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Ab initio calculations of spectroscopic constants and vibrational state lifetimes of diatomic alkali-alkaline-earth cations

Dmitry A. Fedorov, Dustin K. Barnes, and Sergey A. Varganov[a)]
Department of Chemistry, University of Nevada, Reno, 1664 N. Virginia St., Reno, Nevada 89557-0216, USA

We investigate the lifetimes of vibrational states of diatomic alkali-alkaline-earth cations to determine their suitability for ultracold experiments where long decoherence time and controllability by an external electric field are desirable. The potential energy and permanent dipole moment curves for the ground electronic states of $LiBe^+$, $LiMg^+$, $NaBe^+$, and $NaMg^+$ are obtained using the coupled cluster with singles doubles and triples and multireference configuration interaction methods in combination with large all-electron cc-pCVQZ and aug-cc-pCV5Z basis sets. The energies and wave functions of all vibrational states are obtained by solving the Schrödinger equation for nuclei with the B-spline basis set method. To predict the lifetimes of vibrational states, the transition dipole moments, as well as the Einstein coefficients describing spontaneous emission, and the stimulated absorption and emission induced by black body radiation are calculated. Surprisingly, in all studied ions, the lifetimes of the highest excited vibrational states are similar to the lifetimes of the ground vibrational states indicating that highly vibrationally excited ions could be useful for the ultracold experiments requiring long decoherence time. *Published by AIP Publishing.* https://doi.org/10.1063/1.4986818

I. INTRODUCTION

The field of ultracold molecules is one of the fastest growing areas in molecular and optical physics due to a large number of potential applications. Preparing molecules in specific quantum states is a necessary step toward achieving control of chemical reactions, which is one of the most important objectives of ultracold chemistry.[1–3] Ultracold molecules can also be used for high precision measurements of fundamental constants, such as the fine structure constant,[4] proton-to-electron mass ratio,[5] and electron dipole moment.[6] Heteronuclear molecules that have a non-zero dipole moment can be used as qubits in quantum computation devices.[7] In our previous work,[8] we studied the lifetimes of the vibrational states of neutral heteronuclear alkali dimers motivated by use of these molecules in ultracold experiments and the available experimental data on their spectroscopic properties. Our theoretical predictions for the spectroscopic constants were in good agreement with the experimental values. For all heteronuclear alkali dimers, the lifetimes of the ground vibrational states were significantly larger than the lifetimes of the excited vibrational states. In this work, we apply the same methodology to the alkali-alkaline-earth ions $LiBe^+$, $LiMg^+$, $NaBe^+$, and $NaMg^+$, which can be controlled by an external electric field. The permanent dipole moment of a diatomic ion goes to infinity with increasing internuclear distance, whereas for neutral molecules it goes to zero. This permanent dipole moment affects the transition dipole moments between the vibrational states and ultimately the lifetimes of these states.

To our knowledge, there is no experimental spectroscopic data on the four ions investigated in this work; however, several

theoretical studies have been reported. Safonov *et al.* studied the low-lying electronic states of $LiBe^+$ using the Hartree-Fock (HF) method,[9] while Boldyrev and co-workers used the MP2 perturbation theory to calculate the spectroscopic properties of this ion.[10] You *et al.*[11] and Sun *et al.*[12] investigated the ground and low-lying excited states of $LiBe^+$ using a more accurate multireference configuration interaction (MRCI) method with large basis sets.[11] In a recent study, Bala and Nataraj[13] used the coupled cluster with singles, doubles and non-perturbative triples [CCSD(T)] method and extrapolation to the complete basis set limit to calculate the spectroscopic constants for the ground electronic state of $LiBe^+$. The $LiMg^+$ ion was studied by Gao and Gao[14] using the MRCI method. ElOualhazi and Berriche[15] carried out calculations on the electronic ground and 53 excited states of $LiMg^+$ using the configuration interaction method and core polarization potentials. Bala and Nataraj[16] calculated spectroscopic constants of $LiMg^+$ using the CCSD(T) method. Pyykkö performed a theoretical study of a variety of ions, including $LiMg^+$ and $NaBe^+$, using the HF and MP2 methods.[17] We are not aware of previous studies on $NaMg^+$. However, it is important to note the previous theoretical studies of the neutral diatomic alkali-alkaline-earth molecules.[18–22]

The goals of this work are as follows: (1) to obtain highly accurate spectroscopic constants and potential energy and permanent dipole moment curves for the ground electronic state of $LiBe^+$, $LiMg^+$, $NaBe^+$, and $NaMg^+$; (2) to determine the lifetimes of the ground and excited vibrational states of these ions, which is expected to be useful for the design of future ultracold experiments.

