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Study on the spectroscopic parameters and transition probabilities of 25 low-lying states of the AlC$^+$ cation

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ABSTRACT

This paper investigates the spectroscopic parameters and transition probabilities of 25 low-lying states, which come from the first five dissociation channels of AlC$^+$ cation. The potential energy curves are calculated with the complete active space self-consistent field method, which is followed by the valence internally contracted multireference configuration interaction approach with Davidson correction. Of these 25 states, only the $3^5\Sigma^-$ state is repulsive; the $c^1\Sigma^+$, $f^1\Pi$, and $1^5\Pi$ states have the double well; the first well of $c^1\Sigma^+$ state and the second well of $1^5\Pi$ state are very weakly bound; the first well of $c^1\Sigma^+$ state has no vibrational levels; the $2^5\Pi$ state and the double well of $f^1\Pi$ state have only several vibrational states; the $B^3\Sigma^-$, $E^3\Sigma^+$, $D^3\Pi$, $1^5\Sigma^+$, $2^5\Sigma^-$, and $1^5\Pi$ states are inverted when the spin-orbit coupling effect is included. The avoided crossings exist between the $B^3\Sigma^-$ and $3^3\Sigma^-$ states, the $c^1\Sigma^+$ and $d^1\Sigma^+$ states, the $f^1\Pi$ and $3^1\Pi$ states, the $1^5\Pi$ and $2^5\Pi$ states, as well as the $2^5\Pi$ and $3^5\Pi$ states. Core-valence correlation and scalar relativistic corrections are considered. The extrapolation of potential energies to the complete basis set limit is done. The spectroscopic parameters and vibrational levels are determined for all the Λ–S and Ω bound states. The transition dipole moments are calculated. Franck–Condon factors of a great number of electronic transitions are evaluated. On the whole, the spin-orbit coupling effect on the spectroscopic parameters and vibrational levels is small except for very few states. The results determined in this paper could provide some powerful guidelines to observe these states in a spectroscopy experiment.

1. Introduction

It has been proved that Aluminum, fluorine, chlorine, oxygen, and carbon atoms are abundant in space. Some diatomic molecules such as AlF, AlCl, and AlO and some of their ions have been found in various circumstellar environments [1]. Consequently, it is expected that aluminum carbide (AlC) radical and cation (AlC$^+$) can be formed in stellar atmospheres or in interstellar space [2]. That is, AlC radical and AlC$^+$ cation might be of astrophysical interest, though no astronomical observations have reported them till today [1]. In the past several decades, a number of experimental and theoretical investigations have been made for the AlC radical [3]. However, very little work has been done for the AlC$^+$ cation up to date.

For the spectroscopic parameters and transition probabilities of the AlC$^+$ cation, no experimental observations have been reported to date, and only three groups of calculations [2,4,5] are available in the literature. In detail, Largo et al. [4] in 2002 made the first *ab initio* calculations about this cation using the density functional theory (DFT) method with the B3LYP functional and determined the spectroscopic parameters and dipole moments of $X^3\Sigma^-$ and $a^1\Delta$ states. Redondo et al. [2] in 2004 also performed DFT calculations with the B3LYP functional and reported the spectroscopic parameters and dipole moments of $X^3\Sigma^-$ and $a^1\Delta$ states. Feng et al. [5] in 2009 employed the DFT method with the B3LYP functional to calculate the ground-state internuclear equilibrium separation.

Now we discuss what electronic states can be yielded from the first five dissociation channels of the AlC$^+$ cation. The ionization energies of ground-state C and Al atoms are 90,820.45 and 48,278.48 cm^{-1} [6], respectively. Therefore, the first dissociation limit of AlC$^+$ cation should be $Al^+(^1S_g)+C(^3P_g)$. The ground, first and second excited states of Al$^+$ ion are the ^1S_g, ^3P_u and ^1P_u, whose energy levels are approximately 0.00, 37,474.91 ± 62.29, and 59,852.02 cm^{-1}, respectively. The ground, first, second, third and fourth excited states of C atom are the ^3P_g, ^1D_g, ^1S_g, ^5S_u and ^3P_u, whose energy levels are approximately 0.00, 10,192.63, 21,648.01, 33,735.20, and 60,359.73 ± 22.27 cm^{-1}, respectively. According to these energy levels, the first five dissociation channels of the AlC$^+$ cation should be the $Al^+(^1S_g)+C(^3P_g)$, $Al^+(^1S_g)+C(^1D_g)$, $Al^+(^1S_g)+C(^1S_g)$, $Al^+(^1S_g)+C(^5S_u)$, and $Al^+(^3P_u)+C(^3P_g)$.

