Electronic structure of the ZnCl molecule with rovibrational and ionicity studies of the ZnX (X = F, Cl, Br, I) compounds

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ABSTRACT

Based on the complete active space self consistent field (CASSCF) method with multi-reference configuration interaction MRCI calculations including single and double excitations with Davidson correction (+Q), twenty three low lying electronic states in the $^{2s+1}\Lambda^{(\pm)}$ representation of the zinc monochloride ZnCl molecule are investigated considering 7 and 9 valence electrons. The internuclear distance R_e, the harmonic frequency ω_e, the permanent dipole moment μ, the rotational constant B_e and the electronic transition energy with respect to the ground state T_e are calculated for the bound states. The transition dipole moment between some doublet states is used to determine the Einstein spontaneous A_{21} and induced emission B_{21}^ω coefficients, the spontaneous radiative lifetime τ_{spon}, the emission wavelength λ_{21}, the oscillator strength f_{21} and the line strength S_{21}. The fraction of the ground state ionic character f and equilibrium dissociation energy $D_{E,e}$ are also computed. Using the canonical function approach, the eigenvalues E_v, the rotational constants B_v, the centrifugal distortion constants D_v and the abscissas of the turning points R_{min} and R_{max} of the zinc monohalide molecules ZnX (X: F, Cl, Br, I) are calculated. The comparison between the values of the present work and those available in the literature for several electronic states shows good accordance.

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1. Introduction

In view of the increasing interest in spectroscopic information of diatomic molecules in different fields of physics, chemistry and astrophysics, it appears desirable and important to study the compounds of transition-metals. By exothermic reactions of zinc vapor with Cl_2 gas, the ionic ZnCl molecule of the *3d* transition-metal monohalide species is easily produced [1,2]. In order to understand the electronic structure of its low lying states and to learn the characteristic behavior of their chemical bonding, this molecule has been focused on and investigated by many spectroscopic studies, both theoretical and experimental. The previous studies concerning ZnCl are being reviewed and they will be briefly pointed out hereafter. Early experimental studies prior to 1975 were summarized by Huber and Herzberg [3] where the spectroscopic constants as T_e and ω_e are shown for the four lowest lying doublet electronic states. The absorption spectra of ZnCl with 10 heads between 290 and 300 nm was initially reported by Walter and Barratt [4] and the vibrationally resolved emission spectra of the gaseous ZnCl molecule, assigned for the $C^2\Pi - X^2\Sigma^+$ and $E^2\Sigma^+$ -

– $X^2\Sigma^+$ transitions, was recorded by Cornell [5]. From matrix isolation Raman spectroscopy, Givan and Lowenschuss [6] recorded 385 cm^{-1} as the ground state vibrational frequency. Sureshkumar et al. [7] reported that the $A^2\Pi$ state lies at 17987 cm^{-1} above the ground state. From mass spectrometric measurements of gaseous equilibrium, Hildenbrand et al. [8] calculated the ground state dissociation energy to be 54.7 ± 2 kcal/mol and compared this value to that obtained by Corbett and Lynde [9]. Tenenbaum et al. [10] studied the pure rotational spectra of the vibrational ground state of ZnCl molecule using the millimeter-wave direct-absorption techniques to determine the spectroscopic constants for several ZnCl isotopologue. On the other hand, theoretical predictions of the equilibrium bond length, dissociation energy and force constants are calculated from *ab-initio* calculations carried by Bowmaker and Schwerdtfeger [11]. Using the relativistically corrected local density functional method, Liao et al. [12] also studied the ground state of the ZnCl radical and other free molecules. Another theoretical work was performed by Boldyrev and Simons [13] at the QCISD level to determine the spectroscopic constants at the equilibrium geometry of the two lowest electronic states $^2\Sigma^+$ and $^2\Pi$. They concluded that the lowest $^2\Pi$ state is a van der Waals state correlated with the first dissociation asymptote. Kerkines et al. [14] found that the bond length of the ground-state of