The paper is organized as follows. In Sec. II, the electronic structure methods, the method for solving the vibrational Schrödinger equation for nuclei, and the calculations of the lifetimes of vibrational states are described. In Sec. III A,

a)E-mail: svarganov@unr.edu

the obtained spectroscopic constants and potential energy and dipole moment curves are discussed. In Sec. III B, the lifetimes of vibrational states are analyzed. The main results are summarized in Sec. IV.

II. COMPUTATIONAL METHODS

The electronic structure calculations were carried out using the single reference coupled cluster with singles, doubles, and non-perturbative triples (CCSDT) method. The reference wave functions were obtained using the restricted HF method. To determine if the single reference CCSDT method can compensate for the deficiency of the restricted HF wave function at large internuclear distances, we also performed the MRCI with singles and doubles calculations. The MRCI reference wave function was of the complete active space self-consistent field (CASSCF) type with the full valence active space of two electrons on eight orbitals (2s and 2p orbitals of Li and Be; 3s and 3p orbitals of Na and Mg). All valence and core electrons were correlated to recover the correlation energy of the inner shells. The cc-pCVQZ and aug-cc-pV5Z correlation consistent basis sets of Dunning $et\ al.$[23,24] were used. The MRCI calculations were carried out using the quantum chemistry package MOLPRO,[25] while the CCSDT calculations were performed with the CFOUR package.[26]

The equilibrium internuclear distance R_e, the potential energy curves $E(R)$, and the permanent dipole moment curves $\mu(R)$ were calculated with the CCSDT and MRCI methods. For both methods, $E(R)$ and $\mu(R)$ were calculated up to R = 20 Å. For the size-consistent CCSDT method, a dissociation energy was obtained as the difference between $E(R_e)$ and the sum of the energies of separate atomic ions (Li$^+$, Na$^+$) and neutral atoms (Be, Mg). For all four molecular ions, the difference between the energy of the ion (AB$^+$) with an internuclear distance of R = 20 Å and the sum of energies of the corresponding atomic ion (A$^+$) and neutral atom (B) does not exceed 4 cm^{-1}. For the non-size-consistent MRCI method, a dissociation energy was computed as the difference between $E(R_e)$ and $E(R$ = 100 Å). The difference between the MRCI energies calculated for the internuclear distances R = 20 Å and R = 100 Å also does not exceed 4 cm^{-1}.

In all electronic structure calculations, the molecular axis is directed from the less electronegative atom (Li or Na) to the more electronegative atom (Be or Mg). This convention guarantees a positive value of the permanent dipole moment. The origin of coordinates coincides with the center of mass for all ions. The ions are assumed to be in the $J = 0$ rotational states, neglecting the rotational selection rule ($\Delta J = \pm 1$) and the centrifugal distortion.

The methodology for calculating the lifetimes of vibrational states is described in our previous work.[8] Briefly, to obtain the vibrational energies and wave functions, the vibrational Schrödinger equation was solved by expanding the nuclear wave function in the B-spline basis set.[8,27–29] Using the permanent dipole moment $\mu(R)$, the transition dipole moments $\langle i|\mu(R)|f\rangle$ between the initial (i) and final (f) vibrational states were calculated.

