

Accurate *ab initio* calculations of spectroscopic constants and properties of BeLi⁺

Renu Bala^{a,*}, H.S. Nataraj^a, Minori Abe^b, Masatoshi Kajita^c

^a Department of Physics, Indian Institute of Technology Roorkee, Roorkee 247667, India

^b Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

^c National Institute of Information and Communication Technology, Nukui-Kitamachi, Koganei, Tokyo 184-795, Japan

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ABSTRACT

We have calculated the spectroscopic constants and the molecular properties, for the ground-state ($X^1\Sigma^+$) of BeLi⁺, such as dipole moment, quadrupole moment and dipole polarizability at different levels of correlation: many-body perturbation theory (MP2), coupled cluster method with single and double excitations (CCSD) and CCSD with perturbative triples (CCSD(T)). The correlation consistent polarized valence cc-pVXZ (X = D, T, Q) basis sets and also their augmented counterparts are used together with the non-relativistic and relativistic Hamiltonians. The results are extrapolated to the complete basis set limit (CBS) using exponential-Gaussian functions. Thus, accurate and reliable results for BeLi⁺ with the maximum possible error bars on them are reported. The effects of diagonal Born-Oppenheimer corrections (DBOC) and of electron correlations beyond the CCSD(T) level of approximation are also estimated. In addition, by solving the vibrational Schrödinger equation using the potential energy curve obtained at CCSD(T)/QZ level, we have calculated the vibrational parameters such as energies, rotational constants, permanent dipole moments, spontaneous and black-body radiation (BBR) induced transition rates between different vibrational levels of the electronic ground state. The lifetime of the lowest rovibrational state ($\nu = 0$ and $J = 0$) at room temperature, is found to be 4.67 s. Further, the electronic and the vibrational parameters of a few low-lying electronic excited states: $1^3\Sigma^+$, $1^3\Pi$, $2-4^1\Sigma^+$, and $1-2^1\Pi$ are calculated using the EOM-CCSD/QZ method. The dipole moments for the electronic transitions from the ground- to the excited singlet states are also reported.

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1. Introduction

Understanding the complex structure of the molecules, neutral as well as ions, is an outstanding problem of molecular physics. With delicate investigations of such systems, one can obtain a wealth of information which can be used further to explore the various inter-related areas of research. To mention, cold and ultra-cold molecules can be used in the study of the controlled chemical reactions [1], the variation of fundamental physical constants such as the proton-to-electron mass ratio, $\mu \equiv m_p/m_e$ [2–4], the fine structure constant α [4], and also in the search for the symmetry violating exotic property of an electron which hitherto has evaded detection, called the electric dipole moment (EDM) [5,6], etc.

For over a decade, the neutral homonuclear and heteronuclear diatomic molecules of alkali- and alkaline-earth-metals have extensively been studied both theoretically [7–9] and experimen-

tally [10,11,12]. The calculation of spectroscopic constants, permanent dipole moments (PDMs), and vibrational states of electronic ground-state of monohydride ions of group IIA, IIB and Yb have been reported in Ref. [13]. Recently, ground- and first-excited states of the monohydrides of alkaline-earth-metals have been investigated theoretically using multi-reference configuration interaction (MRCI) method for the purpose of laser cooling [14]. The ground and low lying excited states of MgLi and MgLi⁺ have been studied using full valence configuration interaction (FCI) and MRCI methods [15]. Quite recently, structural, electronic and dipolar properties of CaLi⁺ and SrLi⁺ have also been reported in Refs. [16,17].

On continuing with the same isoelectronic sequence, we have a simpler system, BeLi⁺. Although, there is no experimental data available for this system yet, to the best of our knowledge, it is being considered by Rakshit et al. [18] and Ghanmi et al. [19]. There exists, however, several calculations in the literature, such as, the calculation of spectroscopic constants of $1-2^1\Sigma^+$ and $1^3\Sigma^+$ using self-consistent field (SCF) method by Safonov et al.

* Corresponding author.

E-mail address: rbaladph@iitr.ac.in (R. Bala).

[20], thermodynamical stability and physicochemical reaction of several molecular ions including BeLi^+ by Nicolaides et al. [21], the calculation of ground-state spectroscopic constants at MP2 (full) level by Boldyrev et al. [22] using the Gaussian 92 program, calculations of the ground-state and low-lying $1^1\Sigma^+$ electronic states of BeLi^+ by Farjallah et al. [23] using FCI, the studies of ground- and first-excited state potential energy curves (PECs) for predicting the feasibility of the formation of cold molecular ion by photoassociation by Rakshit et al. [18], studies of the ground- and several low-lying excited states by Sun et al. [24] using MRCI+Q method and multi-reference averaged quadratic coupled-cluster (MRAQCC) methods including Davidson correction. An *ab initio* study of ground- and low-lying excited states have been done by You et al. [25] using MRCI method. Recently, Ghanmi et al. [19] have reported their theoretical investigations for tens of excited electronic states of BeLi^+ molecular ion. Those authors have reported the PECs, spectroscopic constants, dipole moment curves, and also the transition dipole moment curves for several of these excited states for the first time and use those results for the photoassociation prediction of BeLi^+ molecular ion. Their calculations are based on the full configuration interaction (CI) method, however, considering only two active valence electrons that are moving in the field of Be^{2+} and Li^+ cores using the pseudo-potential approach. More recently, spectroscopic constants and vibrational state lifetimes of diatomic alkali-alkaline-earth cations have been studied by Fedorov et al. [26]. An accurate knowledge of spectroscopic constants would always be advantageous both theoretically and experimentally. However, the non-inclusion of all electrons and lack of higher basis sets in the calculations may not lead to the level of accuracy desirable for experimental purposes.

In the present work, in order to achieve reliable accuracy we have employed the higher levels of correlation methods and also used a successive hierarchy of three optimized basis sets, which enable us to extrapolate the results easily to the complete basis set (CBS) limit. This is required to achieve the saturation of the results due to the basis size effects. The configuration space considered for electron correlations in our work is also quite large compared to many of the previous works. Thus, we have calculated the spectroscopic constants, potential energy curves and dipole moment curves for the ground state ($X^1\Sigma^+$) of BeLi^+ systematically and more accurately compared to the results available in the literature. In addition, we have calculated the dipole polarizability and the quadrupole moment for the ground-state of BeLi^+ ion, which are being reported for the first time, known to our knowledge. Using PEC calculated at the CCSD(T) level of correlation for the QZ basis set, vibrational Schrödinger equation is solved to obtain the spectroscopy of vibrational energy levels. Thereafter, we have extended our study to the low-lying excited electronic states and their vibrational spectroscopy at the CCSD level of correlation. Our results would be useful for the experimentalists who are seeking accurate theoretical data for BeLi^+ molecular ion.

