–orbit curves’ spectroscopic constants and the splitting values between the spin–orbit states and displayed them with the corresponding spin–orbit PECs in supplementary material SM1. For illustration, we have displayed spin–orbit curves belonging to parents states $(1)^4\Delta$ and $(1)^2\II$ in figures 2 and 3, respectively. A comparison between the spin-free and spin–orbit spectroscopic constants shows that the values are close to each other for states $(1)^2\II$ and $(1)^2\Delta$. States $(1)^4\II$ and $(2)^2\II$ do show a change in the shape of the curves as they are both very close to each other (in fact, in some sections of the curves, they superpose on each other). However, the second minima in the spin–orbit curves emanating from $(2)^2\II$ do show very similar spectroscopic constants of the parent state. By looking at the splitting graphs, we notice that the splitting is minimal, as it is approximately equal to 10 cm$^{-1}$. This is expected as the molecule in question is not very
heavy, and as a consequence, the spin–orbit effect should not be very accentuated in this case. The ground and \( ^2\Sigma^+ \) states seem to have such a negligible splitting energy value that it was not captured through the computations.

3.2.2. CaK\(^+\) cation

Table 3 shows a comparison of our CaK\(^+\) results with work that has been recently published by Zrafi \textit{et al} [36]. The \( T_e \) values that we obtained seem to be higher than those calculated by Zrafi \textit{et al} for the lower-lying electronic states and lower for higher-lying states (starting from \( (2)\Sigma^+ \)). Overall the absolute relative difference varies as \( 0.34\% < |\Delta T_e/T_e| < 15.55\% \). Similarly, to CaK molecule, our calculated values of \( R_e \) for CaK\(^+\) cation are slightly smaller than those found in the literature for the ground and first 13 excited states (relative difference \( |\Delta R_e/R_e| \) varies from 1.66\% to about 7\%, except for \( (1)\Pi \)). Also, the relative differences for \( B_e \) and \( \omega_e \) vary approximately between 5\% and 15\%, except for state \( (1)\Pi \), which shows higher relative differences. As explained previously, the values of the well depth \( D_e \) present a much larger variation than \( R_e \), \( T_e \), \( B_e \), and \( \omega_e \), with the change of the computational method and basis sets used. Again, state \( (1)\Pi \) presents higher relative differences than the remaining states whose values vary as \( 18\% < |\Delta D_e/D_e| < 43\% \). Up to our knowledge, the remaining six excited states’ spectroscopic constants have been calculated here for the first time.

3.2.3. CaK\(^-\) anion

The spectroscopic constants of the negative ion CaK\(^-\) have been computed and presented in table 4. Anions are notoriously difficult systems to treat by electronic-structure theory, especially at the level of the excited state [37], because of electronic excited states that risk to lie within the NMFE (neutral molecule plus free electron) continuum. Anion PECs representing continuum states of a given molecule will usually follow the neutral ground state. They will become closer and closer to the ground state as the basis set is increased. For a typical PEC, the quantity that varies is the bond length. An analogy exists with varying the bond length and the basis set, which can help discriminate unauthentic curves: if a calculated resonance curve of a given molecular system follows its adiabatic curves with increasing internuclear distance, then the curves being described are probably spurious NMFE states [38]. A study on this subject was recently published [39], where pure bound state curves were compared to scattering curves obtained by the \( R \)-matrix method: a
scattering curve of LiH$^-$ was found to be following the avoided crossing of its adiabatic PEC, and it was deduced that they represent the NMFE, and not some bound states of the anion.

In this work, an observation of the neutral ground state of the neutral molecule CaK and the excited states of the CaK$^-$ ion shows that they do not follow well for both the singlet (figure 7) and the triplet (figure 8) states. The only state that seems to follow the neutral molecule’s ground state is that of the negative ion (which should not be admitting any spurious element).

One also has to note that the K atom electron’s affinity is large enough to protect the CaK$^-$ system from electron auto detachment. However, since the ions are among the so far unknown systems, one should take particular care with the results that we present here. Experimental work or stabilization techniques such as $R$-matrix calculations are useful in this case to confirm our findings. We could not compare our results with any previous work as the presented PEC are calculated here for the first time.

### 3.3. Permanent dipole moment

The PDM of a molecule is critical for determining its polarity, the degree of the ionic and covalent character of its bonding, and its long-range dipole–dipole forces. The PDM curves of the investigated electronic states of the CaK molecule and its molecular ions have been plotted in terms of internuclear distance $R$ in figures FS1–FS9 of the supplementary material. The electron density distribution of a molecule usually controls the values of its dipole moments. Considering the Ca atom to be at the origin, a charge transfer from Ca to K leads to negative dipole moment values when the charge density is closer to the K atom. This polarity can be expressed as Ca$^+$K$^-$. A reversed polarity denoted by Ca$^-$K$^+$ reflects a charge transfer from K to Ca atom. For the neutral CaK molecule, the DMCs tend to zero at the dissociation limit of the molecule (except (3)$^2\Pi$ and (2)$^4\Sigma^-$), which reveals a dissociation into neutral fragments.