The lifetime τ_i of vibrational state i was obtained as

$$\tau_i^{-1} = \sum_{f<i} A_{if} + \sum_f B_{if}. \tag{1}$$

The Einstein coefficient A_{if}, describing the probability of spontaneous emission from the vibrational state i to the lower-energy state f reads

$$A_{if} = \frac{4\omega_{if}^3}{3c^3}|\langle i|\mu(R)|f\rangle|^2, \tag{2}$$

where $\omega_{if} = |E_f - E_i|$ is the transition frequency between states i and f. The black body radiation (BBR) coming from the surrounding environment at T = 300 K induces stimulated absorption and emission processes, which are described by the Einstein coefficient $B_{if} = A_{if}N(\omega_{if})$, where $N(\omega_{if})$ is the number of black body photons of frequency ω_{if}.

The harmonic vibrational frequency ω_e and the anharmonic correction $\omega_e\chi_e$ were calculated by expanding the vibration energies in the Taylor series

$$E_\nu = \omega_e\left(\nu + \frac{1}{2}\right) - \omega_e\chi_e\left(\nu + \frac{1}{2}\right)^2, \tag{3}$$

where ν is the vibrational quantum number.

To understand how the quality of the potential energy curves affects the lifetimes of the highly excited vibrational states, the lifetimes were also computed using the analytical Morse potential,

$$V(r) = D_e\left(\left(1 - e^{-a(r-r_e)}\right)^2 - 1\right), \tag{4}$$

where D_e is the dissociation energy, $a = \sqrt{\frac{k_e}{2D_e}}$, and k_e is the force constant. Parameters D_e and r_e were obtained directly from the electronic structure calculations, while k_e was calculated using the reduced mass and the energy gap between the zeroth and first vibrational levels,

$$k_e = \mu_{red}\omega_{01}^2 = \mu_{red}(E_1 - E_0)^2. \tag{5}$$

III. RESULTS AND DISCUSSION

A. Spectroscopic constants and potential energy and dipole moment curves

The values of spectroscopic constants obtained in this and other theoretical works are summarized in Table I. The LiBe$^+$ ion has been studied using the HF, MP2,[9,10] and spin-orbit configuration interaction methods.[30] You $et\ al.$[11] performed calculations with a higher level of theory, MRCI/aug-cc-pwCV5Z, and obtained the equilibrium distance R_e = 4.913a_0, dissociation energy D_e = 4903.6 cm^{-1}, and harmonic vibrational frequency ω_e = 318.4 cm^{-1}. These equilibrium distances and dissociation energies agree well with the values obtained in our work with MRCI/aug-cc-pCV5Z (R_e = 4.918a_0 and D_e = 4888.7 cm^{-1}); the small discrepancy can be explained by a slightly different basis set. Our harmonic frequency value ω_e = 323.8 cm^{-1} is higher by 5 cm^{-1}. Sun $et\ al.$[12] report the longer equilibrium distance, R_e = 4.977a_0, lower dissociation energy, D_e = 4605 cm^{-1}, and smaller harmonic frequency ω_e = 315.5 cm^{-1} obtained with MRCI+Q/ANO-TZVP and the

TABLE I. Equilibrium distances (R_e), permanent dipole moments (μ_e), dissociation energies (D_e), harmonic vibrational frequencies (ω_e), anharmonic corrections ($\omega_e\chi_e$) for the $LiBe^+$, $LiMg^+$, $NaBe^+$, and $NaMg^+$ ions.