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ZnCl molecule is 2.148 Å with a dissociation energy of 52.7 kcal/mol as they studied the HZnCl molecule by the spin-restricted coupled cluster method with single, double, and a non-iterative estimate of triple excitations RCCSD(T). Sefyani and Schamps [15] investigated the spectroscopic constants of five low lying states of the ZnCl molecule in the gaseous phase using the MCSCF-MRCI method. Hayashi [16] also investigated the electronic structure and spectroscopic properties of the ground and some excited doublet electronic states of this molecule based on its potential energy surface obtained at the MRCI+Q levels. More recently, the state-averaged complete active space SCF (CASSCF) calculations of the doubly-charged molecular ion species $ZnCl^{2+}$ were carried out by Fišer [17] and spectroscopic constants were determined from the ground state calculations for the neutral ZnCl and the $ZnCl^+$ monocation. In this work, we investigated the electronic structure of the low lying doublet and quartet states of the ZnCl molecule through the potential energy curves (PECs) and the static dipole moment curves (DMCs) as obtained considering 7 and 9 valence electrons consecutively. The spectroscopic constants as the equilibrium internuclear distance R_e, the harmonic frequency ω_e, the rotational constant B_e, the transition energy with respect to the minimum of the ground state T_e and the permanent dipole moment μ are calculated for the bound states. The ground state dissociation energy D_E and its fraction of ionic character f (also known as the ionicity $q_{ionicity}$) are also estimated using the obtained constants. The transition dipole moment between some doublet low lying states is calculated and employed to determine some emission coefficients, e.g., the Einstein spontaneous coefficient A_{21}, the spontaneous radiative lifetime τ_{spon} and the oscillator strength f_{21}. Based on our calculations [18–20], the vibrational levels with $J = 0$ of the three lowest bound states of the four zinc monohalide molecules (ZnX; X: F, Cl, Br, I) are studied using the canonical function approach such that the eigenvalues E_v, the rotational constants B_v, the centrifugal distortion constants D_v and the abscissas of the turning points R_{min} and R_{max} are determined.

2. Computational approach of the *ab-initio* calculations

The theoretical calculations of ZnCl are carried out using the complete active space self consistent field (CASSCF) method with multi-reference configuration interaction MRCI calculations including single and double excitations with Davidson correction (+Q) by means of the computational chemistry program MOLPRO [21] and taking the advantage of the graphical user interface GABEDIT [22]. The employed method is known to allow correlation effects to be taken into consideration. The zinc atom in the [Ar] $3d^{10}4s^2$ electronic configuration is treated via the effective core potential ECP10MDF [23] as a system of 10 core electrons where the remaining 20 electrons are described by the energy optimized $(12s12p9d3f2g)/[6s6p4d3f2g]$ valence basis sets whereas the chlorine atom Cl [Ne]$3s^23p^5$ is described by the ECP10MWB [24] basis set as a core system of 10 electrons as well. Both ECPs consider relativistic effects where the theoretical level of reference is either relativistic (DF) or quasi-relativistic (WB). Among the 47 electrons explicitly considered for the zinc monohalide molecule (30 electrons for Zn and 17 for Cl), the wavefunctions of 27 electrons are to be determined. Subsequent calculations are done such that the $3s$, $3p$ and $3d$ orbitals of Zn are kept doubly occupied and frozen and the two electrons in $4s$ are valence. Meanwhile two sets of valence electrons of Cl are selected. In the first set, the two electrons occupying the $3s$ orbital of Cl are treated entirely within the core leaving 5 valence chlorine electrons to be described by the $(4s5p)/[2s3p]$ basis sets associated with the ECP. This set yields a total of 7 valence electrons to be treated explicitly for the ZnCl molecule. The second set allows the two chlorine electrons in the