For CaK$^+$ and CaK$^-$ most of the DMCs dissociate in the positive and negative regions at large $R$, respectively, and the remaining ones dissociate into neutral fragments for both. The dipole moment of the ground state $X^2\Sigma^+$ of CaK molecule is positive with a maximum magnitude $|\mu| = 1.27$ a.u. at $R = 3.96$ Å, and decreases beyond 3.96 Å, until reaching zero at the asymptotic limit of dissociation. The absolute values of $\mu_e$ at the PEC minimum were calculated for the ground and excited states for the molecules CaK and CaK$^\pm$ and reported in tables 2–4. The comparison of our calculated absolute values of the PDM $\mu_e$ corresponding to the ground state $X^2\Sigma^+$ of CaK with those reported theoretically by Pototschnig et al [19] using MCSCF/MRCI and CASPT2 methods shows the relative differences $\delta_{\mu_e}/\mu_e = 22.4\%$ and $\delta_{\mu_e}/\mu_e = 30.22\%$, respectively. For the excited states (1)$^3\Pi$ and (1)$^4\Sigma^+$ $|\mu_e|$ the agreement is acceptable,
Figure 7. PECs of the lowest (a) $1^\Sigma^+$, (b) $1^\Delta$, and (c) $1^\Pi$ electronic states of the CaK$^-$ molecule using CASSCF/MRCI method with four valence electrons. X$^2\Sigma^+$ ground state of the neutral molecule is drawn for comparison (dashed line) with the remaining curves.

and it deteriorates for the states (2)$^2\Pi$, (1)$^4\Pi$, (2)$^2\Sigma^+$ and (3)$^2\Sigma^+$. This discrepancy can be attributed to the different theoretical techniques or basis sets used in the calculations.

3.4. The transition dipole moments, the Einstein coefficients, and the radiative lifetimes
The transition dipole moment curves (TDMCs) of the allowed transitions between the ground and the lowest excited states of the molecules CaK, CaK$^+$, and CaK$^-$ are investigated and plotted as a function of the internuclear separation in figures 9–11. For the neutral molecule CaK, the TDMCs for the transitions X$^2\Sigma^+\rightarrow$(1)$^2\Pi$ and X$^2\Sigma^+\rightarrow$(2)$^2\Sigma^+$ tend to a constant value of 3.2 a.u. at $R > 12$ Å, and those for the transitions X$^2\Sigma^+\rightarrow$(2)$^4\Pi$ and X$^2\Sigma^+\rightarrow$(3)$^4\Sigma^+$ transitions tend to zero when $R$ is bigger than 9.4 Å. The
Figure 8. PECs of the lowest \(3\Sigma^+\) and \(3\Delta\), and (b) \(3\Pi\) electronic states of the CaK using CASCCF/MRCI method with four valence electrons. \(X^3\Sigma^+\) ground state of the neutral molecule is drawn for comparison (dashed line) with the remaining curves.

TDMCs of the transitions \(X^1\Sigma^+\)–(1)\(1\Pi\) and \(X^1\Sigma^+\)–(3)\(1\Sigma^+\) for the cation \(Ca^+\) tend to a constant value of 3.0 a.u. while the transition \(X^1\Sigma^+\)–(2)\(1\Sigma^+\) tends to zero when \(R\) is larger than 13.75 Å. For the anion \(CaK^-\) all the TDMC tend to zero for \(R\) larger than 15 Å.

The transition constants values have also been calculated at equilibrium position \(R_e\) of the upper state for each of the considered electronic transitions by using the relations of Hilborn [40]

\[
\omega_{ij} = 2\pi \nu_{ij}
\]
\[
A_{ij} = \frac{2\omega_{ij}^3 \mu_{ij}^2}{3\varepsilon_0\hbar c^3}
\]
\[
\gamma_{cl} = \frac{e^2 \omega_{ij}^2}{6\varepsilon_0 m_e c^2}
\]
\[
f_{ij} = \frac{-A_{ij}}{3\gamma_{cl}}
\]

where \(\nu_{ij}\) is the transition frequency between the two states, \(\varepsilon_0\) is the vacuum permittivity, and \(m_e\) is the mass of an electron, and the emission coefficients for the allowed electronic transitions for the considered CaK and CaK\(^+\). The TDM value \(|\mu_{21}|\), the radiative lifetime \(\tau_{21}\) (\(\tau_i = \sum_j A_{ij}\) where \(j\) runs for the underlying states of \(i\) state), the emission angular frequency \(\omega_{21}\), the Einstein coefficients of spontaneous emissions \(A_{21}\), the oscillator strength constant \(|f_{21}|\) and the classical radiative decay rate of the single-electron oscillator \(\gamma_{cl}\) are reported in table TS3 in the supplementary material. In this table, the largest oscillator strength is for the transition \(X^3\Sigma^+\)–(2)\(2\Sigma^+\) of the neutral CaK molecule and the most considerable value of the radiative lifetime \(\tau_{21}\) is for the transition \(X^1\Sigma^+\)–(1)\(1\Pi\) for the anion CaK\(^-\). Comparing this data with previous work is absent since it is calculated here for the first time.
3.5. Vibration rotation calculation
We have calculated the vibrational energy $E_v$, the rotational constant $B_0$, the centrifugal distortion constant $D_0$ and $R_{\text{min}}$ and $R_{\text{max}}$ for the ground and many excited electronic states, by applying the canonical functions approach [41, 42], on the PECs of CaK and CaK$^+$. These calculations can not be done for some of the electronic states, whose PECs exhibit avoided crossing. The vibrational constants corresponding to the ground state and the excited states are collected in tables TS4–TS6 in the supplementary material. For the CaK molecule, the comparison of the vibrational constant $B_0$ for the ground state calculated for the vibrational level $v = 0$ with those obtained by Gopakumar et al [18] using the CCSD(T) method with three valence electrons shows an excellent agreement with a relative difference 2.9%. To the best of our knowledge, the vibrational parameters for the CaK$^+$ and CaK$^-$ molecular ions are given in the present work for the first time.

