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Ab initio study of the low-lying electronic states of the C_2^- anion

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ABSTRACT

Six low-lying states ($X^2\Sigma_g^+$, $A^2\Pi_u$, $B^2\Sigma_u^+$, $^4\Sigma_g^+$, $^4\Pi_u$ and $^4\Sigma_u^+$) of C_2^- anion are studied by highly correlated *ab initio* calculations. The potential energy curves (PECs) are computed in the internuclear separation from 0.8 to 5.0 Å using the complete active space self-consistent field method, and then performing the internally contracted multireference configuration interaction with Davidson correction. Core–valence correlation and scalar relativistic effect are considered through employing the aug-cc-pcV5Z-dk basis set. The spin–orbit coupling of the $A^2\Pi_u$ state is also calculated using Breit–Pauli Hamiltonian. Based on the PECs derived from the high-level *ab initio* calculations, the spectroscopic parameters are obtained by fitting the ro-vibrational levels that are acquired by solving the ro-vibrational Schrödinger equation. These spectroscopic parameters, especially for low-lying doublet states, are in good agreement with the previously calculated and experimental results. Finally, the electronic transition dipole moment matrix elements, Franck–Condon factors, radiative lifetimes and oscillator strengths of $A^2\Pi_u$–$X^2\Sigma_g^+$ and $B^2\Sigma_u^+ - X^2\Sigma_g^+$ are calculated and discussed as well.

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1. Introduction

The negative ions play an important role in astrophysics [1], and they distribute in upper atmosphere, combustion and chemical reaction [2–9]. At present, only a few anions have been spectroscopically characterized [10–12]. C_2^- is a typical negative ion with high electron affinity and low electronic excited states [13]. In 1980, Vardya and Krishna Swamy suggested that C_2^- might be a possible component in the atmosphere of carbon stars [14], and Wallerstein also searched for the rotational lines of (0–0) vibrational band of the electronic transition in the spectrum of the hydrogen-deficient carbon star [15]. The spectra of the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system in the region 4800–6000 Å were first observed by Herzberg and Lagerqvist in 1968 [16]. In 1972, Lineberger and Patterson studied the two-photon photodetachment of C_2^-, and their results confirmed the previous identification [17]. Poul W. Thulstrup used the valence shell configuration interaction approximation to study the $^1\Sigma_g^+$ state of C_2 and the doublet and quartet states of C_2^- [18]. Due to the significant perturbation to $B^2\Sigma_u^+$ state, the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ transition with sub-Doppler resolution was first observed by Mead et al., and they obtained the corresponding molecular constants for the $A^2\Pi_u$ state [19]. The $A^2\Pi_u$–$X^2\Sigma_g^+$ transition was studied by Brent et al., and they derived the accurate molecular constants for $A^2\Pi_u$ [20]. Transition intensities, lifetimes and oscillator strengths of the $A^2\Pi_u$–$X^2\Sigma_g^+$ and $B^2\Sigma_u^+ - X^2\Sigma_g^+$ systems were also investigated by theoretical calculations and experimental measurements [21–24]. Bruna and Grein calculated the electron-spin g-factors and hyperfine coupling constants by multi reference configuration interaction (MRCI) approach and density functional theory method [25–27]. Graham et al. observed the g-shifts resulting from distortion of the $^2\Sigma_g^+$ through electron spin resonant and optical spectra [28]. Using velocity modulation spectroscopy, Royen and Zackrisson studied the (0,0) band of $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system, and they gave the spin-rotation constant for the $v' = 0$ level of $B^2\Sigma_u^+$ state [29]. Watts et al. used the coupled-cluster method with singles, doubles and noniterative triples to study the three electronic bound states of C_2^- [30]. The (3,4) band of the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ transition at Doppler-limited resolution in the visible region 16,700–17,400 cm^{-1} was first recorded by Shanshan et al. [13]. They performed a rotational analysis and renewed molecular parameters. Recently, three states ($X^2\Sigma_g^+$, $A^2\Pi_u$ and $B^2\Sigma_u^+$) of C_2^- were calculated, and the roational energies of $^{13}C^{12}C^-$ were obtained for the prediction of spectral evidence of C_2^- in laboratory and interstellar medium [11].

