



# *Ab initio* study of band strengths for the $F^2\Sigma^+ - A^2\Pi$ electronic transition of AlO

Nobumitsu Honjou

Oita University, 700 Dannoharu, Oita 870-1192, Japan

## ARTICLE INFO

### Article history:

Received 13 August 2011

Received in revised form 30 September 2011

Accepted 3 October 2011

Available online 17 October 2011

### Keywords:

AlO

Electronic transition

Emission

*Ab initio*

Band strength

Einstein A coefficient

## ABSTRACT

*Ab initio* calculations of band strengths have been carried out for the  $F^2\Sigma^+ - A^2\Pi$  electronic transition of the AlO molecule. The band strength for the 0-0 band, the only band observed, is the largest of the 56 calculated bands. The band strengths for unobserved 19 bands are of the same order of magnitude as the 0-0 band, including the 1-0 and 2-1 bands whose observations are expected to lead to experimental determination of the vibrational constants for the  $F^2\Sigma^+$  state. The Einstein coefficients for spontaneous emission of the F–A bands have been evaluated from the present band strengths and transition energies, and are used to estimate the ratios of the populations in those initial vibrational states, which produce 1-0 and 2-1 bands not weaker in intensity than the detectable 0-0 band, to the population that produces the detectable band.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

A number of experimental and theoretical studies have been made of the electronic states of the aluminum monoxide (AlO) molecule [1–19]. The  $X^2\Sigma^+$ ,  $A^2\Pi$ ,  $B^2\Sigma^+$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$ ,  $E^2\Delta$  and  $F^2\Sigma^+$  states have been identified experimentally [2,3]. The  $F^2\Sigma^+ - A^2\Pi$  electronic transition of the AlO has been observed in the emission spectrum excited in a low pressure arc, where only the ground vibrational level of the  $F^2\Sigma^+$  state was observed and only the 0-0 band was reported [6]. Although molecular constants and intensities are needed for a proper interpretation of emission spectra, no experimental data on the vibrational constants for the  $F^2\Sigma^+$  state, or intensities for the bands in the  $F^2\Sigma^+ - A^2\Pi$  transition, are available.

*Ab initio* calculations [18] show that the potential energy curve for the  $F^2\Sigma^+$  state accommodates excited vibrational levels. Observation of the emission transitions from these levels should clarify the vibrational energy levels of  $F^2\Sigma^+$ , allowing the vibrational constants for the  $F^2\Sigma^+$  state to be determined. Theoretical band strengths are useful in predicting and interpreting experimental emission spectra for electronic transitions, since they provide intensity relations for bands independent of such experimental conditions as the populations of the initial vibrational levels and the sensitivity of the detection system. The band strength is proportional to the square of the vibrational matrix element of the electronic transition moment, and depends on the vibrational quantum numbers in the initial and final states [13]. In addition,

the accuracy of the ratios of the theoretical band strengths for the  $F^2\Sigma^+ - A^2\Pi$  transition can be estimated by comparing the theoretical and the experimental values [10] for the AlO  $B^2\Sigma^+ - X^2\Sigma^+$  transition.

We report here the band strengths for bands in the  $F^2\Sigma^+ - A^2\Pi$  transition, which we have calculated based on the present results for *ab initio* potential energies, electronic wavefunctions, vibrational term values and vibrational wavefunctions for the  $A^2\Pi$  state, and from our previous results for the X, B, D and  $F^2\Sigma^+$  states [18]. The Einstein coefficients for spontaneous emission were evaluated for the bands from the calculated band strengths and transition energies. These coefficients were used to estimate the ratio of the populations in the initial vibrational states, which produce bands not weaker in intensity than the detectable 0-0 band, to the population that produces the detectable band.

## 2. Theoretical approach

### 2.1. Configuration interaction calculations and electronic transition matrix element calculations

We carried out multi-reference configuration interaction (MRCI) calculations to determine the total energies and total electronic wavefunctions for the  $1^2\Pi$  state, using the same basis functions, orbital sets to be used for CI calculations and MRCI procedure as in calculations for the  $1-4^2\Sigma^+$  states [18]. In the MRCI procedure, the reference configurations include all the configurations of the complete-active space (CAS). The configuration state functions (CSFs) with  $^2\Pi$  symmetry include all the CSFs of the CAS (CAS CSFs) and the CSFs of both single and double excitations from the CAS

E-mail address: [n.honjou@helen.ocn.ne.jp](mailto:n.honjou@helen.ocn.ne.jp)

CSFs into the external orbital space. The MRCI calculations were repeated to obtain the potential energy function in the internuclear distance ( $R$ ) range 2.2–6.0  $a_0$  at intervals of 0.2  $a_0$ .