3.6. Laser cooling study
3.6.1. Laser cooling feasibility of CaK molecule
We calculated the FCFs of the transitions $X^2\Sigma^+\rightarrow(1)^2\Pi$, $X^2\Sigma^+\rightarrow(2)^2\Sigma^+$, and $(1)^2\Pi\rightarrow(2)^2\Sigma^+$ for CaK, and $X^1\Sigma^+\rightarrow(1)^1\Pi$ for the anion CaK$^-$ for the vibrational levels, $0 \leq v \leq 6$ of the upper states and $0 \leq v' \leq 6$ of the lower states. We performed the calculations using the LEVEL 11 program [43]. The plottings of the FCF for the mentioned transitions are presented in figures 12–14 and their values are given in tables TS6 and TS7 in the supplementary information section. It is known that obtaining highly diagonal FCFs between non-intervening levels can help determine how much the intervening level would be detrimental to the laser cooling process. Laser cooling of molecules with an intermediate level between the electronic cycling levels has already been proven successful for several molecules (neutral and ionic), as long as specific conditions

| Dissociation of atomic levels | Dissociation energy limit of CaK levels (cm$^{-1}$) | Molecular states of CaK | Total dissociation energy limit of Ca + K atoms (cm$^{-1}$) | Relative error (%) |
|-----------------------------|-----------------------------------------------|------------------------|--------------------------------------------------|-------------------|
| Ca (3p$^6$4s$^2$, 1S) + K (3p$^6$4s$^2$, 1S) | 0$^a$ | $X^2\Sigma^+$ | 0$^b$ | 0.0 |
| Ca (3p$^6$4s$^2$, 1S) + K (3p$^6$4p, 1P$^0$) | 11 341$^a$ | (2)$^3\Sigma^+$, (1)$^3\Pi$ | 13 014$^b$ | 12 |
| Ca (3p$^6$4s$^4$p, 1P$^0$) + K (3p$^6$4s$^2$, 1S) | 13 992$^a$ | (2)$^3\Pi$, (3)$^3\Sigma^+$, (1)$^3\Pi$, (1)$^1\Sigma^+$ | 15 228$^b$ | 8.1 |

| Dissociation limit of atomic levels | Dissociation energy limit of (CaK)$^+$ levels (cm$^{-1}$) | Molecular states of (CaK)$^+$ | Total dissociation energy limit of Ca + K (atoms/ions) (cm$^{-1}$) | Relative error (%) |
|-------------------------------------|-----------------------------------------------|------------------------|--------------------------------------------------|-------------------|
| Ca (3p$^6$4s$^2$, 1S) + K$^+$ (3p$^6$, 1S) | 0$^a$ | $X^2\Sigma^+$ | 0$^b$ | 0.0 |
| Ca (3p$^6$4s$^4$p, 1P$^0$) + K$^+$ (3p$^6$, 1S) | 13 878$^a$ | (1)$^3\Sigma^+$, (1)$^3\Pi$ | 15 228$^b$ | 8.9 |
| Ca$^+$ (3p$^6$4s$^2$, 1S) + K (3p$^6$5s, 2S) | 15 629$^a$ | (2)$^3\Sigma^+$, (2)$^3\Sigma^+$ | 21 026$^b$ | 25.66 |
| Ca (3p$^6$4s$^4$p, 1P$^0$) + K$^+$ (3p$^6$, 1S) | 23 933$^a$ | (3)$^3\Sigma^+$, (1)$^3\Pi$ | 23 652$^b$ | 1.2 |

$^a$Present work.
$^b$Experimental data from NIST atomic spectra database.
were met [45, 46]. Among these conditions, figure a much higher probability of transitions from the excited state (1)2 Σ to the ground state (X)2 Σ+.

To evaluate the suitability of the transition (2)+2 Σ (v′ = 0) → XΣ (v′ = 0) for laser cooling, and the degree of interference of state (1)+Π in the spontaneous decays of molecules from the state (2)+2 Σ+ to the state XΣ, we propose:

(a) To evaluate the Einstein coefficients of the vibrational transitions between states (XΣ and (2)+Σ), and ((2)+Σ and (1)+Π), using level 1 program.
(b) To deduce the vibrational radiative lifetime for transitions between (XΣ and (2)+Σ+), and ((2)+Σ+ and 1Π states).
(c) To calculate the vibrational branching ratio loss between states ((2)+Σ+ and (1)+Π).

