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Ab initio study of the molecular vibrations and electronic structure of the X, B, D and $F^2\Sigma^+$ states of AlO

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ABSTRACT

Molecular vibrations and electronic structure of the $X^2\Sigma^+$, $B^2\Sigma^+$, $D^2\Sigma^+$, and $F^2\Sigma^+$ states of AlO are studied by carrying out *ab initio* configuration interaction calculations and molecular vibration calculations using accurate potential energy functions. An avoided crossing between the $D^2\Sigma^+$ and $F^2\Sigma^+$ potential energy curves occurs in the neighborhood of 4.0 a_0 and results in irregular vibrational levels of the D and $F^2\Sigma^+$ states. The vibrational constants for the $F^2\Sigma^+$ state are predicted from the vibrational levels not involved in the irregularity. Configuration mixing is important in describing the B, D, and $F^2\Sigma^+$ states. The $F^2\Sigma^+$ state at and around its well minimum and the D and $F^2\Sigma^+$ states in the avoided crossing region are characterized in terms of their main configurations and dipole moment functions.

1. Introduction

The electronic states of the aluminum monoxide (AlO) molecule have been examined in a number of experimental [1–11] and theoretical [12–19] studies. Seven electronic states of $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, $C^2\Pi$, $D^2\Sigma^+$, $E^2\Delta$, and $F^2\Sigma^+$ have been identified experimentally [2,3]. Extensive studies have provided accurate molecular constants of the $X^2\Sigma^+$ and $B^2\Sigma^+$ states [9–11]. Of higher excited $^2\Sigma^+$ states, $D^2\Sigma^+$ was observed in the emission bands $D^2\Sigma^+$–$X^2\Sigma^+$ [4] and $D^2\Sigma^+$–$A^2\Pi$ [5,8], and $F^2\Sigma^+$ in an emission band $F^2\Sigma^+$–$A^2\Pi$ [6]. Theoretical studies have derived the potential energy curves (PECs) [18,19] and electric dipole moments [18] for the D and F states, and transition moments for the D–X, D–A, and F–A bands [18].

Information on the $D^2\Sigma^+$ and $F^2\Sigma^+$ states nevertheless remains limited. For example, no vibrational constants of the $F^2\Sigma^+$ state are known experimentally. A theoretical study [18] has indicated that the $D^2\Sigma^+$ state forms an avoided crossing with the $F^2\Sigma^+$ state for internuclear distance close to 3.5 a_0, near to the $F^2\Sigma^+$ potential well minimum at 3.4325 a_0 [2], but no studies have been reported on the effects of the avoided crossing on the vibrational levels of the $D^2\Sigma^+$ and $F^2\Sigma^+$ states. The electronic structure for the F state at and around its well minimum has not been published in detail, nor the D and F states in the avoided crossing region.

The present work studies the molecular vibrations and electronic structure of the X, B, D, and $F^2\Sigma^+$ states of AlO. *Ab initio* state-averaged complete-active-space self-consistent-field (SA-CASSCF)/multi-reference configuration interaction (MRCI) calculations and molecular vibration calculations were performed for the 1–$4^2\Sigma^+$ states, adopting the CASSCF procedure used by Lengsfield and Liu [15] for the calculations of the $X^2\Sigma^+$ and $B^2\Sigma^+$ states. The X, B, D, and $F^2\Sigma^+$ states were characterized according to the calculated PECs, vibrational energies, spectroscopic constants, dipole moments, and MRCI wavefunctions.

Irregularities were found in both vibrational levels of the $D^2\Sigma^+$ and $F^2\Sigma^+$ states due to the avoided crossing. Vibrational constants of the F state were determined from the vibrational levels not involved in the irregularity. The $F^2\Sigma^+$ state in the neighborhood of its well minimum keeps nearly constant dipole moment, implying a transfer of negative charge from O to Al. The D and F states in the avoided crossing region are described by the change in the mixing among ion-pair and neutral configurations in their MRCI wavefunctions, with internuclear distance.