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Table 1
Dissociation relationships of 25 states yielded from the first five dissociation channels of the AlC$^+$ cation.

Dissociation limit	State	Relative energy/cm^{-1}	
		This work[a]	Exp. [6]
Al$^+$(^{1}S$_g$) + C(^{3}P$_g$)	X$^3\Sigma^-$, A$^3\Pi$	0.0	0.0
Al$^+$(^{1}S$_g$) + C(^{1}D$_g$)	a$^1\Delta$, b$^1\Pi$, c$^1\Sigma^+$	10,109.22	10,192.63
Al$^+$(^{1}S$_g$) + C(^{1}S$_g$)	d$^1\Sigma^+$	21,427.80	21,648.01
Al$^+$(^{1}S$_g$) + C(^{5}S$_u$)	1$^5\Sigma^-$	33,890.03	33,735.20
Al$^+$(^{3}P$_u$) + C(^{3}P$_g$)	B$^3\Sigma^-$, C$^3\Delta$, D$^3\Pi$, E$^3\Sigma^+$, e$^1\Sigma^-$, f$^1\Pi$, g$^1\Delta$, 3$^1\Sigma^+$, 2$^5\Sigma^-$, 3$^3\Pi$, 3$^1\Pi$, 1$^5\Pi$, 2$^5\Pi$, 1$^5\Delta$, 3$^5\Sigma^-$, 1$^5\Sigma^+$, 3$^3\Sigma^-$, 2$^1\Sigma^-$	37,462.36	37,474.91 ± 62.29[b]

[a] obtained by the icMRCI + Q/Q5 + CV + DK calculations;
[b] obtained by averaging the atomic energy levels of the ^{3}P$_2$, ^{3}P$_1$ and ^{3}P$_0$ states.

Employing the molecular group theory, we affirm that the first five dissociation asymptotes can generate the 25 Λ–S states, which are the 1$^3\Sigma^-$ (X$^3\Sigma^-$), 1$^3\Pi$ (A$^3\Pi$), 1$^1\Delta$ (a$^1\Delta$), 1$^1\Pi$ (b$^1\Pi$), 1$^1\Sigma^+$ (c$^1\Sigma^+$), 2$^1\Sigma^+$ (d$^1\Sigma^+$), 1$^5\Sigma^-$, 2$^3\Sigma^-$ (B$^3\Sigma^-$), 1$^3\Delta$ (C$^3\Delta$), 2$^3\Pi$ (D$^3\Pi$), 1$^3\Sigma^+$ (E$^3\Sigma^+$), 1$^1\Sigma^-$ (e$^1\Sigma^-$), 2$^1\Pi$ (f$^1\Pi$), 2$^1\Delta$ (g$^1\Delta$), 3$^1\Sigma^+$, 2$^5\Sigma^-$, 3$^3\Pi$, 3$^1\Pi$, 1$^5\Pi$, 2$^5\Pi$, 1$^5\Delta$, 3$^5\Sigma^-$, 1$^5\Sigma^+$, 3$^3\Sigma^-$, and 2$^1\Sigma^-$, respectively. These Λ–S states together with their dissociation channels are collected in Table 1. For reasons of comparison with the present theoretical results, we also tabulate the experimental energy separations [6] between each higher dissociation asymptote and the lowest one, Al$^+$(^{1}S$_g$) + C(^{3}P$_g$), in this table.

In the next section, we will briefly introduce the methodology used. In Section 3, the potential energy curves (PECs) of 25 states are reported. The spectroscopic parameters and vibrational levels are predicted. The transition dipole moments (TDMs) are determined. Franck–Condon (FC) factors of a large number of transitions between different electronic states are calculated. The spin-orbit coupling (SOC) effect on the spectroscopic parameters and vibrational levels is evaluated. Finally in Section 4, some conclusions are drawn. The spectroscopic parameters, vibrational levels and transition probabilities obtained in this paper should be considered very reliable.