### Table 2. The spectroscopic parameters and relative errors for the XΣ+ and 18 excited electronic states of the CaK molecule.

| States          | Method reference | Method | T_rot (cm⁻¹) | ΔT_rot/T_rot (%) | R_rot (Å) | ΔR_rot/R_rot (%) | ω_rot (cm⁻¹) | Δω_rot/ω_rot (%) | B_rot (cm⁻¹) | ΔB_rot (cm⁻¹) (%) | D_rot/ΔD_rot (D) | ΔD_rot/ΔD_rot (%) |
|-----------------|------------------|--------|--------------|------------------|-----------|------------------|--------------|------------------|--------------|------------------|-------------------|------------------|
| (XΣ)            | This work        | 0      | 4.404        | 65.76            | 0.0439    | 1245             | 2.809        |                  |              |                  |                   |                  |
| (XΣ)            | CCSD(T) [19]     | 0      | 4.320        | 71.00            | 0.0547    | 1001             | 3.207        |                  |              |                  |                   |                  |
| (XΣ)            | MDCM/RMCI [20]   | 0      | 4.200        | 70.60            | 0.08      | 300              | 2.207        |                  |              |                  |                   |                  |
| (XΣ)            | CASED [20]       | 0      | 4.071        | 6.90             | 0.08      | 300              | 2.207        |                  |              |                  |                   |                  |
| (XΣ)            | Laser and Fourier transform spectroscopy [18] | 0 | 4.200 | 71.00 | 0.0547 | 1001 | 3.207 |                  |              |                  |                   |                  |
| (XΣ)            | This work        | 0      | 4.571        | 71.00            | 0.0547    | 1001             | 3.207        |                  |              |                  |                   |                  |
| (XΣ)            | CASED [20]       | 0      | 4.200        | 70.60            | 0.08      | 300              | 2.207        |                  |              |                  |                   |                  |
| (XΣ)            | Laser and Fourier transform spectroscopy [18] | 0 | 4.200 | 71.00 | 0.0547 | 1001 | 3.207 |                  |              |                  |                   |                  |
| (XΣ)            | This work        | 0      | 4.571        | 71.00            | 0.0547    | 1001             | 3.207        |                  |              |                  |                   |                  |
| (XΣ)            | CASED [20]       | 0      | 4.200        | 70.60            | 0.08      | 300              | 2.207        |                  |              |                  |                   |                  |
| (XΣ)            | Laser and Fourier transform spectroscopy [18] | 0 | 4.200 | 71.00 | 0.0547 | 1001 | 3.207 |                  |              |                  |                   |                  |
| (XΣ)            | This work        | 0      | 4.571        | 71.00            | 0.0547    | 1001             | 3.207        |                  |              |                  |                   |                  |
| (XΣ)            | CASED [20]       | 0      | 4.200        | 70.60            | 0.08      | 300              | 2.207        |                  |              |                  |                   |                  |
| (XΣ)            | Laser and Fourier transform spectroscopy [18] | 0 | 4.200 | 71.00 | 0.0547 | 1001 | 3.207 |                  |              |                  |                   |                  |

To deduce the vibrational radiative lifetime for transitions between (XΣ and (2)+Σ+), and ((2)+Σ+ and 1Π states).

(c) To calculate the vibrational branching ratio loss between sates ((2)+Σ+ and (1)+Π).
To compare the FCF and radiative lifetimes for transitions between the states (X2Σ+ and (2)2Σ+) and (2)Π).

We calculated the Einstein coefficients for transitions (from a vibrational state \( \nu' \) to a vibrational state \( \nu \)) by using:

\[
A_{\nu'\nu} = (3.136 \times 10^{19}) (\Delta \nu)^3 \langle \psi_{\nu'} | M(r) | \psi_\nu \rangle^2,
\]

where \( A_{\nu'\nu} \) has as units \( \text{s}^{-1} \), \( \Delta \nu \) is the emission frequency (in \( \text{cm}^{-1} \)) and \( M(r) \) is the electronic transition dipole moment between the two electronic states that are considered (in Debye) [45]. We deduced the radiative lifetimes between the lowest vibrational levels in tables 5 and 6. These show that the radiative lifetime between the lowest vibrational transitions of states X2Σ+ and 2Σ+ varies between 75 ns and 225 ns. On the other hand, the radiative lifetime between the vibrational transitions of states 1Π and 2Σ+ is 104 times longer, with values that vary between 0.08 ms and 0.26 ms. A comparison between the vibrational radiative lifetimes obtained in tables 5 and 6 and the electronic radiative lifetimes in table TS3 of the supplementary material SM1 shows comparable values among the transitions. However, the difference in the order of magnitude between the

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### Table 3. The spectroscopic parameters for the X2Σ+ and 13 excited states of the CaK+ molecule.

| States \((\Lambda)\) | Method | \( T_e \) (cm⁻¹) | \( \Delta T_e/T_e \) (%) | \( R_e \) (Å) | \( \Delta R_e/R_e \) (%) | \( \omega_e \) (cm⁻¹) | \( \Delta \omega_e/\omega_e \) (%) | \( B_e \) (cm⁻¹) | \( \Delta B_e/B_e \) (%) | \( D_e \) (cm⁻¹) | \( \Delta D_e/D_e \) (%) | \( |\mu_e| \) (D) |
|-------------------|--------|----------------|------------------|-----------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| X2Σ+ | This work | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |
| (1)Σ+ | This work | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |
| (1)Π | This work | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |
| (1)Σ | This work | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |
| | CIPCI | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |

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### Table 4. The spectroscopic parameters for the X2Σ+ and 18 excited states of the CaK+ molecule.

| States \((\Lambda)\) | \( T_e \) (cm⁻¹) | \( R_e \) (Å) | \( \omega_e \) (cm⁻¹) | \( B_e \) (cm⁻¹) | \( D_e \) (cm⁻¹) | \( |\mu_e| \) (D) |
|-------------------|----------------|-----------|----------------|----------------|----------------|----------------|
| X2Σ+ | This work | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |
| (1)Σ+ | This work | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |
| (1)Π | This work | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |
| (1)Σ | This work | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |
| | CIPCI | 3234 | 4.621 | 65.51 | 0.0399 | 3047 | 0.00 | 13.456 |

---

(d) To compare the FCF and radiative lifetimes for transitions between the states (X2Σ+ and (2)2Σ+) and (2)Π).
vibrational radiative lifetimes of \((1^2\Pi\text{ and } 2^2\Sigma^+\text{)}\) and \((X^2\Sigma^+\text{ and } (2)^2\Sigma^+\text{)}\) transitions emanates from the difference of the vibrational levels’ coupling among the respective electronic states.

The vibrational branching loss ratio expresses the extent of an intervening state’s influence numerically in a given laser cooling cycle that is taking place between two other states. In our case, we are trying to investigate the influence of the intermediate state \((1)^3\Pi\) on a cycle between \((2)^2\Sigma^+\text{ and } X^2\Sigma^+\text{ states. We}
Figure 11. TDMCs between the ground state $X^1\Sigma^+$ and the lowest-excited singlet states of the CaK$^-$ molecule using CASSCF/MRCI method with four valence electrons.

Figure 12. The FCF plotting for the $X^1\Sigma^+\rightarrow(1)^1\Pi$ transition of CaK$^-$ molecule using CASSCF/MRCI method with four valence electrons.

find that the vibrational branching loss ratio to the state $(1)^2\Pi$, is in the order of:

$$\eta = \frac{A_{0\nu(2^1\Sigma^+\rightarrow X^1\Sigma^+)}^{\nu\gamma}}{A_{0\nu(2^1\Sigma^+\rightarrow 1^2\Pi)}^{\nu\gamma}} = 2.81 \times 10^{-4}.$$  

A very comparable value with what has been recently demonstrated for YO molecule [46]

$$\eta = \gamma_A/\gamma_x < 4 \times 10^{-4}$$

Similar vibrational branching loss ratios have been previously demonstrated for other laser cooling candidates with an intermediate state such as ScO ($\eta = 1.44 \times 10^{-5}$) [47].
Finally, the FCF between the ground vibrational levels of $2^2\Sigma^+$ and $(1)^2\Pi$ is given by $f_{00} = 5.70 \times 10^{-5}$, which is very small compared to the FCF between the ground vibrational levels of $(2)^2\Sigma^+$ and $X^2\Pi$. $f_{00} = 0.9566$.

With such values in mind, we can confirm the feasibility of laser cooling between states $X^2\Sigma^+$ and $(2)^2\Sigma^+$ of CaK molecule: (i) the radiative lifetimes $\tau$ for vibrational transitions between the $X^2\Sigma^+$ and $2^2\Sigma^+$ states are in the order of the ns, which is ideal for their usage in the Doppler laser cooling technique, as a minimal radiative lifetime maximizes the rate of cooling between two vibrational states and produces a strong Doppler force [48–50]. (ii) The radiative lifetimes of transitions between $((1)^2\Pi$ and $(2)^2\Sigma^+\rangle$ states are much longer than those between $(X^2\Sigma^+$ and $(2)^2\Sigma^+\rangle$, and consequently the spontaneous decay toward the ground state is much faster than that of the decay to the intermediate state. (iii) The vibrational branching loss ratio shows quantitatively that the intervening $(1)^2\Sigma^+$ state’s influence is negligible. (iv) The value of $f_{00}$ between $(2)^2\Sigma^+\rightarrow X^2\Sigma^+$ states is much higher than $f_{00}$ between $(2)^2\Sigma^+\rightarrow (1)^2\Pi$ states, which means there is a much higher probability for the molecules to decay through the $(2)^2\Sigma^+\rightarrow X^2\Sigma^+$ channel, than that of the $(2)^2\Sigma^+\rightarrow (1)^2\Pi$ channel. The decay of excited molecules through that channel can be considered negligible and would not perturb the cooling cycle.

To characterize the temperatures that can be reached within this process, we calculated the Doppler limit temperature $T_D$ and recoil temperature $T_r$, which are given by:

$$T_D = \frac{h}{4 \times \pi \times \tau \times k_b} = 51 \text{ mK} \quad \text{and} \quad T_r = \frac{h^2}{m \times \lambda_0^2 \times k_b} = 156 \text{ nK}$$

$\tau$ is the radiative lifetime, $m$ the mass of the molecule, $\lambda_0$ is the wavelength, and $k_b$ is the Boltzmann constant [51, 52]. Here the Doppler limit temperature is higher than the recoil temperature, which can be reached using Sisyphus cooling techniques. Additionally, the radiative width ($\Gamma_r$) for the vibrational transitions between states $2^2\Sigma^+\rightarrow X^2\Sigma^+$ are given in table 6.