The present paper is divided into four sections. After the introduction, Section 2 briefly reports the methodology involved in the calculations, Section 3 details the discussions on the calculated results and Section 4 summarizes the current work.

2. Methodology

CFOUR [27] and DIRAC15 [28] software suites are used to carry out the non-relativistic and relativistic ground-state calculations, respectively, of the spectroscopic constants, at the equilibrium point, such as: bond lengths (R_e), dissociation energies (D_e), harmonic frequencies (ω_e), anharmonic constants ($\omega_e x_e$), rotational

constants (B_e and α_e) together with the molecular properties such as: dipole moments (μ_e), quadrupole moments (Θ_{zz}) and components of static dipole polarizability (α_{\parallel} , α_{\perp}) at MP2, CCSD and CCSD(T) level of correlation. The uncontracted cc-pVXZ and aug-cc-pVXZ basis sets of Dunning et al. [29] with $X = [D, T, Q]$, available in the DIRAC15 package, are used in the present calculations. The nuclear masses of 9.0121822 au for Be and of 7.0160030 au for Li have been used. Further, C_{2v} molecular point group symmetry is utilized in our calculations. The origin of the coordinate system is at the center-of-mass of the molecule. All the electrons are kept active both for diatomic constants and also for property calculations. Furthermore, the energies and PDMs are calculated for the range 0.4–30 Å with a step size of 1 Å and around the equilibrium point a finer step size of 0.001 Å is adopted. The maximum distance of 30 Å is chosen based on the saturation of energies limited to the threshold set. The dissociation energies are evaluated by taking the difference between the energies at equilibrium bond length and those at a distance of 30 Å.

For non-relativistic calculations, the basis sets have been taken from the EMSL library [30]. The harmonic frequencies and anharmonic constants are calculated using the second-order vibrational perturbation theory, i.e., with VPT2 keyword in the CFOUR package. The average polarizabilities ($\bar{\alpha}$) and anisotropic polarizabilities (γ) are obtained, respectively, using:

$$\bar{\alpha} = (\alpha_{\parallel} + 2\alpha_{\perp})/3, \quad (1)$$

and

$$\gamma = \alpha_{\parallel} - \alpha_{\perp}. \quad (2)$$

The z-component of the quadrupole moment, Θ_{zz} , is related to the other diagonal components by the relation,

$$\Theta_{zz} = -(\Theta_{xx} + \Theta_{yy}). \quad (3)$$

For linear molecules, $\Theta_{xx} = \Theta_{yy}$, and therefore,

$$\Theta_{zz} = -2\Theta_{xx}. \quad (4)$$

Further, we have performed vibrational spectroscopy using VIBROT program available in MOLCAS package [31]. PEC and dipole moment data for bond distance varying from 0.4 to 30 Å at CCSD(T) level of correlation are used to obtain vibrational wavefunctions, vibrational-state energies (E_v), transition dipole moments (TDMs) between the vibrational levels, and rotational constants (B_v). The spontaneous and black-body radiation induced transition rates at surrounding temperature, viz. $T = 300$ K, are calculated using TDM values and vibrational energy differences as [32],

$$\Gamma_v^{spont} = \sum_{v'' < v} \Gamma^{emis}(v \rightarrow v'') \quad (5)$$

$$\Gamma_v^{BBR} = \sum_{v'' < v} \bar{n}(\omega) \Gamma^{emis}(v \rightarrow v'') + \sum_{v'' > v} \bar{n}(\omega) \Gamma^{abs}(v \rightarrow v'') \quad (6)$$

The average number of photons $\bar{n}(\omega)$ at frequency, ω , is given by the relation,

$$\bar{n}(\omega) = \frac{8\pi\omega^2}{c^3} \frac{1}{e^{(\hbar\omega/k_B T)} - 1}, \quad (7)$$

where $\hbar\omega = |E_v - E_{v'}|$, is the energy difference between the two vibrational levels involved, with $\tilde{\nu}$ is v'' for emission and v' for absorption and k_B is the Boltzmann constant.

The emission and absorption rates required for Γ^{spont} and Γ^{BBR} in above equations are calculated using the equation,

$$\Gamma^{emis \text{ or } abs}(v \rightarrow \tilde{\nu}) = \frac{\omega}{3\epsilon_0 \hbar} (TDM_{v \rightarrow \tilde{\nu}})^2 \quad (8)$$

Thus, the lifetimes of the vibrational states can be obtained as the inverse of the sum of spontaneous and BBR-induced transition rates ($\Gamma^{\text{total}} = \Gamma^{\text{spont}} + \Gamma^{\text{BBR}}$).

In addition to the ground electronic state, a few low-lying electronic excited states are also studied using EOM-CCSD method with QZ basis set.

For the relativistic case, the Dirac-Fock-Coulomb Hamiltonian is used with the DIRAC15 package. The contribution from the (SS|SS) integrals is taken in an approximate manner, as suggested in Ref. [33], by including an interatomic (SS|SS) correction. The energy calculations at MP2, CCSD and CCSD(T) levels are carried out with the RELCCSD module. The VIBROT program of MOLCAS is used for calculating the spectroscopic constants as discussed earlier for the non-relativistic case. The results calculated systematically using the three progressively large basis sets, both for relativistic and non-relativistic cases, are extrapolated to CBS limit using a function of the form [34,35]:

$$f(x) = f_{\text{CBS}} + B e^{-(x-1)} + C e^{-(x-1)^2} \quad (9)$$

where B and C are constant parameters, $x = 2, 3, 4$ is the cardinal number for basis sets DZ, TZ and QZ, respectively, $f(x)$ is the property that is calculated with the basis set characterized by cardinal number x and f_{CBS} is the complete basis set limit for the property of interest.

The estimation of uncertainty on the calculated quantities, in general, is little involved; there can be two possible error sources: one arising due to the choice of the basis set (*viz.* the size) and the other arising from the negligence of higher order correlation effects beyond what is considered in the present work. As we have done a series of calculations with a successive hierarchy of optimized basis sets, and extrapolated the results systematically to the CBS limit, we least expect the error to come from the former source. As the contributions from the higher order correlation effects are not expected to be larger than that of the leading order triples considered perturbatively in our work, we have quoted the entire contribution from the latter, *i.e.* CCSD(T) - CCSD at CBS level, as the maximum possible error bar (Δ) on our results. Thus, we recommend the final result, f_{final} , of the calculated property to be:

$$f_{\text{final}} = f_{\text{CCSD(T)@CBS}} \pm (|\Delta|) \quad (10)$$

where $f_{\text{CCSD(T)@CBS}}$ is the CBS value of the property of interest at CCSD(T) level.