	Method	Basis	R_e, a_0	μ_e, D	D_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})
$LiBe^+$	CCSDT[a]	cc-pCVQZ	4.919	3.56	4881.0	325.9	5.6
	MRCI[a]	cc-pCVQZ	4.921	3.62	4870.7	323.3	5.1
		aug-cc-pCV5Z	4.918	3.60	4888.7	323.8	5.1
	MRCI+Q[12]	aug-cc-pCVQZ	4.978		4605.0	315.5	4.965
	MRCI[11]	aug-cc-pwCV5Z	4.913		4903.6	318.4	4.31
	MP2[10]	6-311+G*	4.968		4616.8	320	
	Full SOCI[24]	STO-6G	4.980		4516	311	4.8
	CCSD(T)[13]	cc-pCVQZ	4.923		4868	322	4.85
$LiMg^+$	CCSDT[a]	cc-pCVQZ	5.476	5.44	6658.8	265.9	2.0
	MRCI[a]	cc-pCVQZ	5.481	5.44	6649.2	265.4	2.0
		aug-cc-pCV5Z	5.481	5.44	6640.8	266.1	2.1
	MRCI+Q[14]	aug-cc-pV5Z	5.546		6508.9	263.5	2.37
	MRCI+Q+DK[14]	aug-cc-pV5Z	5.533		6557.3	266.4	2.48
	MRCI+Q[14]	aug-cc-pVQZ	5.548		6484.7	262.9	2.35
	MRCI+Q+DK[14]	aug-cc-pVQZ	5.544		6476.6	262.9	2.36
	MP2[10]	6-311+G*	5.546		6470.5	261	
	CI[15]	Custom[b]	5.470		6575	264.22	2.63
	CCSD(T)[16]	cc-pVQZ	5.493		6712.4	267.3	2.30
$NaBe^+$	CCSDT[a]	cc-pCVQZ	5.624	1.14	3064.7	199.0	3.2
	MRCI[a]	cc-pCVQZ	5.617	1.21	3018.8	193.0	1.9
		aug-cc-pCV5Z	5.614	1.21	3085.2	194.6	1.9
	MP2[25]	6-31G*	5.686			202	
$NaMg^+$	CCSDT[a]	cc-pCVQZ	6.097	3.22	4522.9	150.9	1.2
	MRCI[a]	cc-pCVQZ	6.141	3.35	4452.8	149.3	1.2
		aug-cc-pCV5Z	6.140	3.34	4492.0	150.3	1.2

[a]This work.
[b]Li: 9s8p5d/8s6p3d; Mg: 9s7p5d4f/7s7p4d4f.

complete active space with 2 electrons on 16 orbitals. Using the CCSD(T)/cc-pVQZ level of theory, Bala *et al.* obtained the values, R_e = 4.923a_0, D_e = 4881 cm^{-1}, and ω_e = 322 cm^{-1}, that agree well with our CCSDT/cc-pCVQZ values (R_e = 4.919a_0, D_e = 4868.0 cm^{-1}, and ω_e = 325.9 cm^{-1}). Because of the non-perturbative treatment of the triple excitations and the inclusion of the core electron excitations, we expect our CCSDT values to be more accurate.

For the $LiMg^+$ ion, using the MRCI method with the relativistic Douglas-Kroll (DK) and Davidson (Q) corrections, Gao and Gao[14] obtained the following ranges for spectroscopic constants: R_e = 5.533-5.546a_0, D_e = 6476.6-6557.3 cm^{-1}, ω_e = 262.9-266.4 cm^{-1}, and $\omega_e\chi_e$ = 2.35-2.48 cm^{-1}. The specific values depend on the size of the basis set and inclusion of the DK and Q corrections. These values should be compared with our MRCI results: R_e = 5.481a_0, D_e = 6640.8 cm^{-1}, ω_e = 266.1 cm^{-1}, and $\omega_e\chi_e$ = 2.0 cm^{-1}. One of the reasons for the discrepancies in the equilibrium distance and dissociation energies is that in the work of Gao, the core electrons were frozen, whereas in our study all core electrons were correlated. ElOualhazi and Berriche[15] used the configuration interaction method with effective core potentials, reducing $LiMg^+$ to a two-electron system, and reported the values of R_e = 5.470a_0, D_e = 6575.0 cm^{-1}, and ω_e = 264.2 cm^{-1}. The equilibrium distance agrees well with our value. The dissociation energy is lower by about 100 cm^{-1} compared to our

value, likely due to the use of the effective core potentials. In the recent study, Bala and Nataraj[16] calculated spectroscopic constants of $LiMg^+$ using the CCSD(T)/cc-pVQZ level of theory and obtained the following values: R_e = 5.493 a_0, D_e = 6712.4 cm^{-1}, ω_e = 267.3 cm^{-1}, and $\omega_e\chi_e$ = 2.3 cm^{-1}. These values are very close to the ones calculated in this work using the higher CCSDT/cc-pCVQZ level of theory (R_e = 5.476 a_0, D_e = 6658.8 cm^{-1}, ω_e = 265.9 cm^{-1}, and $\omega_e\chi_e$ = 2.0 cm^{-1}).