Usually, the cooling of molecules in a molecular beam requires scattering of a few thousand photons [53]. The laser cooling scheme for the molecule CaK in figure 15 maximizes the number of cycles for photon absorption/emission. The proposed laser-driven transitions are shown by arrows and annotated with their corresponding wavelength. The spontaneous decays are represented with dotted lines, along with their calculated FCF ($f_{\nu',\nu}$) and vibrational branching ratios ($R_{\nu',\nu}$). The intermediate state $(1)^2\Pi$ is drawn on the side, with its vibrational branching loss ratio. The principal cooling transition is for the $(2)^2\Sigma^+ (\nu' = 0) \rightarrow X^2\Sigma^+ (\nu'' = 0)$ transition with a principal laser-driven cycling of $\lambda_0 = 1265.2$ nm. Three repump lasers of wavelengths $\lambda_{01} = 1275.6$ nm, $\lambda_{02} = 1284.6$ nm, and $\lambda_{13} = 1281.2$ nm are used to reduce the vibrational branching loss and repump the molecules populated at vibrational excited states of $X^2\Sigma^+$ for the transitions $(2)^2\Sigma^+ (\nu' = 0) \rightarrow X^2\Sigma^+ (\nu'' = 1)$, $(2)^2\Sigma^+ (\nu' = 0) \rightarrow X^2\Sigma^+ (\nu'' = 2)$, and $(2)^2\Sigma^+ (\nu' = 1) \rightarrow X^2\Sigma^+ (\nu'' = 3)$ respectively. Table 6 shows the vibrational branching ratios among these transitions, and we use them to calculate the number of cycles ($N$) for photon absorption/emission in this configuration [54, 55]:

![Figure 13. The FCF plotting for the $X^2\Sigma^+-(2)^2\Sigma^+$ transition of CaK molecule using CASSCF/MRCI method with three valence electrons.](image)
Figure 14. The FCF plotting for the (a) (1)$^2\Pi$–(2)$^2\Sigma^+$ and (b) (1)$^2\Pi$–$X^2\Sigma^+$ transitions of CaK molecule using CASSCF/MRCI method with three valence electrons.

\[
N = \frac{1}{[1 - ([R_{00} + R_{01} + R_{02}) + R_{03}(R_{10} + R_{11} + R_{12} + R_{13})])]
\]

\[
N = \frac{1}{[1 - ([0.96002 + 0.03586 + 0.00249] + 0.00155(0.03207 + 0.83554 + 0.12436 + 0.00123))]} \approx 12120.
\]

Typical values for the number of cycles ($N$) have been previously calculated for other molecules such as thallium chloride (ThCl) and bismuth hydride (BH) and were in the order of a few thousand absorptions/emissions, with values smaller than the one we obtained for CaK molecule. More specifically, laser cooling schemes for these molecules led to the following values of $N$: $N_{\text{ThCl}} \approx 5400$ and $N_{\text{BiH}} \approx 10 200$ [54, 55]. The use of any additional repump laser seems unnecessary in this scheme, as the probability of decay for the vibrational ($v' > 4$) vibrational states of $X^2\Sigma^+$ from the (2)$^2\Sigma^+$ state is negligible. In fact, about $N_{\text{scat}} = 1/f_{04} > 10^4$ photons are scattered before higher vibrational levels are populated.

The length of the slowing region ($L$) is an important parameter to take into account when performing Doppler laser cooling. Usually, a distance up to $L \approx 1$ m is reasonable for a molecular beam apparatus [56]. From the above laser cooling scheme, we can calculate the velocity that would correspond to the number of cycles $N$ as [55]:

\[
V = \langle hN \rangle/m\lambda_{00} \approx 49 \text{ m s}^{-1}
\]
We have approximated the value of \( N_e/N_{tot} \) and excited states and ignoring any hyperfine structure \([57]\).

Buffer gas cooling of calcium bearing molecules has been proven successful for species such as calcium gas, whose role is to dissipate the molecules’ translational energy. We model the CaK atoms to be produced through a typical laser ablation technique before being driven into a buffer cooling cell, to be then sent in the Doppler laser cooling setup. Standard buffer cooling setups usually depend on the buffer cooling cell.

\[ \nu = 0 \quad A_{\nu} \quad 17.9 \quad 1.65 \times 10^4 \quad 1.07 \times 10^7 \quad 2.53 \times 10^1 \quad 6.34 \times 10^2 \quad 1.30 \times 10^3 \quad 2.29 \times 10^3 \]

\[ \nu = 1 \quad A_{\nu} \quad 1.84 \times 10^7 \quad 1.37 \times 10^7 \quad 8.87 \times 10^4 \quad 1.32 \times 10^1 \quad 2.52 \times 10^2 \quad 3.84 \times 10^3 \quad 4.79 \times 10^3 \]

\[ \nu = 2 \quad A_{\nu} \quad 9.04 \times 10^4 \quad 5.32 \times 10^4 \quad 3.44 \times 10^1 \quad 2.87 \times 10^1 \quad 3.78 \times 10^2 \quad 3.58 \times 10^3 \quad 2.33 \times 10^3 \]