3. Results and discussion

3.1. Ground-state spectroscopic constants and molecular properties

Fig. 1 shows the potential energy curves for the ground-state of BeLi⁺, obtained at the CCSD(T) level of correlation with DZ, TZ and QZ basis sets, using the non-relativistic Hamiltonian. The spectroscopic constants computed, using the non-relativistic Hamiltonian, at various levels of correlation considered in this work are shown in Table 1. In addition, the results extrapolated to CBS limit at each level of correlation are shown. Our results of the spectroscopic constants show a good agreement with those available in the literature [19–26,36]. The difference between our CBS values at the SCF level and those quoted in Ref. [20] is not more than 7% in all the spectroscopic constants barring the anharmonic constant. The latter which depends on other diatomic constants shows a larger deviation. The MP2 results of Ref. [22] also compare quite well with our results at the similar level of approximation. The results reported in Ref. [23], calculated at FCI level and our recommended CCSD(T) values, highlighted in bold fonts, agree extremely well. Leaving aside the anharmonic constant, the difference between our CBS results at CCSD(T) level and those reported in Refs. [25,19] at MRCI and FCI

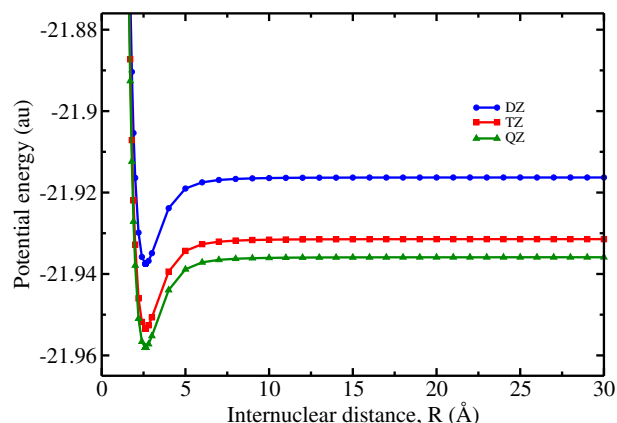


Fig. 1. Potential energy curves for the ground-state of BeLi⁺ using CCSD(T) method, in the non-relativistic case.

level of correlation, respectively, is less than 3% for all diatomic constants. The values for R_e , D_e , and ω_e obtained in the current work at CCSD(T) level with cc-pVQZ basis set are very close to those reported in Ref. [26] at MRCI level of correlation with cc-pCVQZ basis set. The difference between present results for R_e , D_e , and ω_e using cc-pVQZ basis set and CCSD(T) method is not more than 1.2% from those reported in Ref. [26] at CCSDT level with cc-pCVQZ basis set. The fundamental vibrational frequency of BeLi⁺ ion calculated using the CBS results of ω_e and $\omega_e x_e$ at the CCSD(T) level of theory is 314.26 cm⁻¹.

In order to understand the dissociative nature of the ground-state of BeLi⁺, we have performed ionization energy calculations on neutral BeLi and singly charged ion, BeLi⁺. We have found that the first ionization energy of BeLi is 43,437 cm⁻¹, which agrees with the ionization energy of Li atom to within 0.1% to that reported in NIST database [37]. In addition, D_e calculated by taking the difference between the sum of Be and Li⁺ energies, and the energy at the equilibrium point of BeLi⁺ molecule in the PEC reassures that the ground-state of BeLi⁺ will dissociate to Be + Li⁺.

The results of spectroscopic constants derived from the PECs computed using the relativistic Hamiltonian are given in Table 2. As is obvious, due to the small charge of Be and Li, we did not observe an appreciable difference between the relativistic and the non-relativistic results in all the spectroscopic constants.

Thus, we continue to use the non-relativistic Hamiltonian for the calculation of molecular properties such as dipole moments, quadrupole moments, components of static dipole polarizability, isotropic and anisotropic polarizabilities, and parallel-component of the dipole polarizabilities at super molecular limit (100 au) symbolized as α_{100} , and these results are tabulated in Table 3. Fig. 2 shows the absolute value of PDM as a function of internuclear distance R at CCSD(T) level of correlation using QZ basis set. This dipole moment curve shows an almost linear behaviour from 6 Å to 30 Å exactly in agreement with that reported by Farjallah et al. [23]. The value of PDM at equilibrium point reported in the current work using CCSD(T) method is 0.005 au larger and 0.018 au smaller than those reported in Ref. [26] at CCSDT and MRCI levels of theory, respectively, at the similar standard of basis set. We have observed that, as we go towards the higher basis set, the results for spectroscopic constants and molecular properties converge. Further, the R -variation of quadrupole moment and components of dipole polarizability at CCSD(T) level of correlation using QZ basis set is shown in Figs. 3 and 4, respectively. The complete list of the computed values of potential energies, permanent dipole moments, quadrupole moments and polarizabilities are collected together and are reported in the Supplementary Table S1.

Table 1
The computed spectroscopic constants for the ground-state of BeLi⁺, in the non-relativistic case. Comparison with the available results in the literature.

Basis	Method	R_e (au)	D_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)
DZ	SCF	5.006	5068	305	5.01	0.608	0.0138
	MP2	4.966	4994	320	4.80	0.618	0.0130
	CCSD	4.957	4644	318	4.84	0.621	0.0131
	CCSD(T)	4.955	4655	318	4.93	0.621	0.0131
TZ	SCF	5.008	5105	302	5.16	0.608	0.0139
	MP2	4.947	5145	324	4.82	0.623	0.0129
	CCSD	4.942	4799	319	4.84	0.624	0.0131
	CCSD(T)	4.940	4812	319	4.82	0.625	0.0131
QZ	SCF	5.004	5116	300	5.15	0.609	0.0144
	MP2	4.930	5222	326	4.95	0.627	0.0132
	CCSD	4.927	4859	321	4.86	0.628	0.0134
	CCSD(T)	4.923	4868	322	4.85	0.629	0.0133
CBS	SCF	5.001	5122	299	5.14	0.610	0.0147
	MP2	4.919	5269	327	5.04	0.630	0.0134
	CCSD	4.917	4894	322	4.87	0.631	0.0136
	CCSD(T)	4.912	4900	324	4.87	0.631	0.0134
Error bar		±0.005	±6	±2	±0.0006	±0.0009	±0.0002
Published works							
	SCF [20]	5.027	5001	320	8.2	0.601	–
	MP2 [22]	4.968	–	320	–	–	–
	MP4* [22]	–	4757	–	–	–	–
	QCISD(T)** [22]	–	4617	–	–	–	–
	FCI [23]	4.96	4849	321.2	6.48	0.6395	–
	CCSD(T) [24]	4.964	–	315.5	–	0.623	–
	MRCI [25]	4.913	4903.6	318.4	4.310	0.6173	–
	FCI [19]	4.940	4862	323.7	5.45	0.6395	–
	CCSDT [26]	4.919	4881.0	325.9	5.6	–	–
	MRCI [26]	4.921	4870.7	323.3	5.1	–	–
	MRD-CI*** [36]	5.083	–	–	–	–	–

