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Theoretical study on the electronic absorption spectra of C_3Cl and its ions

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Abstract

Optimized geometries of small carbon clusters C_3Cl and its ions in their ground and selected excited states have been obtained by CASSCF approach. The vertical excitation energies for the electronic excitations to low-lying excited states have been calculated by the CASPT2 method using cc-pVTZ basis set. The predicted vertical excitation energies are in good agreement with available experimental values. The spin–orbit effect on the spin-forbidden transitions is generally small, with oscillator strengths in the magnitude of 10^{-7}–10^{-13}. The vertical emission energies for the selected excited states were calculated at CASPT2/cc-pVTZ level of theory based on the CASSCF optimized geometries of the corresponding excited states.

Keywords: C_3Cl; Ion; Vertical excitation energy; Vertical emission energy; CASPT2

1. Introduction

There has been a growing interest in heteroatom-terminated carbon clusters [1–6], because of their important involvement in nanoscience and astrochemistry [7–9]. The chlorine-containing carbon chains, which are thought to be good candidates for astronomical detection [10], also attract extensive attention.

Many experimental and theoretical studies of the C_nCl family were reported in the past 20 years. Among the carbon–chlorine compounds, small molecules such as CCl, CCl^+ and C_2Cl were investigated extensively in the laboratory [11–19]. The electronic absorption spectra of linear C_5Cl, C_6Cl, C_5Cl^+ and C_6Cl^+ have also been observed with mass selective neon matrix isolation spectroscopy [20]. Redondo et al. performed *ab initio* calculations for C_3Cl and its cation on geometry, stability and energy. According to their report, the ground state structure for C_3Cl was a cyclic triatomic carbon ring with an exocyclic chlorine, whereas both quasilinear and cyclic structures were similar in energies [21]. For longer chlorine-doped carbon chain, DFT with the B3LYP hybrid functional has been carried out to predict the ground state electronic structures, vibrational frequencies, ionization potentials and electronic affinities [22,23].

Recently, using mass-selective deposition in neon matrices the electronic absorption spectra of C_3Cl and its ions have been observed in experiment by Maier and co-workers [24]. For bent C_3Cl, the absorption bands of $5^2A' \leftarrow X^2A'$ and $3^2A'' \leftarrow X^2A'$ transitions are observed at 336.1 nm (3.70 eV) and 428.7 nm (2.89 eV), respectively. For carbon-cyclic structure of C_3Cl, the absorption wavelength of $^2A_1 \leftarrow X^2B_2$ transition lies at 1047 nm (1.18 eV). The band systems for bent C_3Cl^- and linear C_3Cl^+ are 435.2 nm (2.85 eV) and 413.2 nm (3.00 eV), which correspond to $2^1A'' \leftarrow X^1A'$ and $^1\Pi \leftarrow X^1\Sigma^+$ transitions.

In our previous work [25], we have carried out theoretical studies on the carbon cluster $C_{2n}Cl^+$ ($n = 1$–5). Although the electronic absorption spectra of C_3Cl and

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its ions have been observed and assigned, the calculated value 4.55 eV for the absorption band $5^2A' \leftarrow X^2A'$ of bent C_3Cl is 0.85 eV higher than the observed 3.70 eV [24]. Moreover, few high level theoretical studies about excited states of C_3Cl and its ions have been reported by former literatures. In order to obtain more precise vertical excitation energies and more information about excited states for C_3Cl and its ions, in the present work, a theoretical study on the low-lying excited states of these species has been performed, and the results show good agreement with the available observed values.

2. Computational method

The equilibrium geometries for bent C_3Cl and C_3Cl^-, cyclic C_3Cl and linear C_3Cl^+ (abbreviated as *b*-C_3Cl, *b*-C_3Cl^-, *c*-C_3Cl and *l*-C_3Cl^+, respectively) in their ground states were determined at CCSD(T)/cc-pVTZ level from Ref. [24]. The vertical excitation energies of the selected excited states have been calculated by CASPT2 [26] method with cc-pVTZ basis set. The transition moments were computed simultaneously using CASSCF [27,28] with state-averaged orbitals. In the CASPT2 calculation, the CASSCF active spaces are as follows:

b-C_3Cl: $12a'$–$17a'$, $2a''$–$5a''$, with 11 active electrons;

b-C_3Cl^-: $12a'$–$17a'$, $2a''$–$5a''$, with 12 active electrons;

c-C_3Cl: $8a_1$–$12a_1$, $2b_1$-$4b_1$, $7b_2$–$12b_2$, $1a_2$, with 15 active electrons;

l-C_3Cl^+: 9σ–12σ, 2π–4π, with 14 active electrons.