\[ \nu = 3 \quad A_{\nu} \quad 2.86 \times 10^6 \quad 1.27 \times 10^6 \quad 8.19 \times 10^4 \quad 3.15 \times 10^4 \quad 2.23 \times 10^5 \quad 6.79 \times 10^6 \quad 22.9 \]

\[ \nu = 4 \quad A_{\nu} \quad 6.52 \times 10^5 \quad 2.05 \times 10^5 \quad 1.33 \times 10^4 \quad 1.56 \times 10^4 \quad 1.66 \times 10^5 \quad 3.05 \times 10^6 \quad 1.58 \times 10^6 \]

\[ \nu = 5 \quad A_{\nu} \quad 1.14 \times 10^5 \quad 3.23 \times 10^5 \quad 1.51 \times 10^4 \quad 9.71 \times 10^4 \quad 4.91 \times 10^5 \quad 1.66 \times 10^6 \quad 1.44 \times 10^6 \]

\[ \nu = 6 \quad A_{\nu} \quad 1.60 \times 10^4 \quad 1.83 \times 10^4 \quad 1.36 \times 10^4 \quad 1.44 \times 10^4 \quad 9.38 \times 10^5 \quad 1.73 \times 10^6 \quad 1.73 \times 10^6 \]

The corresponding initial temperatures and Doppler frequency shift are: \( T_{ini} = mV^2/(2k_B) \approx 11.15 \) K.

\( \Delta f = V/\lambda_0 \approx 9 \) MHz

\( N \) is the number of cycles \((N)\) for photon absorption/emission, \(h\) is Planck’s constant, \(m\) is the mass of the molecule, \(\lambda_0\) the principal laser wavelength, \(k_B\) Boltzmann’s constant.

The maximum acceleration is then estimated to be:

\[ a_{max} = hN_e/(N_{tot}m \cdot \tau \cdot \lambda_0) \approx 10 \text{ km/s}^2 \]

\( N_e \) is the number of excited states in the main cycling transition.

\( N_{tot} \) is the number of ground states connected to the excited state of the leading cycling transition plus \(N_e\). We have approximated the value of \(N_e/N_{tot} = 1/5\) by only taking into account the vibrational ground and excited states and ignoring any hyperfine structure \([57]\). \(\tau\) is the leading cycling transition radiative lifetime. From there, we can approximate the length of the slowing region as: \(L = k_B T_{ini}/(m a_{max}) \approx 10 \) cm, which is suitable for this type of experiment. In the SrF cooling setup, the length of the slowing window was about 15 cm \([57]\).

The molecules’ initial velocity and temperature imply that one needs to find a cooling process that would lead to the initial temperature of 11 K before it reaches the kN regime through Sisyphus cooling. We propose using buffer gas cooling, as it is a flexible method that is applicable to a multitude of molecules \([58, 59]\). Buffer gas cooling of calcium bearing molecules has been proven successful for species such as CaH, which were cooled to temperatures close to the \(\mu \)K \([60]\).

The buffer gas cooling technique consists of thermalizing species through collisions with a cold buffer gas, whose role is to dissipate the molecules’ translational energy. We model the CaK atoms to be produced through a typical laser ablation technique before being driven into a buffer cooling cell, to be then sent in the Doppler laser cooling setup. Standard buffer cooling setups usually depend on the buffer cooling cell.
Figure 15. Laser cooling scheme of the $X^2\Sigma^+ \rightarrow (2)^2\Sigma^+$ transition of CaK molecule using CASSCF/MRCI method with three valence electrons.

length, cross-section, and aperture diameter [61]. According to the hard-sphere collision model, the equation that relates the temperature of a molecule before and after $N$ collisions is given by:

$$
TN / T = (T' / T - 1) \exp(-N/k) + 1
$$

where $\kappa = (M + m)^2/(2mM)$,

$T$ is the temperature of the buffer gas, $T'$ is the initial temperature of the diatomic molecule, and $T_N$ its temperature after $N$ collisions. $M$ and $m$ are the masses of the molecule and the buffer gas atom, respectively. We have chosen to take: $T_l = 11$ K (desired precooling temperature of the CaK molecules), $T' = 10\,000$ K (set as the typical temperature of molecules that were created though laser ablation), $T = 1$ K (initial temperature of the helium atoms).

Solving for the number of collisions $N$ gives $N \approx 75$ collisions, which is relatively close to the typical number of collisions for molecules previously cooled through buffer laser cooling, such as vanadium oxide, where $N_{VO} \approx 100$ collisions.

In such buffer cooling processes, molecules need to be produced, thermalized, and exit the cell within a concise time scale. Consequently, one must ensure the thermalization process time remains relatively short, i.e., ranges within values typically less than 10 ms. To calculate this time in the case of the CaK molecule, we rely on the work of Iwata [62]; we first consider the velocity of a molecule before a given $N$th collision:

$$
v_N = \frac{\lambda}{t_N}
$$

$\lambda$ the mean free path of the molecule between each collision, and $t_N$ is the time to follow the given route, i.e., the time that passes between the $N - 1$ and $N$th collision.