* MP4: Fourth-order many-body perturbation theory, ** QCISD(T): Quadratic CI including singles, doubles and partial triples, *** MRD-CI: Multi-reference double-excitation CI.

Table 2
The computed spectroscopic constants for the ground-state of BeLi⁺, in the relativistic case.

Basis	Method	R_e (au)	D_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)
DZ	SCF	5.005	5067	320	5.13	0.607	0.0116
	MP2	4.966	4993	322	5.05	0.616	0.0113
	CCSD	4.955	4644	320	5.13	0.619	0.0116
	CCSD(T)	4.954	4654	320	5.11	0.620	0.0116
TZ	SCF	5.006	5104	318	4.99	0.605	0.0112
	MP2	4.947	5149	323	4.73	0.619	0.0109
	CCSD	4.942	4799	321	5.24	0.622	0.0115
	CCSD(T)	4.940	4811	322	5.22	0.623	0.0114
QZ	SCF	5.003	5114	319	5.02	0.605	0.0113
	MP2	4.929	5221	327	4.99	0.622	0.0106
	CCSD	4.926	4858	324	5.31	0.626	0.0116
	CCSD(T)	4.922	4868	324	5.30	0.627	0.0116
CBS	SCF	5.001	5119	320	5.05	0.605	0.0114
	MP2	4.917	5264	330	5.18	0.624	0.0104
	CCSD	4.916	4893	326	5.35	0.629	0.0116
	CCSD(T)	4.910	4901	325	5.35	0.630	0.0117
Error bar		±0.006	±8	±1	±0.003	±0.001	+0.0001

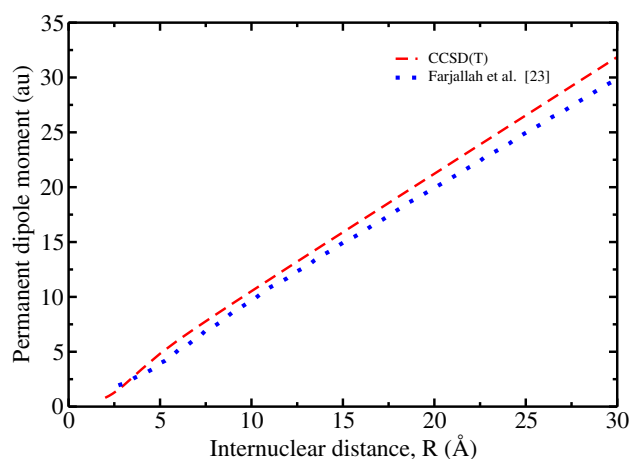
The augmentation of the basis sets with diffuse functions does not appreciably alter the results of the spectroscopic constants and the molecular properties. The difference in our final results between the augmented and un-augmented basis sets is about 0.001 au in R_e , 1 cm⁻¹ in D_e and ω_e , 0.2 cm⁻¹ in $\omega_e x_e$, 0.0003 cm⁻¹ in B_e , 0.0001 cm⁻¹ in α_e , 0.0004 au in μ_e and Θ_{zz} , 0.066 au in $\bar{\alpha}$, and 0.051 au in γ , at the CCSD(T) level. All of these, except γ , are well within the error bars that we have reported in Table 1 and in Table 3. The polarizability results, with and without augmentation, in the super-molecular limit seem to have a noticeable difference. At the CCSD(T) level, the CBS value of $\alpha_{100} = (37.944 \pm 0.167)$ au with augmented basis set, while

$\alpha_{100} = (37.085 \pm 0.189)$ au without augmentation. The former is significantly close to the sum of polarizabilities of the Be [38] and Li⁺ [39], viz. $\alpha_{Be} + \alpha_{Li^+} = 37.71 + 0.191 = 37.901$ au. Due to the unavailability of experimental value of polarizability for Li⁺ in the literature, we have taken its calculated value at the CCSD(T) level from the Ref. [39] and combined it with the experimental value for Be. The recent work in Ref. [19] also reports $\alpha_{Be} = 37.4932$ au which lies almost in the middle of our two estimates for α_{100} discussed above.

In order to understand the effects of higher-order electron correlation, beyond the CCSD(T) level considered here for most of the calculations, we have performed potential energy calculations at

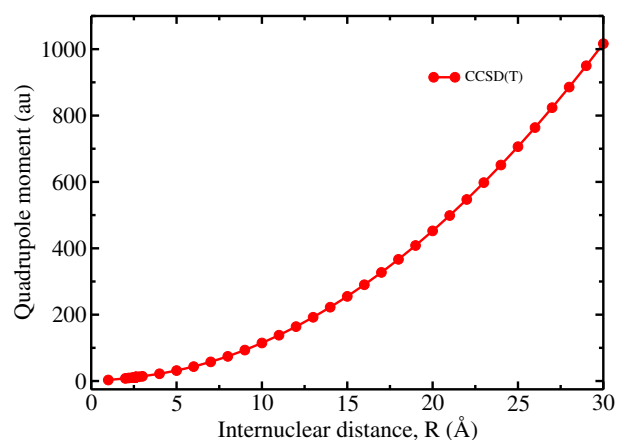
Table 3Dipole moment, quadrupole moment, components of dipole polarizability at equilibrium point, and polarizability at super-molecular limit, for the ground-state of BeLi⁺.