The spin–orbit coupling in these species has been estimated by the spin–orbit coupling configuration interaction (SOC-CI) calculation [29]. The oscillator strengths (*f*) are calculated with the following formula:

$$f = \frac{2}{3}\Delta E|TM|^2,$$

where ΔE denotes the transition energy in atomic unit, and TM refers to the transition dipole moment in atomic unit.

The geometries of the selected excited states were optimized using the CASSCF method with 6-31G* basis set. For comparison the geometries of ground states have also been optimized at the same level. After the excited states were located, vertical emission energies of selected emission band systems have been estimated by CASPT2 calculations with the cc-pVTZ basis set. The active space here is the same as that in calculation of vertical excitation energy. All calculations were performed using the MOLPRO2002 software package [30].

3. Results and discussion

3.1. Electronic structures in ground states

The electronic configurations and their coefficients in CASSCF wavefunction in the ground states of *b*-C_3Cl, *b*-C_3Cl^-, *c*-C_3Cl and *l*-C_3Cl^+ are listed in Table 1. Table 1 shows that the neutral *b*-C_3Cl and *c*-C_3Cl with open-shell electronic configurations have the ground states of doublet $^2A'$ and $^2B_2$, and *b*-C_3Cl^- and *l*-C_3Cl^+ with closed-shell electronic configurations have singlet ground states $^1A'$ and $^1\Sigma^+$, respectively. CASSCF wavefunction analysis shows that these configurational coefficients are 0.8541, 0.9188, 0.8809 and 0.9000, respectively. Such large coefficients indicate that the contributions of these configurations are dominant in their ground states.

3.2. Vertical excitation energies

3.2.1. Bent C_3Cl

Table 2 presents CASPT2/cc-pVTZ calculated vertical transition energies and calculated oscillator strengths of selected seventeen low-lying excited states (A′, A″) for bent C_3Cl, including 11 spin-allowed doublet states and six spin-forbidden quartet states.

For doublet states, the lowest excited state in energy is found to be $1^2A''$, only 0.73 eV ($f = 2.20 \times 10^{-4}$) higher than the ground state, while the highest is 6 $^2A'$, 5.33 eV ($f = 2.82 \times 10^{-2}$) above the ground state. Compared these excited states, only 4 $^2A'$ and $6^2A'$ states are due to double electronic excitations, and the other states are derived from single electronic excitations. All the oscillator strengths for spin-allowed $^2A' \leftarrow X^2A'$ and $^2A'' \leftarrow X^2A'$ transitions are in the magnitude of 10^{-2}–10^{-4}. It is noticeable that the vertical excitation energies predicted for the $5^2A' \leftarrow X^2A'$ and $3^2A'' \leftarrow X^2A'$ transition are 3.70 and 2.89 eV, with larger oscillator strengths 3.68×10^{-2} and 9.19×10^{-3}, respectively. The theoretical values are quite close to the observed values 3.59 and 2.90 eV [24]. Compared with the results predicted by CASSCF/cc-pVTZ method, the vertical excitation energies predicted by CASPT2/cc-pVTZ method are more precise.

For quartet systems, all the excited states considered here are caused by single excitations, except $2^4A'$, due to $3a''14a' \rightarrow 15a'4a''$ double electronic excitation. The lowest quartet state is $1^4A''$, 1.30 eV above the ground state. To examine accessibility of the spin-forbidden quartet excited states, SOC-CI calculations have been carried out for the low-lying quartet excited states. As shown in Table 2, the oscillator strengths for spin-forbidden $^4A' \leftarrow X^2A'$ and $^4A'' \leftarrow X^2A'$ transitions are in the magnitude of 10^{-9}–10^{-11}. The oscillator strengths are so little that such quartet states are less accessible by direct doublet–quartet transition.

3.2.2. Cyclic C_3Cl

For cyclic C_3Cl, fifteen low-lying excited states (A_1, A_2, B_1, B_2) have been calculated using the CASPT2 method with the cc-pVTZ basis set. Table 3 displays the predicted vertical transition energies and calculated oscillator strengths for these selected electronic excited states.

For doublet states, the lowest excited state is 1^2A_1, and $1^2A_1 \leftarrow X^2B_2$ transition is predicted at 1.24 eV ($f = 1.47 \times 10^{-2}$), very close to the observed value 1.18 eV [24]. The highest excited state 1^2B_2 is 5.17 eV higher than