The $NaBe^+$ ion was studied with the MP2 perturbation theory by Pyykkö *et al.*[17] who obtained the equilibrium distance R_e = 5.686a_0 and the harmonic frequency ω_e = 202 cm^{-1}. These results are in fairly good agreement with our CCSDT/cc-pCVQZ (R_e = 5.624a_0 and ω_e = 199.0 cm^{-1}) and MRCI/cc-pCVQZ (R_e = 5.617a_0 and ω_e = 193.0 cm^{-1}) values. The anharmonic corrections computed in this work with MRCI/cc-pCVQZ and CCSDT/cc-pCVQZ are $\omega_e\chi_e$ = 3.2 cm^{-1} and $\omega_e\chi_e$ = 1.9 cm^{-1}, respectively. The discrepancy in harmonic frequencies and anharmonic corrections between the two methods can be explained by the fact that the CCSDT method produces a more accurate potential energy curve near the equilibrium distance than MRCI. For the $NaBe^+$ ion, the differences in the CCSDT and MRCI potential energy curves are the largest compared to other ions, which results in largest differences in harmonic frequency and anharmonic correction.

The potential energy and dipole moment curves and the vibrational state lifetimes for the LiBe$^+$, LiMg$^+$, NaBe$^+$, NaMg$^+$ ions calculated with the CCSDT/cc-pCVQZ level of theory are presented in Fig. 1. The potential energy curves calculated with MRCI and CCSDT are in excellent agreement and cannot be distinguished on the plot. The differences in D_e (up to 46 cm^{-1} for NaBe$^+$) can be explained by the fact that MRCI, which based on the multireference wave function, better describes a dissociation limit, while CCSDT provides more accurate results close to the equilibrium distance because of the ability to recover more dynamic electron correlation. The dipole moment curves calculated with two methods are also in very good agreement, with MRCI predicting slightly higher dipole moments than CCSDT for the same internuclear distances. The largest difference for the dipole moment at the equilibrium distance is 0.13 D for NaMg$^+$. To estimate the basis set error, we performed the MRCI/aug-cc-pCV5Z calculations. Expansion of the basis set size did not have any significant effect on the dipole moments; the biggest difference

between the MRCI dipole moments obtained with cc-pCVQZ and aug-cc-pCV5Z basis sets is 0.02 D for LiBe$^+$. The changes in equilibrium distance do not exceed 0.003a_0, while the differences in dissociation energy vary from 9 cm^{-1} for LiMg$^+$ to 67 cm^{-1} for NaBe$^+$.

B. Vibrational state lifetimes

The lifetimes of the ground vibrational states of alkali-alkaline-earth ions calculated using the CCSDT potential energy and dipole moment curves are presented in Table II. The vibrational state lifetimes as functions of vibrational level ν are shown in Fig. 1(c). The same lifetimes as functions of energy are plotted in Fig. S1 of the supplementary material. The ions can be divided into two groups: LiBe$^+$ with LiMg$^+$ and NaBe$^+$ with NaMg$^+$. Interestingly, the LiBe$^+$ and LiMg$^+$ ions have essentially the same vibrational state lifetimes up to $\nu = 10$, with the ground state lifetimes around $\tau = 2.8$ s. Similarly, the lifetimes of NaBe$^+$ and NaMg$^+$ show the same behavior up to $\nu = 10$, but with a different ground state lifetime of around $\tau = 14$ s. Surprisingly, for all ions, the lifetimes of the several highest excited vibrational states are similar, or even larger, than the lifetimes of the ground states. This is in contrast to our early finding for the neutral heteronuclear alkali dimers where the ground vibration state lifetimes are at least an order of magnitude larger than the lifetimes of the highest excited states.[8]