Basis	Method	$ \mu_e $ (au)	Θ_{zz} (au)	$\alpha_{ }$ (au)	α_{\perp} (au)	$\bar{\alpha}$ (au)	γ (au)	α_{100} (au)
DZ	SCF	1.274	12.642	46.086	36.843	43.005	9.243	44.586
	MP2	1.335	12.713	43.881	34.285	37.483	9.596	40.403
	CCSD	1.449	11.732	42.010	32.071	35.384	9.939	35.921
	CCSD(T)	1.450	11.712	41.942	32.006	35.318	9.936	35.838
TZ	SCF	1.276	12.622	45.941	36.713	42.865	9.228	45.520
	MP2	1.310	12.130	43.652	34.306	37.421	9.346	41.348
	CCSD	1.421	11.711	42.223	32.347	35.639	9.876	37.012
	CCSD(T)	1.422	11.687	42.143	32.273	35.563	9.870	36.911
QZ	SCF	1.274	12.621	45.895	36.745	42.845	9.150	45.721
	MP2	1.291	12.097	43.499	34.407	37.438	9.092	41.572
	CCSD	1.405	11.680	42.197	32.466	35.710	9.731	37.191
	CCSD(T)	1.406	11.645	42.087	32.363	35.604	9.724	37.037
CBS	SCF	1.273	12.621	–	–	42.836	9.098	45.826
	MP2	1.279	12.095	–	–	37.452	8.929	41.691
	CCSD	1.395	11.660	–	–	35.749	9.635	37.274
	CCSD(T)	1.396	11.617	–	–	35.623	9.628	37.085
Error bar		± 0.001	± 0.043	–	–	± 0.126	± 0.007	± 0.189
	CCSDT [26]	1.401	–	–	–	–	–	–
	MRCI [26]	1.424	–	–	–	–	–	–

**Fig. 2.** Permanent dipole moment curve using CCSD(T)/QZ method.

the CCSDT level using QZ basis set. The difference in the potential energies calculated using CCSD(T) and CCSDT method, in the vicinity of equilibrium point and at the dissociative limit is about 9 cm⁻¹ and 6 cm⁻¹, respectively. We have found that the values of R_e and B_e remain unaffected by the inclusion of missing non-leading order triples to CCSD(T) at least for up to the accuracies reported in this work. On the other hand, the value of D_e increases by 3 cm⁻¹, and ω_e decreases by 0.06 cm⁻¹. These contributions are well within the error bars that we have quoted in Table 1. Further, the adiabatic effects are also estimated by including the diagonal Born-Oppenheimer (DBOC) corrections at the CCSD level of theory using QZ basis set. The calculated DBOC energy correction is significantly large, about 332 cm⁻¹, similar to that reported for BeH molecule in Ref. [40]. However, the consideration of DBOC correction for the energy in our calculation does not seem to alter the R_e as well as the D_e results since it has been observed to be more or less uniform throughout the region of PEC of BeLi⁺. The computed values of DBOC are given in the Supplementary Table S2.

Using PEC and PDM curve obtained at CCSD(T) level of correlation with QZ basis set we have solved the vibrational Schrödinger equation taking the rotational quantum number, $J = 0$ and obtained the vibrational parameters. The vibrational energies

**Fig. 3.** Quadrupole moment curve using CCSD(T)/QZ method.

(E_v), rotational constants (B_v), PDMs (μ_v), transition rates: both spontaneous (Γ_v^{spont}), and BBR-induced (Γ_v^{BBR}); are tabulated for some low-lying vibrational states in Table 4. The relative energy spacings between the adjacent vibrational states observed in this work compare well with those reported by Fedorov et al. [26]. As expected, the value of dipole moment for $v=0$ is close to the dipole moment calculated at the equilibrium point of the PEC. We have observed that the PDM increases as the vibrational quantum number increases, whereas, the rotational constant shows an opposite trend. It has been reported in the literature [41] that the TDMs between the vibrational states and hence, the lifetimes of vibrational states depend on the numerical grid size used for the integration for solving vibrational Schrödinger equation. In order to verify this, we have used four different grid sizes ranging from 1000 to 2200. The grid dependent TDM values used to calculate transition rates can be found in the Supplementary Table S3. From the reciprocal of total transition rates, the lifetimes of the vibrational states are evaluated and plotted in Fig. 5 for different grid sizes. It can be seen explicitly that there is a convergence of results for the lifetimes of the vibrational states at higher grid sizes and hence, we report the lifetime for the rovibronic ground-state to be 4.67 s calculated with 2200 grid size. This result is 1.89 s larger than the value reported in Ref. [26]. The reason for this discrepancy

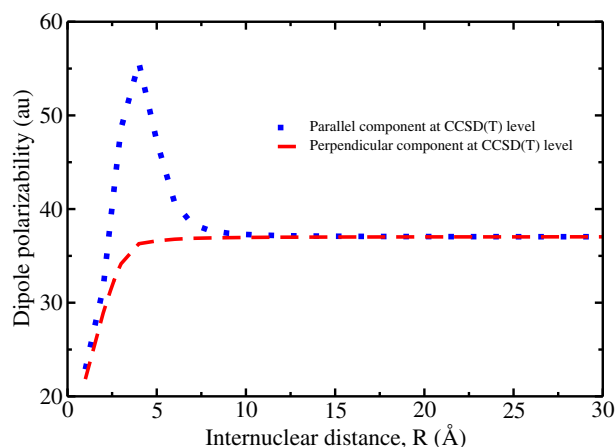


Fig. 4. Components of dipole polarizability as a function of R using CCSD(T)/QZ method.

could be from the difference in the PDM values between the two calculations and the numerical convergence issues related to grid size considered in Ref. [26]. As anticipated, the lower vibrational states have longer lifetimes than that of the higher vibrational states and also, the difference between the lifetimes of consecutive states for higher v is much smaller than the lower states.

3.2. Excited-state spectroscopic constants and dipole moment

The PECs for the excited states: $1^3\Sigma^+$, $1^3\Pi$, $2-4^1\Sigma^+$, and $1-2^1\Pi$, as a function of internuclear distance, R , at EOM-CCSD level of theory using QZ basis set are shown in Fig. 6. The corresponding data for the PECs is provided in the Supplementary Table S4. These calculations are performed using the EOM-CCSD method alone due to the current unavailability of higher-order EOM-CC methods. By extracting the spectroscopic constants from the PECs of the excited states and on comparing them with the available results, we have confirmed the accuracy of our results. The calculated spectroscopic constants for the excited states are shown in Table 5. The dissociative product states of these electronic excited states are shown in Table 6. In order to identify the molecular states to which these excited states dissociate, we have compared their energies at dissociation limit (100 au) with the sum of atomic/ionic energies

taken from the NIST database [37]. The maximum percentage error between our values and those from Ref. [37] is 1.97% as shown in the last column of Table 6.