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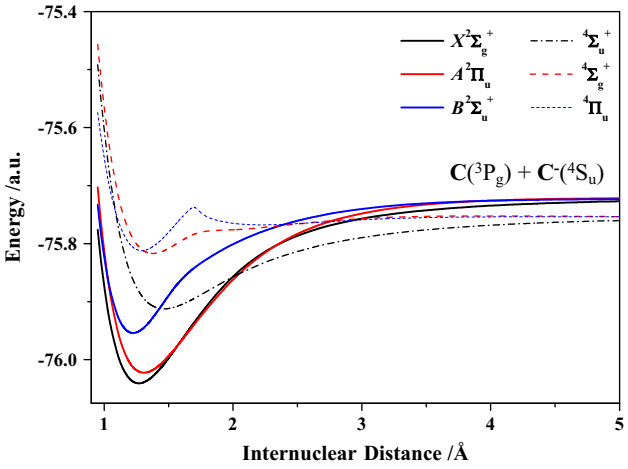

Fig. 1. Potential energy curves of $X^2\Sigma_g^+$, $A^2\Pi_u$, $B^2\Sigma_u^+$, $^4\Sigma_g^+$, $^4\Sigma_u^+$ and $^4\Pi_u$ states of C_2^-.

However, most of the previous theoretical and experimental researches focused on the spectral properties of doublet states. Though, the previous investigations of quartet states are physically correct, the data are quantitatively less accurate. Moreover, the spin–orbit coupling effect that plays an important role in the spectroscopy of diatomic molecules was not concerned in the previous theoretical study. In present article, the low-lying electronic states of C_2^- are investigated by employing the MRCI with a large correlation-consistent quintet basis set augmented with diffuse functions [31–37]. Based on the calculation of the scanning single point energy of the $X^2\Sigma_g^+$, $A^2\Pi_u$, $B^2\Sigma_u^+$, $^4\Sigma_g^+$, $^4\Pi_u$ and $^4\Sigma_u^+$ states, the corresponding vibrational and rotational constants are acquired. The Franck–Condon (F–C) factors and the *ab initio* transition dipole moments (TDMs) for the $A^2\Pi_u$–$X^2\Sigma_g^+$ and $B^2\Sigma_u^+ - X^2\Sigma_g^+$ systems are computed, of which values are used to compute the relative lifetimes of the $A^2\Pi_u$ and $B^2\Sigma_u^+$ states. Besides, we calculate the spin–orbit (SO) coupling of the $A^2\Pi_u$ state with Breit–Pauli operator [38].

2. Computational details

In the present work, the *ab initio* calculations are performed by Molpro2012 suite of quantum chemistry package [39]. C_2^- is a homonuclear diatomic anion and belongs to the $D_{\infty h}$ point group. The low-lying electronic states of C_2^- result from a combination of the ^3P_g ground state of C and the ^4S_u ground state of C^-, correlating with $^{2,4,6}\Sigma_g^+$, $^{2,4,6}\Sigma_u^+$, $^{2,4,6}\Pi_g$ and $^{2,4,6}\Pi_u$ molecular electronic states. Due to the limitation of the MOLPRO package, the calculations are performed in the D_{2h} symmetry group substituting the $D_{\infty h}$ symmetry group. There are eight irreducible representations, A_g, B_{3u}, B_{2u}, B_{1g}, B_{1u}, B_{2g}, B_{3g}, and A_u, in the D_{2h} point group. The corresponding symmetry operations for both $D_{\infty h}$ and D_{2h} are $\Sigma_g^+ \rightarrow A_g$, $\Sigma_g^- \rightarrow B_{1g}$, $\Pi_g \rightarrow B_{2g} + B_{3g}$, $\Delta_g \rightarrow A_g + B_{1g}$, $\Sigma_u^+ \rightarrow B_{1u}$, $\Sigma_u^- \rightarrow A_u$, $\Pi_u \rightarrow B_{2u} + B_{3u}$, and $\Delta_u \rightarrow A_u + B_{1u}$, respectively [40]. In the

Table 1
Computed and experimental spectroscopic parameters for the $X^2\Sigma_g^+$, $A^2\Pi_u$, $B^2\Sigma_u^+$, $^4\Sigma_g^+$, $^4\Sigma_u^+$ and $^4\Pi_u$ states of C_2^-.