The behavior of the vibrational lifetime curves can be explained by analyzing the transition dipole moments and the transition frequencies. The vibrational state lifetime is the inverse sum of the Einstein coefficients, which depend quadratically on the magnitude of transition dipole moment and cubically on the transition frequency between levels i and f [Eqs. (1) and (2)]. The magnitude of transition dipole moment depends on the permanent dipole moment and the overlap of the vibrational wave functions of levels i and f. The transition frequency ω_{if}, the energy difference between levels i and f, becomes very small for the highly excited vibrational states due to the large anharmonicity of the potential energy curve. Both transition dipole moment and transition frequency contribute to the rates of spontaneous emission and the BBR-induced stimulated absorption and emission.
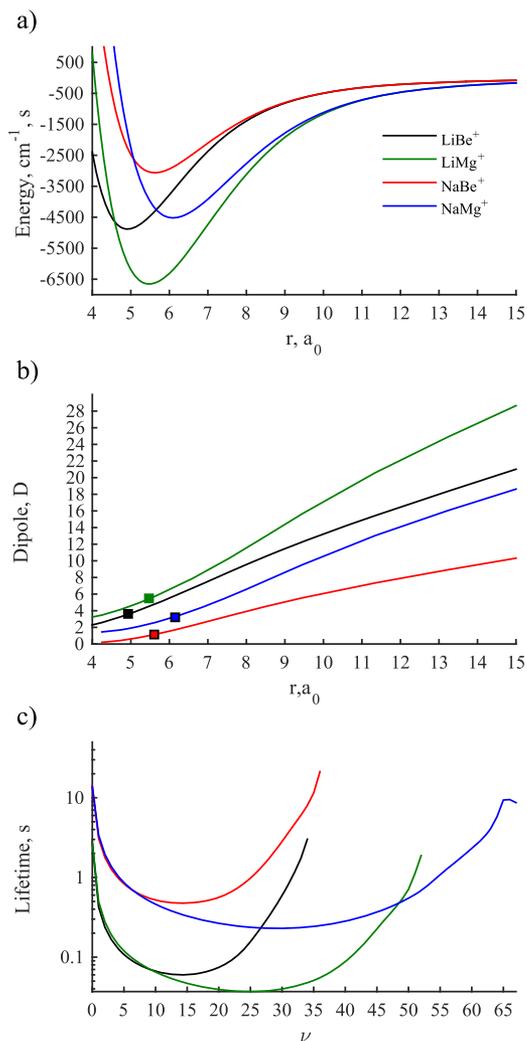
FIG. 1. [(a) and (b)] Potential energy and dipole moment curves calculated using the CCSDT method with the cc-pCVQZ basis set. Dipole moment values at the equilibrium distance indicated by squares. (c) Vibrational lifetimes as functions of vibrational level ν calculated with the CCSDT/cc-pCVQZ level of theory. The MRCI curves in (a)–(c) are indistinguishable from CCSDT and not plotted in this figure.

TABLE II. Ground state $\nu = 0$ vibrational lifetimes.

	Method	Basis set	Lifetime (s)
LiBe$^+$	CCSDT	cc-pCVQZ	2.78
	MRCI	cc-pCVQZ	2.76
		aug-cc-pCV5Z	2.77
LiMg$^+$	CCSDT	cc-pCVQZ	2.76
	MRCI	cc-pCVQZ	2.77
		aug-cc-pCV5Z	2.76
NaBe$^+$	CCSDT	cc-pCVQZ	14.0
	MRCI	cc-pCVQZ	14.8
		aug-cc-pCV5Z	14.4
NaMg$^+$	CCSDT	cc-pCVQZ	13.8
	MRCI	cc-pCVQZ	14.0
		aug-cc-pCV5Z	14.1
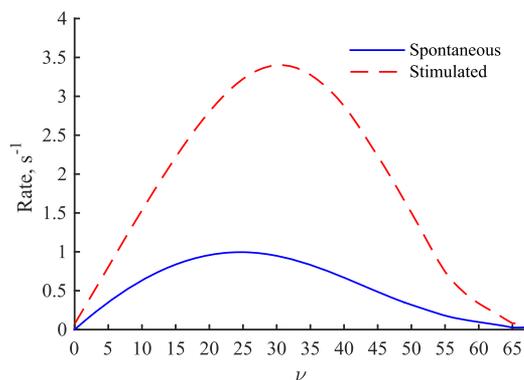
FIG. 2. Spontaneous (blue) and stimulated (red) rates of transitions from NaMg$^+$ vibrational states with quantum number ν calculated with the CCSDT/cc-pCVQZ level of theory.