The MRCI wavefunctions for the A  $1^2\Pi$  state, and those for the X  $1^2\Sigma^+$ , B  $2^2\Sigma^+$  and F  $4^2\Sigma^+$  states obtained in the previous study [18], were used to calculate the electronic transition matrix elements of  $\langle F^2\Sigma^+ | x | A^2\Pi \rangle$  ( $= \langle F^2\Sigma^+ | y | A^2\Pi \rangle$ ) and  $\langle B^2\Sigma^+ | z | X^2\Sigma^+ \rangle$  (in a.u.), i.e. the nonvanishing components of the electronic transition dipole moments, where  $x$ ,  $y$  and  $z$  respectively denote the  $x$ ,  $y$  and  $z$  components of the position vector of an electron in the molecule fixed system whose internuclear axis is the  $z$  axis. The electronic transition matrix element calculations were repeated so as to obtain electronic transition matrix element functions  $\mu(R)$  in the range 2.4–5.0  $a_0$  at intervals of 0.2  $a_0$ . The ALCHEMY II computer program package [20] was used for the CI and electronic transition matrix element calculations [21].

## 2.2. Molecular vibration calculations

We performed molecular vibration calculations of vibrational term values  $G(v)$  of states with vibrational quantum numbers  $v$  and wavefunctions for  $A^2\Pi$  in the same way as in our previous study for the  $2^2\Sigma^+$  states [18]. The one-dimensional Schrödinger equation for the vibration of a diatomic molecule with no rotational energy was solved numerically using the potential energy function for  $A^2\Pi$ , which was input to the equation as cubic natural spline (CNS) curves fitted to the MRCI energies for 2.2–6.0  $a_0$ .

## 2.3. Band strength calculations

The band strength  $S_{v'v''}$  for an electronic transition from an upper state with vibrational quantum number  $v'$  to a lower state with  $v''$  is calculated from  $S_{v'v''} = g_{A''} \gamma (\mu_{v'v''})^2$  (in a.u.) [13]. Here,  $g_{A''}$  is the degeneracy of the lower electronic state  $A''$ :  $g_{A''} = 2$  for  $A'' = 2^2\Sigma$  symmetry, and  $g_{A''} = 4$  for  $A'' = 2^2\Pi$  symmetry;  $\gamma$  is the number of possible nonvanishing components of the electronic transition moment because of axial symmetry, taking value  $\gamma = 1$  for the  $\Sigma$ – $\Sigma$  transition and  $\gamma = 2$  for the  $\Sigma$ – $\Pi$  transition; and  $\mu_{v'v''}$  denotes the transition matrix element of the electronic transition matrix element function  $\mu(R)$  between the vibrational wavefunction for the upper state  $\psi_{v'}$  and that for the lower state  $\psi_{v''}$ :  $\mu_{v'v''} = \langle \psi_{v'} | \mu(R) | \psi_{v''} \rangle$ . To the equation for  $\mu_{v'v''}$ , the  $\mu(R)$  functions were input as the CNS curves fitted to the electronic transition matrix elements for 2.4–5.0  $a_0$ , and as the CNS linear extrapolation functions for 2.2–2.4  $a_0$  (5.0–6.0  $a_0$ ) having gradient equal to the CNS curve at 2.4  $a_0$  (5.0  $a_0$ ) and passing through the point at 2.4  $a_0$  (5.0  $a_0$ ). We used the vibrational wavefunctions for the X, B, and  $F^2\Sigma^+$  states obtained in the previous study [18]. A computer program constructed by the author [22] was used for computations of the vibrational term values and wavefunctions, and the transition matrix elements.

## 3. Results and discussion

### 3.1. Transition energies and band strengths

#### 3.1.1. Potential energy function and spectroscopic constants for the $A^2\Pi$ state

The electronic term value  $T_e$ , the equilibrium internuclear distance  $R_e$ , the vibrational constant  $\omega_e$  and the anharmonicity constant  $\omega_e x_e$  were calculated for the  $A^2\Pi$  state. The values were respectively 5005  $\text{cm}^{-1}$  (5406.110  $\text{cm}^{-1}$  [23]), 1.775 Å (1.7678 Å), 728  $\text{cm}^{-1}$  (729.762  $\text{cm}^{-1}$ ), and 4.4  $\text{cm}^{-1}$  (4.888  $\text{cm}^{-1}$ ); the experimental values [9] are in parentheses. Here, the values of  $T_e$ ,  $R_e$ ,