$3s$ orbital to interact with the valence shell giving rise to 7 valence electrons of Cl to be described by the augmented correlation-consistent polarized valence quadruple zeta basis set with diffuse functions over the s, p, d, f and g primitives as provided by the basis set library of the program [21]. Therefore, the second set is used to investigate the low lying electronic states of ZnCl with 9 valence electrons. The quality of the different selected basis sets for the considered molecules is checked by comparing our CI calculations for the ground and several excited electronic states of isolated zinc and chlorine atoms to the experimental data in NIST Atomic Spectra database [25] from literature where the relative difference for the two atoms ranges between $(0.91\% \leqslant \Delta E_e/E_e \leqslant 3.90\%)$. The active space contains at least 6σ (Zn: $4s$, $4p_0$, $5s$; Cl: $3p_0$, $4s$, $4p_0$) and 3Π (Zn: $4p_{\pm1}$; Cl: $3p_{\pm1}$, $4p_{\pm1}$) orbitals in the C_{2v} symmetry distributed into irreducible representations a_1, b_1, b_2, and a_2 in the following way $6a_1$, $3b_1$, $3b_2$, $0a_2$ noted by [6,3,3,0]. In the range of the internuclear distance R around the equilibrium position of its ground state, the ZnCl molecule is assumed to be mainly ionic. The calculation of the potential energy curves of the doublet and quartet electronic states was performed within the range between $1.8 \text{ Å} \leqslant R \leqslant 4.3 \text{ Å}$.

3. Results and discussion

The calculations with the first set, of basis sets and valence electrons described above, enabled the investigation of 13 doublet and 6 quartet low lying electronic states (five $^2\Sigma^+$, four $^2\Pi$, two $^2\Delta$, two $^2\Sigma^-$, two $^4\Sigma^+$, two $^4\Pi$, one $^4\Delta$ and one $^4\Sigma^-$). The second set enabled the study of these states as well as 5 additional quartet states which are $(3)^4\Sigma^+$, $(4)^4\Sigma^+$, $(3)^4\Pi$, $(4)^4\Pi$, $(2)^4\Delta$ and $(2)^4\Sigma^-$. Their PECs and DMCs are plotted as function of the internuclear distance R and given in Figs. 1 and 2 and Figs. (SM.1–SM.7). The energy data around the equilibrium position corresponding to the minimum energy is fitted into a polynomial in terms of the internuclear distance R in order to calculate the spectroscopic constants R_e, T_e, ω_e and B_e. The calculated constants together with the experimental and theoretical values available in literature are given in Table 1. The comparison of our calculated constants corresponding to the ground state $X^2\Sigma^+$ with respect to those found in literature shows very good agreements with relative differences $(0.23\%$ [11] $\leqslant \Delta R_e/R_e \leqslant 4.27\%$ [10]$)$, $(0.22\%$ [15] $\leqslant \Delta \omega_e/\omega_e \leqslant 9.47\%$ [17]$)$ and $(2.18\%$ [15] $\leqslant \Delta B_e/B_e \leqslant 8.55\%$ [10]$)$ respectively. The calculated values of the anharmonicity correction $\omega_e \chi_e = 1.73 \text{ cm}^{-1}$ and 1.78 cm^{-1}, obtained with the two calculation sets respectively, also show good accordance with respect to the experimental value of 1.7 cm^{-1} [10]. Though theoretical calculations of reliable dissociation energies D_E are known to be relatively difficult because of the limited basis sets and the selected active space, our value of $D_{E,e} = 53.61 \text{ kcal/mol}$ which is calculated as an approximation [26] using our determined spectroscopic constants has yielded $D_{E,v=0} = 53.09 \text{ kcal/mol}$ which is in excellent agreement with the 54.7 kcal/mol [8] and 53.06 kcal/mol [9] obtained experimentally. Table 2 shows the values of D_E as calculated in this work together with those available in literature and the corresponding relative differences. Our first excited $(1)^2\Pi$ electronic state is determined to be unbound and correlating with the first dissociation asymptote. In literature, the QCISD calculations had considered this electronic state to be a Van der Waals complex with $R_e = 4.685 \text{ Å}$ and $T_e = 15881 \text{ cm}^{-1}$ [13]. While the experimental work of Sureshkumar et al. [7] had reported that this state lies at about 17987 cm^{-1} above the ground state. However, this value has not been confirmed by any other experimental work, but rather a higher energy is recorded for the lowest $^2\Pi - ^2\Sigma^+$ transition from the analysis of the emission and absorption band spectra [3]. In this work, the avoided crossing region between the two lowest $^2\Pi$ states at 2.19 Å has yielded a ver-