2. Theory and method

All the PECs involved in this paper are calculated with the complete active space self-consistent field (CASSCF) method, which is followed by the internally contracted multireference configuration interaction (MRCI) approach with Davidson correction (icMRCI + Q) [7,8]. Here, the CASSCF is used as the reference wavefunction for the icMRCI calculations. The calculations are carried out with the aug-cc-pVQZ (AVQZ) and aug-cc-pV5Z (AV5Z) basis sets [9–11] for internuclear separations from 1.0 to 11.0 Å All the PECs are calculated with the MOLPRO 2010.1 program package [12] in the C_{2v} point group. In this work, the point spacing interval used is 0.2 Å for each state. To accurately determine each PEC, the point spacing interval used is 0.02 Å for internuclear separations approximately 1.5–5.0 Å because the equilibrium separations are fallen into this range for all the bound states. These point spacing intervals are used for various calculations, including the SOC splitting energies, as well as core-valence correlation and scalar relativistic corrections.

The molecular orbitals (MOs) employed for the icMRCI calculations come from the CASSCF results. The state-averaged technique is used in the CASSCF calculations. To accurately determine the interaction between different PECs (such as avoided crossings), we altogether put the 37 electronic states into the calculations. Each state has the same weight factor of 0.0270270. In this paper, we only report the PECs of 25 states arising from the first five dissociation limits. In the icMRCI calculations, we put the 8 outermost MOs ($4a_1$, $2b_1$ and $2b_2$) into the active space, corresponding to the 5- 8σ, 2π and 3π MOs in the AlC$^+$ cation. No additional MOs are added to the active space. That is, the 6 valence electrons are distributed into the 8 valence MOs of AlC$^+$ cation. Consequently, this active space is referred to as CAS (6, 8). We put the rest 12 inner electrons into the 6 lowest MOs (1 - 4σ and 1π). For the AV5Z basis set, the total number of external orbitals is 244, corresponding to $86a_1$, $60b_1$, $60b_2$, and $38a_2$ MOs. In summary, we altogether use the 14 MOs ($8a_1$, $3b_1$ and $3b_2$) for the reference wavefunction.

The extrapolation of potential energies to the complete basis set (CBS) limit is made with the AVQZ and AV5Z basis sets. The energy obtained by the extrapolation is denoted as Q5 in this paper. The extrapolation scheme [13] is written as,

$$\Delta E_X^{ref} = E_\infty^{ref} + A^{ref} X^{-\alpha}, \quad (1)$$

$$\Delta E_X^{corr} = E_\infty^{corr} + A^{corr} X^{-\beta}. \quad (2)$$

where, $\Delta E_X^{ref}$and ΔE_X^{corr} are the CASSCF and correlation energies obtained by the aug-cc-pVXZ basis set, respectively. $\Delta E_\infty^{ref}$and ΔE_∞^{corr} are the CASSCF and correlation energies extrapolated to the CBS limit; and the extrapolation parameters α and β are taken as 3.4 and 2.4 for the CASSCF and correlation energies [13], respectively.

To improve the quality of the PECs, core-valence correlation and scalar relativistic corrections are accounted for. Core-valence correlation correction is included with the cc-pCVQZ basis set [14,15]. In detail, we first calculate the potential energy using the cc-pCVQZ basis set and the potential energy using the frozen-core cc-pCVQZ basis set at the same internuclear separation, and then we determine the difference between the two energies. The difference is the contribution to the total energy by core-valence correlation correction, which is denoted as CV here. Scalar relativistic correction is calculated with the cc-pVQZ-DK basis set [16]. Its contribution to the total energy is denoted as DK. The SOC effect is determined by the state interaction approach with the Breit–Pauli operator [17] at the level of icMRCI theory with the all-electron cc-pCVQZ basis set. The all- electron cc-pCVQZ basis set with and without Breit–Pauli operator is used to calculate the contribution to the potential energy by the SOC effect. The difference between the two energies is the SOC splitting energy and is denoted as SOC.

With the PECs, the spectroscopic parameters, including the excitation energy term T_e referred to the ground state, dissociation energy D_e, harmonic frequency ω_e, equilibrium separation R_e, vibration coupling constant α_e, first and second anharmonic constant $\omega_e x_e$ and $\omega_e y_e$, and rotational constant B_e, are evaluated. All the PECs are fitted to an analytical form by cubic splines. The rovibrational constants are first obtained from the analytic potential by solving the rovibrational Schrödinger equation, and then the spectroscopic parameters are evaluated by fitting the vibrational levels. For a certain state, when the number of its vibrational levels is not less than ten, we use the first ten vibrational levels to fit the spectroscopic parameters; and when the number of its vibrational levels is less than ten, we employ all the vibrational levels to evaluate the spectroscopic parameters.

When the extrapolation, core-valence correlation and scalar relativistic corrections are included into the PECs, we denote such