$\omega_e$  and  $\omega_e x_e$  were determined from the MRCI energies, and the vibrational term values  $G(v)$  for the observed states with vibrational quantum numbers  $v = 0$ –8 [9] were calculated in the same way as in our previous work [18]. We had previously examined the calculated potential energy curves (PECs) for the X, B, D and  $F^2\Sigma^+$  states by comparing calculated spectroscopic constants with experiment, and found that each of the PECs is accurate at and around its  $R_e$  [18]. The absolute values of the discrepancies between the calculated and experimental values for the  $A^2\Pi$  state are within or close to the largest absolute values among the discrepancies for the X, B and  $D^2\Sigma^+$  states [18], i.e. within 25  $\text{cm}^{-1}$  for  $\omega_e$ , 0.7  $\text{cm}^{-1}$  for  $\omega_e x_e$  and 0.011 Å for  $R_e$  or close to 185  $\text{cm}^{-1}$  for  $T_e$ . This implies that the  $A^2\Pi$  PEC at and around its  $R_e$  is accurate.

#### 3.1.2. Transition energies

The transition energies (wave numbers) for the bands corresponding to transitions between two electronic states are given by  $\nu_{v'v''} = (T'_e - T''_e) + [G'(v') - G''(v'')]$ , where the single-primed letters refer to the upper state and the double-primed letters refer to the lower state [1]. The theoretical transition energies were obtained from the  $T_e$  and  $G(v)$  values for the X, B and  $F^2\Sigma^+$  states calculated in our previous study [18] and the present  $T_e$  and  $G(v)$  values for the  $A^2\Pi$  state. Table 1 gives the theoretical  $\nu_{v'v''}$  values in  $\text{cm}^{-1}$ .

The error in any theoretical transition energy is given as the sum of the discrepancy between the theoretical and experimental values for the  $T'_e - T''_e$  and the discrepancy for the  $G'(v') - G''(v'')$ . The errors for the bands with  $v' = 0$ –7 and  $v'' = 0$ –6 are estimated to lie between  $-21 \text{ cm}^{-1}$  and  $466 \text{ cm}^{-1}$ , and the error for each band is within 1.1% of its transition energy. Here, the discrepancy in  $T'_e - T''_e$  of 240  $\text{cm}^{-1}$ , which is common to all the calculated bands of the  $F^2\Sigma^+ - A^2\Pi$  transition, is the difference between the discrepancy in  $T'_e$  for  $F^2\Sigma^+$  of  $-161 \text{ cm}^{-1}$  [18] and the discrepancy in  $T''_e$  for  $A^2\Pi$  of  $-401 \text{ cm}^{-1}$  (cf. subsection 3.1.1). The discrepancies in  $G'(v') - G''(v'')$ , which depend on both  $v'$  and  $v''$ , are estimated to be in the range between  $-261 \text{ cm}^{-1}$  and  $226 \text{ cm}^{-1}$  for the calculated bands [24] based on the Dunham series expansion [25].

#### 3.1.3. Electronic transition matrix element functions and band strengths

Fig. 1 shows the theoretical electronic transition matrix element functions  $\mu(R)$  for the  $F^2\Sigma^+ - A^2\Pi$  and  $B^2\Sigma^+ - X^2\Sigma^+$  transitions. The  $\mu(R)$  curve for the F–A transition has an extremum of 0.9563 a.u. at 3.23  $a_0$ , beyond which it falls monotonically to zero a.u. at 4.06  $a_0$  and then reaches another extremum of  $-0.3669$  a.u. at 4.43  $a_0$ . Table 1 gives values for the theoretical Franck-Condon factor  $q_{v'v''}$  and band strength  $S_{v'v''}$  (a.u.) for the  $F^2\Sigma^+ - A^2\Pi$  electronic transition.

The accuracy of the relative band strengths for the  $F^2\Sigma^+ - A^2\Pi$  transition is estimated from a comparison of the theoretical and the experimental [10] values of the relative band strengths of the  $v' - v''$  and  $v' - u''$  bands  $S_{v'v''}/S_{v'u''} = (\mu_{v'v''}/\mu_{v'u''})^2$  for the  $B^2\Sigma^+ - X^2\Sigma^+$  transition, since no experimental intensities are available for the F–A transition. Here,  $(\mu_{v'v''}/\mu_{v'u''})^2$  is the ratio of the square of transition matrix elements. We calculated the band strengths for the B–X transition using the same method as the F–A transition. Table 2 compares the present results for the relative band strength for the B–X transition with experimental values [10]. The present values agree with experiment to within 0.08. The relative band strengths for the F–A transition are given to the same accuracy as the B–X transition.

Download English Version:

<https://daneshyari.com/en/article/5394919>

Download Persian Version:

<https://daneshyari.com/article/5394919>

[Daneshyari.com](https://daneshyari.com)