2. Theoretical approach

2.1. Configuration interaction calculations

We used Slater-type functions (STFs) centered on each nucleus as basis functions. The basis set consists of an (8*s*6*p*) set augmented with (1*s*1*p*4*d*1*f*) for aluminum atom and a (6*s*4*p*) set augmented with (1*s*1*p*2*d*1*f*) for oxygen atom. The types and exponents (ζ) for the aluminum (8*s*6*p*) set were taken from the work of McLean et al. [20], and those for the oxygen (6*s*4*p*) set were from the work of Clementi and Roetti [21]. For aluminum atom, four 3*d*-type STFs (ζ = 1.840,1.062,0.613,0.354) were added to describe both the occupied orbitals for excited states and polarization. The

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$\zeta = 1.840$ was taken from Ref. [20] and the remaining three were obtained through dividing 1.840 by 1.732, 3.000, and 5.196 (i.e. an even-tempered set of the ratio $\sqrt{3}$). One 4*f*-type STF ($\zeta = 1.17$) was added to describe the polarization, whose ζ value was determined by taking geometric means between the ζ values of 1.44 and 0.95 given in Ref. [15]. For oxygen atom, two 3*d*-type STFs ($\zeta = 2.0$, 1.0) which were taken from Ref. [22] and one 4*f*-type STF ($\zeta = 2.5$) which were from Ref. [15] were added as polarization functions. The (1*s*1*p*) sets used to describe diffuse orbitals were the 3*s*-type ($\zeta = 0.5$) and 3*p*-type (0.4) STFs for aluminum atom, and the 2*s*-type (0.8) and 2*p*-type (0.6) STFs for oxygen atom. Their values were obtained by dividing the smallest ζ value of the 3*s*- (or 3*p*-) type STFs of the (8*s*6*p*) set by 2 for aluminum atom and that of the 2*s*- (or 2*p*-) type STFs of the (6*s*4*p*) set by 2 for oxygen atom.

Orbital sets to be used for configuration interaction (CI) calculations (CI orbitals) were obtained by means of state-averaged complete-active-space self-consistent-field (SA-CASSCF) calculations [23–28] and natural orbital transformations. The core orbitals for both the CASSCF and CI calculations consist of the innermost five σ and one π orbitals. All the configuration state functions (CSFs) with the $^2\Sigma^+$ symmetry that were generated by distributing seven electrons among the 6–9σ and 2–4π active orbitals were taken into account in the SA-CASSCF calculations. The active space includes all orbitals correlating with Al 3*s*, 3*p* and O 2*p*, 3*p* orbitals, which Lengsfield and Liu [15] used in their CASSCF calculations on the $X^2\Sigma^+$ and $B^2\Sigma^+$ states to take into account both the O^- 2*p* in–out correlation and the Al 3*s*-3*p* near degeneracy effect. The total numbers of CSFs for the SA-CASSCF calculation (CAS CSF) are 1556 for the $^2\Sigma^+$ symmetry. The external orbital space is made up of the 10–36σ and 5–20π orbitals. The value of the SA-CASSCF weight vector (1/4) was chosen so that it specifies equal contribution of each of the lowest four states to the averaged energy functional.

For correlation energy correction, we carried out multi-reference configuration interaction (MRCI) calculations to obtain accurate total energies for the 1–4$^2\Sigma^+$ states. Reference configurations include all the configurations of the CAS space. The CSFs include the CSFs for the SA-CASSCF calculations (CAS CSFs) and the CSFs of both single and double excitations from the CAS CSFs into the external orbital space of 10–30σ, 5–18π, 1–8δ, and 1–2ϕ, where the 31–36σ and 19–20π orbitals were treated as the core complements.

The SA-CASSCF and MRCI calculations were repeated to obtain potential energy curves at 23 internuclear distance (R) points in the range 2.2–4.4 a_0 at intervals of 0.1 a_0 and 8 R points in the range 4.6–6.0 a_0 at intervals of 0.2 a_0. The ALCHEMY II computer program package [29] was used for the CASSCF and CI calculations [30].

2.2. Molecular vibration calculations

Vibrational term values $G(v)$ and wavefunctions were computed for AlO 1–4$^2\Sigma^+$ (vibrational quantum number $v = 0$–18) in the same way as our previous study on the F_2 [31] and CS^+ [32]. The one-dimensional Schrödinger equation for the vibration of a diatomic molecule with no rotational energy was solved numerically using potential energy functions (PEFs) for AlO 1–4$^2\Sigma^+$ which were fed to the equation as the cubic natural spline curves fitted to the MRCI energies for 2.2–6.0 a_0. A computer program constructed by the author [31–33] was used for the computations of the $G(v)$ values and vibrational wavefunctions.

3. Results and discussion

3.1. Potential energy curves and spectroscopic constants

Fig. 1 shows the MRCI potential energy curves (PECs) for the 1–4$^2\Sigma^+$ states of AlO. The 3$^2\Sigma^+$ state is found to have a double potential well. The electronic term values T_e and the equilibrium internuclear distances R_e of the 1–4$^2\Sigma^+$ were determined by cubic natural spline (CNS) fitting to the MRCI energies. The vibrational constant ω_e and the anharmonicity constant $\omega_e x_e$ were obtained from a Dunham series expansion of vibrational term value $G(v)$ for the vibrational quantum number v [34] as in our previous work [32], except for the outer-well of the 3$^2\Sigma^+$ state, for which ω_e value was determined by the CNS fitting to the MRCI energies. The results are listed in Table 1, together with the experimental values [2,6].