Both of the triplet excited states considered here: $1^3\Sigma^+$ and $1^3\Pi$ dissociate into the same final states: $\text{Be}(2s2p)^3\text{P} + \text{Li}^+$. There is a small energy separation of $\sim 2\text{ cm}^{-1}$ between these triplet states at the dissociation limit in our calculation, however they are shown to be degenerate in NIST database [37]. The spectroscopic constants that we have obtained for these states are reasonably in good agreement with other published calculations [19,24,25]. The disagreement ranges between 0.01 and 0.06 au for R_e , 12 and 626 cm^{-1} for D_e , 0.4 and 8.6 cm^{-1} for ω_e , 0.62 and 2.4 cm^{-1} for $\omega_e x_e$, 0.001 and 0.002 cm^{-1} for B_e , and 0.002 and 0.003 cm^{-1} for α_e , respectively.

We have evaluated the contribution of relativistic effects for the $^3\Pi$ state using Kramers-restricted configuration interaction with single and double excitations (KRCSID) method available in the KRCSID module of DIRAC [28]. The $^3\Pi_1$ and $^3\Pi_2$ states are found to lie 1.96 cm^{-1} and 3.92 cm^{-1} , respectively, above the $^3\Pi_0$ state at the equilibrium point. Hence, the transition energy, T_e , reported in Table 5 may have an error of about 4 cm^{-1} , while the error in the reported dissociation energy, harmonic frequency, and anharmonic constant for $^3\Pi$ state is estimated to be 0.8 cm^{-1} , 0.01 cm^{-1} and 0.001 cm^{-1} , respectively, due to the negligence of spin-orbit splitting.

There is an apparent disagreement between the results of Sun et al. [24] and Ghanmi et al. [19] for the case of $2-3^1\Sigma^+$ states. The former reports these PECs as repulsive while the latter reports them to be attractive with a potential depth of 1976 cm^{-1} for $2^1\Sigma^+$ and 737 cm^{-1} for $3^1\Sigma^+$. In the present work, we have found both of these states to be attractive similar to that of Ref. [19] and calculated the potential depths to be 1937 cm^{-1} and 1803 cm^{-1} , respectively. The relative difference between our results and those reported in Ref. [19] is; $\Delta(R_e) < 0.32\%$, $\Delta(\omega_e) < 2.32\%$, $\Delta(\omega_e x_e) < 5.4\%$, and $\Delta(B_e) < 0.8\%$ for $2^1\Sigma^+$ state. However, for $3^1\Sigma^+$ state, some of our results show a noticeable disagreement. Our dissociation energy ($D_e = 1803\text{ cm}^{-1}$) is 1066 cm^{-1} larger, and the anharmonic constant ($\omega_e x_e = 0.81\text{ cm}^{-1}$) is 8.43 cm^{-1} smaller than that of [19]. The difference in the values of potential depths may arise due to the method of calculation employed and the choice of basis set. On the other hand, our findings for $4^1\Sigma^+$ state compare well with those given in Ref. [19]. Our results of

Table 4
Energies, rotational constants, PDMs, spontaneous and BBR-induced transition rates for vibrational levels of the ground electronic state.

v	E_v (cm^{-1})	B_v (cm^{-1})	$ \mu_v $ (au)	Γ_v^{spont} (s^{-1})	Γ_v^{BBR} (s^{-1})
0	159.72	0.623	1.435		0.214
1	471.78	0.609	1.509	0.731	0.649
2	773.92	0.596	1.588	1.426	1.102
3	1066.1	0.582	1.671	2.078	1.571
4	1348.19	0.568	1.759	2.682	2.048
5	1620.14	0.554	1.852	3.239	2.541
6	1881.78	0.539	1.951	3.726	3.018
7	2132.99	0.524	2.057	4.168	3.504
8	2373.58	0.509	2.169	4.516	3.946
9	2603.42	0.494	2.290	4.811	4.462
10	2822.31	0.478	2.418	4.978	4.932
11	3030.08	0.462	2.556	5.105	5.253
12	3226.55	0.445	2.705	5.140	5.564
13	3411.53	0.428	2.865	5.077	5.747
14	3584.84	0.410	3.039	4.913	5.945
15	3746.34	0.391	3.227	4.705	6.021
16	3895.91	0.372	3.430	4.411	5.577
17	4033.44	0.353	3.653	4.081	3.700
18	4158.92	0.332	4.151	3.013	0.930

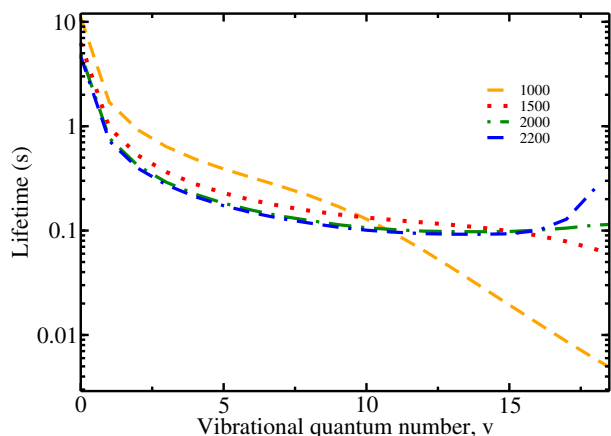


Fig. 5. Lifetimes of the vibrational states (with $J = 0$) of the electronic ground state, at $T = 300$ K, calculated with different grid size.

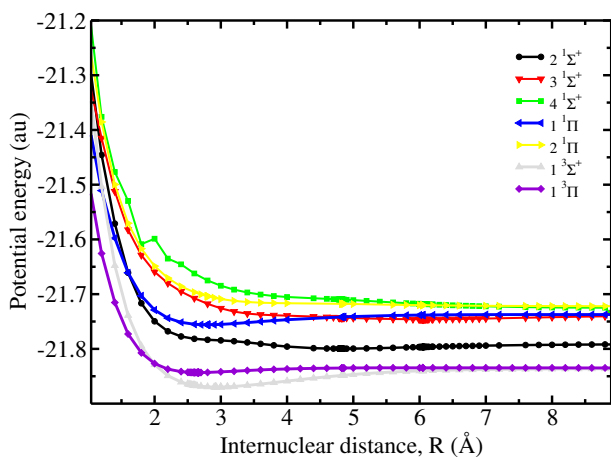


Fig. 6. Potential energy curves for the excited states of BeLi^+ using EOM-CCSD/QZ method.

all spectroscopic constants, except D_e , of $1^1\Pi$ state are in good agreement with the results available in literature [24,25,19]. On the other hand, the $2^1\Pi$ molecular state is found to be repulsive in our work and as well as in Ref. [19].