Figure 2 shows the sum of the Einstein coefficients B_{if} for stimulated absorption and emission and the sum of the coefficients A_{if} for spontaneous emission as functions of vibrational state i for the NaMg$^+$ ion. The initial rapid decay of the lifetime as a function of the vibrational quantum number is explained by the fact that the excited vibrational states can spontaneously decay to the lower states, whereas the ground state can only decay to the excited through stimulated absorption. Because the transition rates from the intermediate-energy vibrational states are higher, they also have shorter lifetimes. The shortest lifetime ($\nu = 30$) corresponds to the peak of the stimulated transition rate and close to the maximum of the spontaneous transition rate. In the region $\nu > 30$, both spontaneous and stimulated rates monotonically decrease because the transition frequencies ω_{if} between the highly excited vibrational states become lower, i.e., highly excited states are energetically closer than the lower-energy states. Thus, for the highly excited states, the lifetime starts to increase again and, for the highest state, it reaches the value close to the ground state lifetime. This behavior is observed for all four studied ions. It is important to note that the long vibrational lifetimes of the highly excited vibrational states have been predicted for the neutral KRb molecule.[31,32]

The potential energy and dipole moment curves obtained with the CCSDT and MRCI methods predict similar vibrational state lifetimes, except for the highly excited vibrational states of NaMg$^+$. For this ion, the CCSDT-based lifetime curve has a small cusp around the 65th vibrational level, which is not observed on the MRCI-based lifetime curve (Fig. 3). To check if this is an artifact of the CCSDT potential energy curve, we computed the lifetimes using the Morse potential with the CCSDT dissociation energy and force constant [Eqs. (4) and (5)]. The Morse potential reproduces the CCSDT potential energy curve around the equilibrium quite accurately. However, for larger internuclear distances, the Morse potential deviates significantly from the CCSDT potential. This deviation results in the smaller number of vibrational states and different lifetimes for $\nu > 30$ states. However, the lifetime curve obtained with the Morse potential does not have a cusp, similar to the MRCI curve. Therefore, we conclude that the cusp is an artifact associated with the low quality of the CCSDT potential energy curve in the dissociation region. Similar artifacts, which are related to the single reference nature of the
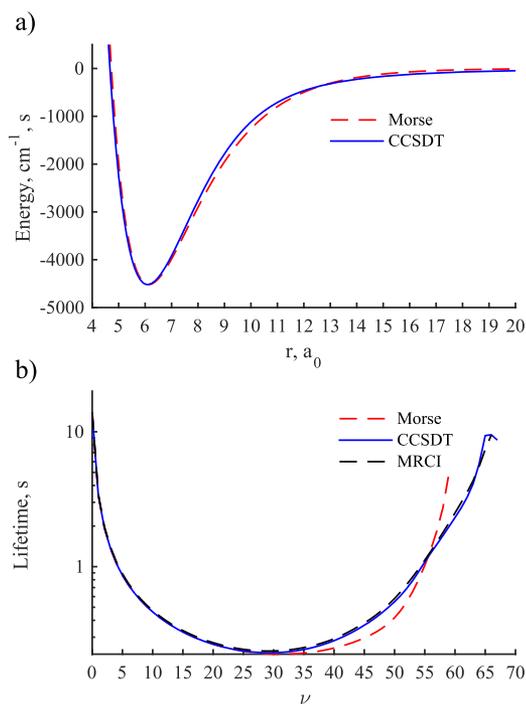
FIG. 3. (a) Potential energy curves for NaMg$^+$ calculated with the CCSDT method (solid blue line) and the Morse potential (dashed red line). (b) Lifetimes of NaMg$^+$ calculated with the CCSDT (blue line) and MRCI (dashed black line) methods. The dashed red line represents the lifetime calculated with the Morse potential using the CCSDT dipole moment curve.