We calculate the mean free path $\lambda$ of the molecule in the buffer gas as:

$$
\lambda = \frac{1}{\sigma \cdot n_{He}} \cdot \frac{1}{\sqrt{(1 + \frac{M}{m})}}
$$

where $\sigma$ is the scattering cross-section between a CaK molecule and He, $n_{He}$ is the density of the buffer gas, $M$ the mass of CaK molecules, and $m$ the mass of He atoms. Typically, depending on the buffer cell’s
geometry and length, a buffer gas density of $\approx 1 \times 10^{20}$ atoms/m$^3$ corresponds to a value of $\sigma \approx 10^{-18}$ cm$^2$. Using these values and the corresponding masses of CaK and He, we obtain $\lambda \approx 0.220$ cm.

Using the kinetic theory of ideal gases and summing over the total number of collisions $N$, we can calculate the complete time $t$ for the buffer cooling process as:

$$t = \sum_{N=0}^{75} \sqrt{\frac{N_M}{N}} \left( \frac{\lambda}{(T' - T)e^{-N/\kappa} + T} \right) \approx 3.26 \text{ ms.}$$

Thus, given the short time for the molecules’ thermalization, we predict that it may be possible to buffer cool the CaK molecule to a temperature that would be suitable enough to reach the desired $\mu K$ regime.

### 3.6.2. Comparison with previously laser-cooled molecules

Table 7 summarizes the laser cooling properties of the CaK molecule and other proposed molecular candidates that would be suitable for laser cooling. We notice that in general, CaK stands well among other molecules for the realization of laser cooling. The values of $f_{00}$ are closer to one for CaK compared to TiO, LiRb, Krb, GaH, and BBr. It also presents a shorter lifetime than the majority of the remaining molecules, with $\tau = 0.075 \mu s$. This represents an advantage as a smaller radiative lifetime leads to stronger Doppler forces. The Doppler temperature mainly depends on the leading transition’s radiative lifetime. Molecules whose radiative lifetime is in the nanosecond order, such as CaF, YO, and CaK, show Doppler temperatures $(T_D)$ within the same range. $T_D$’s value of $T_D$ for CaK falls well within the inverse proportionality relationship among the three molecules: as the value of the radiative lifetime increase, that of the Doppler temperature decreases. In table 7, $\tau_{CaK} < \tau_{YO} < \tau_{CA}$ leads to $T_{DCA} > T_{DYO} > T_{DCA}$. The main cycling laser value $\lambda_{00}$ for CaK is in the infrared range, similar to the molecules constituted of group I metallic elements such as LiRb and Krb. Also, the recoil temperatures of CaK and Krb are very close, with $T_r(CaK) = 0.156 \mu K$ and $T_r(Krb) = 0.14 \mu K$. The recoil temperature of LiRb is unavailable in the literature so that suitable comparison with that of CaK is not possible. Such results show that diatomic molecules constituted of elements I and II may prove suitable candidates for laser cooling, especially given their short radiative lifetime and very low recoil temperature. Their primary cycle laser wavelengths are within the near-infrared range, which can be attained through readily available lasers.

### 4. Conclusion

This paper reported \textit{ab initio} calculations of the ground and excited electronic states for the molecule CaK and its molecular ions CaK$^\pm$. We studied the PECs and DMCs of these molecules via CASSCF/MRCI technique, employing the ECP10MWB basis set for Ca atom and the wCV5Z basis set for K atom. The PDMs have been calculated for the investigated electronic states. The ground state of the molecule CaK has been compared with the data available in the literature. The spectroscopic constants $T_1$, $\omega_1$, $B_1$, $R_e$ and the dissociation energy $D_e$ has been calculated for most of the bound states and compared with previously published papers. A very good agreement is obtained for the calculated constants, especially with previous work using the same calculation method. Also, the ro-vibrational constants $E_v$, $B_v$, $D_v$ with the absicissas of turning points $R_{\min}$ and $R_{\max}$ have been obtained for different vibrational levels of the ground and some low lying electronic states of the CaK and CaK$^+$ and CaK$^-$ molecules through the canonical function approach.

Aiming at a laser cooling study, the TDMs between specific lowest electronic transitions for the three molecules have been determined, considering the selection rule for electronic transitions. The transition dipole moment value of the upper state at its equilibrium position $|\mu|$, the emission angular frequency $\omega_{21}$, the Einstein coefficients $A_{21}$ with several important parameters such as the emission oscillator strength $f_{11}$, the spontaneous radiative lifetime $\tau_{\text{spont}}$, the wavelength $\lambda_{21}$ and the classical radiative decay rate of the
single-electron oscillator $\gamma_c$ for the considered transitions are also reported. These values and the calculation of the FCFs for the different transitions of CaK and CaK$^+$ showed that the molecule CaK is a suitable candidate for Doppler laser cooling while the two ions CaK$^+$ are not. The results that we obtained in the present work may pave the way for experimentalists to produce ultracold CaK molecules.

Acknowledgments

This publication is based upon work supported by the Khalifa University of Science and Technology under Award No. CIRA-2019-054. The authors would also like to thank Dr Israa Zeid and Dr Sergio Martinez for thoughtful discussions. Khalifa University High power computer system was used for the completion of this work.

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