The molecular states [$2^1\Sigma^+$], [$3^1\Sigma^+$, $1^1\Pi$], and [$4^1\Sigma^+$, $2^1\Pi$] dissociate, respectively, into [$\text{Be}^+(2s) + \text{Li}(2s)$], [$\text{Be}(2s2p)^1P + \text{Li}^+$], and [$\text{Be}^+(2s) + \text{Li}(2p)$]. The nature of the asymptotic molecular states for $X^1\Sigma^+$, $2^1\Sigma^+$ and $1^3\Sigma^+$ reported in this work agree well with those reported in Ref. [19]. However, the dissociative nature of $1^3\Pi$ electronic states reported in Ref. [19] seems to be ambiguous to compare with.

The variation of PDMs against the internuclear distance, R , for the excited electronic states is shown in Fig. 7 and the corresponding data is provided in the Supplementary Table S5. As the structure of the molecule changes from BeLi^+ to Be^+Li , the polarity of the dipole moment changes from negative to positive at large distance in the present work *viz.* the following electronic states: $2^1\Sigma^+$, $4^1\Sigma^+$, and $2^1\Pi$, which dissociate into Be^+Li , as can be seen from Table 6, show a common trend together, while the remaining electronic states, shown in Table 6, which dissociate into BeLi^+ show an opposite trend at large distances in Fig. 7. However, the phase convention adopted in Ref. [19] seems to be the opposite. The electronic transition dipole moments from ground-state to singlet excited states as a function of R are shown in Fig. 8 and the corresponding TDM values are provided in the Supplementary Table S6.

The behaviour of TDM curves for $X^1\Sigma^+ - 2^1\Sigma^+$ and $X^1\Sigma^+ - 3^1\Sigma^+$ transitions compares well with those reported in Ref. [23]. The TDM value for the transitions: $X^1\Sigma^+ - 2^1\Sigma^+$, $X^1\Sigma^+ - 4^1\Sigma^+$, and $X^1\Sigma^+ - 2^1\Pi$ goes to zero at large internuclear separation. The molecular excited states involved in these transitions are dissociating into $\text{Be}^+(2s) + \text{Li}(2s \text{ or } 2p)$. On the other hand, the remaining transitions: $X^1\Sigma^+ - 3^1\Sigma^+$, and $X^1\Sigma^+ - 1^1\Pi$ whose TDM attains a constant non-zero value after 13 Å bond distance, are dissociating into $\text{Be}(2s2p) + \text{Li}^+(2s^2)$. The value of TDM (= 1.889 au) at the dissociative limit for $X^1\Sigma^+ - 3^1\Sigma^+$, and $X^1\Sigma^+ - 1^1\Pi$ molecular transitions agrees extremely well with the value of 1.887 au, reported in Ref. [23]. This is also comparable to the theoretical (= 1.801 au) [42] as well as experimental (1.645 au) [43] value of TDM available in the literature for the pure allowed atomic transition between $\text{Be}(2s^2)$ to $\text{Be}(2s2p)$. The maximum TDM value of $X^1\Sigma^+ - 2^1\Sigma^+$ transition is found to be 1.975 au at 3 Å bond distance.

The electronic excitation energies (T_e) as reported in Ref. [19] and our results shown in Table 5 are in very good agreement. The maximum difference between the two is about 2.3% for all states, except for the $3^1\Sigma^+$ state for which the difference is about 29%. On solving the Schrödinger equation using the electronic energies calculated at different bond lengths varying from 0.4 to 30 Å and taking 1000 grid points, we have obtained the maximum vibrational levels to be: 45 for $1^3\Sigma^+$, 11 for $1^3\Pi$, 31 for $2^1\Sigma^+$, 41 for $3^1\Sigma^+$, 32 for $4^1\Sigma^+$, and 25 for $1^1\Pi$. The Supplementary Table S7 provides the relative energies of vibrational states and the vibrationally coupled rotational constants for all the excited electronic states considered. We have shown variation of the energy spacing between the adjacent vibrational states, ($E_{v+1} - E_v$), for the ground- and for the low-lying excited electronic states as a function of vibrational quantum number in Fig. 9. This separation which is not a constant is a hallmark of anharmonic effects.

4. Summary

To summarize, we have carried out the *ab initio* calculations of the spectroscopic constants and the molecular properties of the ground-state ($X^1\Sigma^+$) of BeLi^+ molecular ion that dissociates into $\text{Be} + \text{Li}^+$. The saturation of the results with respect to the size of the basis sets and the higher levels of correlations up to CCSD(T) is observed for the ground electronic state. Further, we have investigated the effect of including DBOC and the contribution of non-leading order triples which were missing in CCSD(T) on the spectroscopic parameters. Although, the DBOC in itself is significant, it does not affect the spectroscopic constants that we have considered. The contributions of CCSDT-CCSD(T) are well within the error bars that we have quoted. Our findings of diatomic constants and equilibrium dipole moment are reasonably in good agreement with the available results. Moreover, the results of the dipole polarizability and the quadrupole moment for this ion are being reported here for the first time, to the best of our knowledge. On solving vibrational Schrödinger equation, we have obtained vibrational wavefunctions, spectroscopic constants for all vibrational states and vibrational TDMs. Further, we have also calculated the spontaneous and the BBR induced transition rates, and hence the lifetimes of vibrational states. The lifetime of the rovibronic ground-state ($X^1\Sigma^+$ with $v = 0$ and $J = 0$) of BeLi^+ , at room temperature, is found to be 4.67 s.

In addition, we have calculated the spectroscopic parameters and studied the PDM curves of a few low-lying electronic excited states using the EOM-CCSD method and compared them with the available results in the literature. The nature of electronic TDM curves for the transitions from the ground- to the excited singlet states is also presented and analyzed.

Table 5
The spectroscopic constants for the excited states of BeLi⁺ computed using EOM-CCSD/QZ method. Comparison with the available results in the literature.