	T_e (cm^{-1})	R_e (Å)	B_e (cm^{-1})	α_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	$\omega_e\gamma_e$ (cm^{-1})	Main configurations at R_e (%)
$X^2\Sigma_g^+$	0[a]	1.2689	1.7438	0.0161	1781.56748	11.5247	0.00972	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^1$(89)
Exp. [19]	0	1.2684	1.74649(16)	0.016557(76)	1781.202(20)	11.6716(48)	0.00998(28)	
Exp. [20]	0	1.26831(13)	1.74666(32)	0.01651(46)	1781.189(18)	11.6717(48)	0.009813	
Cal. [11]	0	1.2685	1.7464	0.01651	1787.4	11.56		
Cal. [47]	0	1.318			1680			
Cal. [48]	0	1.277535						
Cal. [23]	0	1.276	1.726	0.016	1780	12		
Cal. [49]		1.284306						
Cal. [18]	0	1.34			1690			
Cal. [30]	0	1.267			1799			
Cal. [51]	0	1.2704		0.0165	1776.5			
$A^2\Pi_u$	4004.91162	1.3075	1.64241	0.01573	1668.72707	10.79763	0.02015	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^3 3\sigma_g^2$(93)
Exp. [19]	4064(91)	1.313	1.630(5)	0.0152	1656(10)	10.80(26)		
Exp. [20]	3985.83(50)	1.30768(13)	1.64305(334)		1666.4(10)	10.80(26)		
Cal. [11]	4050.6	1.3066	1.6458	0.0159	1679.04	11.61		
Cal. [47]	4800	1.32			1700			
Cal. [48]	3250	1.31721						
Cal. [23]	3548.8375	1.318	1.619	0.016	1646	11		
Cal. [18]	10485.2018	1.41			1510			
Cal. [30]	4463	1.307			1676			
Exp. [50]	3928.660(17)	1.30767(20)	1.64307(51)	0.01625(72)				
Cal. [51]	3887.5902	1.309		0.0161	1664.5			
$B^2\Sigma_u^+$	18981.3074	1.2238	1.87477	0.01764	1976.17619	14.75376	0.07515	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^1 1\pi_u^4 3\sigma_g^2$(85)
Exp. [19]	18390.723(35)	1.2234	1.87718(27)	0.01887(28)	1969.542(84)	15.100(57)	0.135(16)	
Cal. [11]	18763.9	1.2234	1.8713	0.0129	1964.72	10.28		
Cal. [47]	24,630	1.265			1910			
Cal. [48]	18,830	1.22199						
Cal. [23]	18954.0186	1.231	1.855	0.017	1983	16		
Cal. [49]		1.235268						
Cal. [18]	26616.2815	1.33			1330			
Cal. [30]	19,783	1.222			2013			
Cal. [51]	18728.1836	1.2256		0.018	1963.6			
$^4\Sigma_u^+$	33226.969	1.4641	1.30975	0.01814	1128.97168	11.26472	0.04326	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^3 3\sigma_g^1 1\pi_g^1$(83)
Cal. [47]	22,900	≈1.52			900			
Cal. [48]	29,910	≈1.47062						
Cal. [18]	28229.3895	1.57			1070			
$^4\Sigma_g^+$	54173.8414	1.3768	1.40281	0.09125	1744.7585	88.32409	1.06646	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^1 1\pi_u^3 3\sigma_g^2 1\pi_g^1$(77)
Cal. [18]	54845.6711	1.82			710			
$^4\Pi_u$	55238.1851	1.4641	1.68356	0.01502	1638.8344	11.6269	0.04598	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^1 1\pi_u^4 3\sigma_g^1 1\pi_g^1$(85)

[a] The total energy calculated here for the ground state at equilibrium is −76.0407 a.u.

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