CCSDT method, were observed in our earlier study of the neutral heteronuclear alkali dimers. To estimate the effect of the basis set on lifetimes, the MRCI calculations were carried out with the larger aug-cc-pCV5Z basis set. The lifetime values do not change significantly compared to ones obtained with the cc-pCVQZ basis set; the largest discrepancy is 0.4 s for the ground state lifetime of NaBe$^+$.

IV. SUMMARY

We investigated the lifetimes of vibrational states of four diatomic alkali-alkaline-earth ions (LiBe$^+$, LiMg$^+$, NaBe$^+$, and NaMg$^+$) to determine their suitability for ultracold experiments where long decoherence time and controllability by an external electric field are desirable. The CCSDT and MRCI methods with large one-electron basis sets were used to calculate the potential energy and dipole moment curves for the ground electronic states of these ions. These potential energy and dipole moment curves were used to evaluate the lifetimes of the ground and excited vibrational states.

The spectroscopic constants obtained with the MRCI and CCSDT methods in combination with the cc-pCVQZ basis set were compared for all four ions. The largest discrepancy between two methods in the equilibrium distance is $0.044a_0$, for NaMg$^+$ ion, and the smallest is $0.002a_0$, for LiBe$^+$. MRCI predicts slightly larger values of permanent dipole moment than CCSDT with the largest difference of 0.13 D for NaMg$^+$. The CCSDT method predicts larger dissociation energies compared to MRCI with the largest difference of 70 cm^{-1} for NaMg$^+$. The largest discrepancy between two methods in harmonic frequencies is only 6 cm^{-1}, for the NaBe$^+$ ion. The

spectroscopic properties are well converged with respect to the one-electron basis set, as demonstrated by the MRCI calculations on NaBe$^+$ with the cc-pCVQZ and aug-cc-pCV5Z basis sets. The differences in values obtained with these basis sets are 0.003 a_0 for equilibrium distance, 0.008 D for dipole moment, and 1.6 cm^{-1} for harmonic frequency.

We used the CCSDT and MRCI potential energy curves to calculate the wave functions and energies for the ground and excited vibrational states by solving the Schrödinger equation for nuclear motion. Transition dipole moments between all vibrational states were computed using the vibrational wave functions and the permanent dipole moment curves obtained from the electronic structure calculations. Lifetimes of all vibrational states as functions of the vibrational quantum number ν were obtained for all four ions. Two pairs of ions with distinct behavior of the vibrational state lifetimes (LiBe$^+$ with LiMg$^+$ and NaMg$^+$ with NaBe$^+$) were identified. Vibrational state lifetimes of the ions within each pair have very similar values up to $\nu = 10$ vibrational level. The pair of ions containing Li have the ground state lifetimes of approximately $\tau = 2.8$ s, while the ions containing Na have the lifetimes $\tau = 14$ s. For all ions, after initial decay as a function of ν, the lifetime reaches a minimum and then increases reaching the values closer, or even larger, than the lifetime of the ground vibrational state. It is important to note that the obtained values provide the upper limits for the lifetimes of highly excited states because in this study, and in our previous work on neutral alkali-alkali dimers,[8] we did not consider the vibrational state decay leading to dissociation into neutral atoms and atomic ions. Increasing the basis set has no significant effect on the predicted lifetimes. The CCSDT and MRCI methods predict essentially the same lifetime values. The small cusp on the CCSDT curve, also observed in our earlier study of neutral heteronuclear alkali dimers, is likely caused by the incorrect behavior of the CCSDT potential energy curve at the dissociation limit. This incorrect behavior is associated with a single reference nature of CCSDT and is not observed in the MRCI method and if the analytical Morse potential is used.

The accurate spectroscopic constants and potential energy and dipole moment curves are expected to be useful in the future experimental and theoretical studies of diatomic alkali-alkaline-earth ions. The long lifetime of the highly excited vibrational states of these ions could be useful in designing the ultracold experiments, where electric field control and long decoherence time of the vibrational states are desirable.

SUPPLEMENTARY MATERIAL

See supplementary material for the plot of lifetimes as functions of the energy of vibrational states, as well as potential energy curves, dipole moment curves, and vibrational state lifetimes calculated with different levels of theory.

ACKNOWLEDGMENTS

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