State	R_e (au)	D_e (cm ⁻¹)	T_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)	Ref.
$2^1\Sigma^+$	9.121	1937	34656.36	126	2.15	0.185	0.0025	This work
	9.150	1976	34,729	123.15	2.04	0.1836	–	[19] [24] ^a
Repulsive								
$1^3\Sigma^+$	5.556	7603	19262.19	270	1.62	0.484	0.0042	This work
	5.530	7615	19,648	275.47	4.06	0.5016	–	[19]
	5.605	6976.85	–	271.9	2.679	0.489	0.00678	[24] ^a
	5.546	7527.0	–	274.2	2.290	0.4949	6.894×10^{-3}	[25]
$1^3\Pi$	5.040	1793	25077.82	245	6.22	0.597	0.0163	This work
	5.02	1650	25,613	244.33	7.57	0.6100	–	[19]
	5.104	1661.54	–	236.4	6.848	0.589	0.02025	[24] ^a
	5.029	1754.2	–	244.6	5.501	0.5984	1.402×10^{-2}	[25]
$3^1\Sigma^+$	11.439	1803	46457.07	83	0.81	0.111	0.0015	This work
	11.74	737	35,967	75.50	9.24	0.1111	–	[19] [24] ^a
Repulsive								
$1^1\Pi$	5.285	4027	44238.18	267	4.61	0.545	0.0115	This work
	5.320	3183	45,279	256.6	5.12	0.5428	–	[19]
	5.365	3395.67	–	256.6	4.446	0.533	0.01228	[24] ^a
	5.263	7224.7	–	281.1	1.572×101	0.5329	4.875×10^{-3}	[25]
$4^1\Sigma^+$	16.863	418	51087.32	37	1.18	0.056	0.0023	This work
	17.27	535	51,075	37.17	1.90	0.0515	–	[19]
$2^1\Pi$	Repulsive							This work
	Repulsive							[19]

^a At MRAQCC level.

Table 6
Energies of few low-lying electronic states of BeLi⁺ at the dissociative limit.

Molecular state	Asymptotic molecular state	E (cm ⁻¹)		% error
		This work	NIST [37]	
$X^1\Sigma^+$	Be (2s ²) + Li ⁺	0.0	0.0	
$2^1\Sigma^+$	Be ⁺ (2s) + Li(2s)	31,734	31,706	0.09
$1^3\Sigma^+$	Be (2s2p) ³ P + Li ⁺	22,009	21979.49	0.13
$1^3\Pi$	Be (2s2p) ³ P + Li ⁺	22,011	21979.49	0.14
$3^1\Sigma^+$	Be (2s2p) ¹ P + Li ⁺	43,403	42565.35	1.97
$1^1\Pi$	Be (2s2p) ¹ P + Li ⁺	43,405	42565.35	1.97
$4^1\Sigma^+$	Be ⁺ (2s) + Li(2p)	46,644	46609.83	0.07
$2^1\Pi$	Be ⁺ (2s) + Li(2p)	46,647	46609.83	0.08

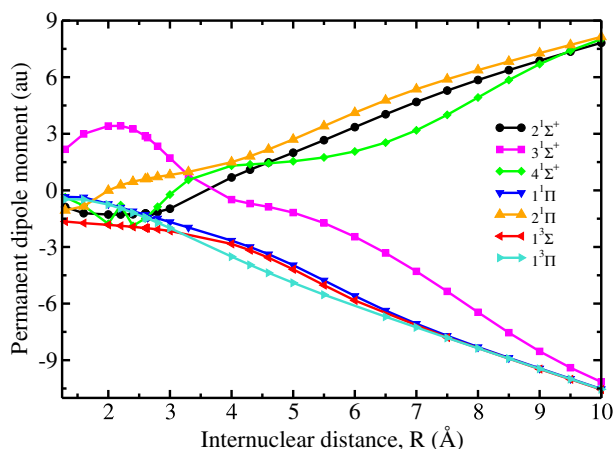


Fig. 7. Permanent dipole moment curves for the excited states of BeLi⁺ using EOM-CCSD/QZ method.

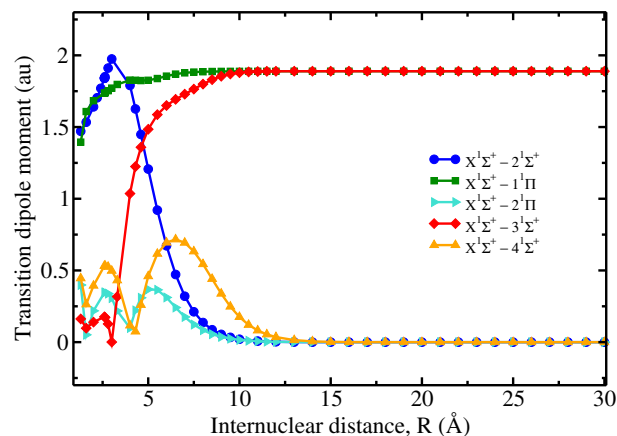


Fig. 8. Transition dipole moment from the ground-state to the excited singlet electronic states of BeLi⁺ using EOM-CCSD/QZ method.

We have considered all electrons as well as virtual orbitals active for correlation calculations even in the largest basis sets considered and also we have used accurate correlation methods available. We have taken extreme care in estimating the error bars,

limited to the theoretical approximations considered, on the ground-state spectroscopic parameters by extrapolating our results to complete basis set limit. Further, the complete convergence of the results, with respect to numerical grid size, of the

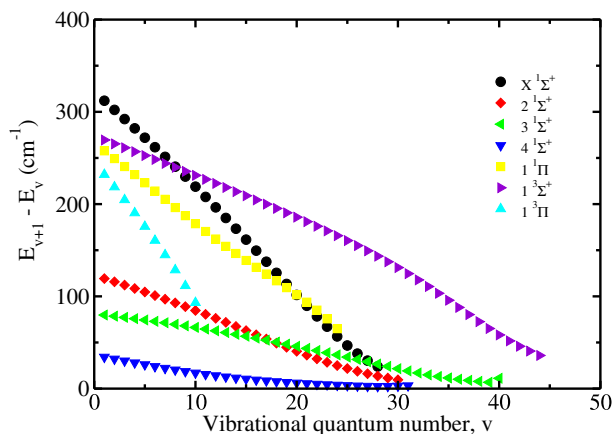


Fig. 9. Spacing between adjacent vibrational energy levels for ground- (using CCSD (T)/QZ method) and excited electronic states (using EOM-CCSD/QZ method).

vibrational lifetimes of the electronic ground-state are obtained. Thus, the results reported in this work for the ground-state should be considered more reliable than many of the existing calculations for this molecular ion. Our results on the excited state PECs and the derived spectroscopic parameters settle the discrepancies in some of the existing theoretical calculations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jms.2018.03.013>.

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