Experimental values are available for T_e, ω_e, $\omega_e x_e$, and R_e of the $X^2\Sigma^+$, $B^2\Sigma^+$, and $D^2\Sigma^+$ states, and T_e [2] (T_{00} [6]) and R_e [2] of the $F^2\Sigma^+$ state. The theoretical ω_e and $\omega_e x_e$ values for the 1$^2\Sigma^+$, 2$^2\Sigma^+$, and 3$^2\Sigma^+$ states were determined from the calculated $G(v)$ values for the observed vibrational states ($X^2\Sigma^+$ $v = 0$–6 [9], $B^2\Sigma^+$ $v = 0$–9 [9], and $D^2\Sigma^+$ $v = 0$–5 [5]) using the Dunham series expansion of $G(v)$ up to the fourth-order term of $(v + 1/2)$. The MRCI values of the 1$^2\Sigma^+$, 2$^2\Sigma^+$ and 3$^2\Sigma^+$ (inner-well) states agree excellently with the experimental values of the X, B, and D states, respectively, to within 185 cm^{-1} for T_e, 25 cm^{-1} for ω_e, 0.7 cm^{-1} for $\omega_e x_e$, and 0.011 Å for R_e. The values of T_e, ω_e, and R_e for the D 3$^2\Sigma^+$ outer-well are predicted in Table 1. Vibrational levels of the $D^2\Sigma^+$ double potential well will be considered in Section 3.2.

The MRCI T_e (T_{00}) and R_e values of the 4$^2\Sigma^+$ state agree well with the experimental values of the F state [2], to within 160 cm^{-1} (72 cm^{-1}) and 0.015 Å, indicating that the 4$^2\Sigma^+$ PEC at and around its R_e is accurate. The present calculations found an irregularity in the separation values of successive vibrational levels of the F 4$^2\Sigma^+$ state. The vibrational constants for the 4$^2\Sigma^+$ state of values 451 cm^{-1} for ω_e and 8.7 cm^{-1} for $\omega_e x_e$ were determined from the calculated $G(v)$ values for $v = 0$–2 using the Dunham series expansion of $G(v)$ up to the second-order term of $(v + 1/2)$. Our ω_e value is smaller by 399 cm^{-1} than the theoretical value reported previously [18]. More detail about the determination of the 4$^2\Sigma^+$ vibrational constants, taking into account the irregularity, is given in Section 3.2.

The $D^2\Sigma^+$ and $F^2\Sigma^+$ PECs are close in value to a separation 0.19 eV at internuclear distance $R = 4.0$ a_0; the $D^2\Sigma^+$ PEC has a barrier top at 4.229 a_0; the $F^2\Sigma^+$ PEC bends upward around 4.1 a_0. These result from an avoided crossing between the D and F states

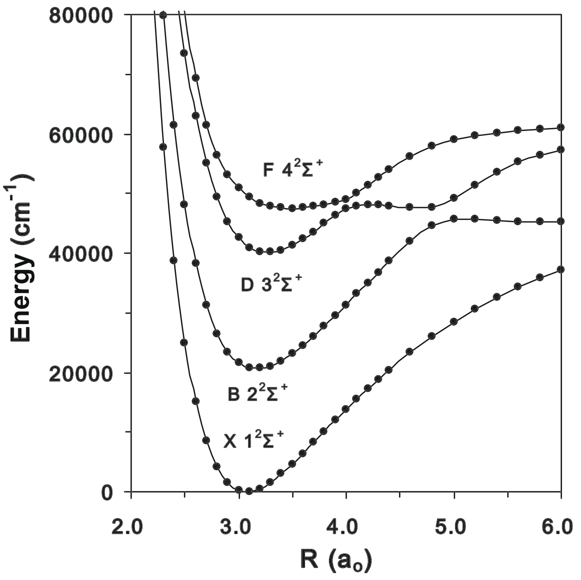

Fig. 1. Potential energy curves for the X 1$^2\Sigma^+$, B 2$^2\Sigma^+$, D 3$^2\Sigma^+$, and F 4$^2\Sigma^+$ states which were drawn by using the MRCI energies. The MRCI total energy value for the 1$^2\Sigma^+$ state at internuclear distance $R = 3.1$ a_0 is −316.998378 hartree.