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Extensive spectroscopic calculations of the 21 Λ-S and 74 Ω states of the AsN molecule including the spin–orbit coupling effect

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ABSTRACT

The potential energy curves (PECs) of 74 Ω states generated from the 21 Λ-S states of AsN molecule are studied for the first time for internuclear separations from 0.1 to 1.0 nm. Of these 21 Λ-S states, the $X^1\Sigma^+$, $a'^3\Sigma^+$, $1^5\Sigma^+$, $1^3\Delta$, $1^3\Sigma^-$, $a^3\Pi$, $1^5\Pi$, $2^5\Sigma^+$, $3^5\Sigma^+$, $2^3\Delta$, $2^3\Pi$, $3^3\Pi$, $3^5\Pi$, and $A^1\Pi$ states are found to be bound, and the $2^3\Sigma^+$, $3^3\Sigma^+$, $1^5\Sigma^-$, $1^5\Delta$, $2^5\Delta$, $2^5\Pi$, and $1^7\Sigma^+$ states are found to be repulsive ones. The $3^3\Pi$ state possesses the double well. The $2^5\Sigma^+$, $3^5\Sigma^+$, $3^5\Pi$, and $3^3\Pi$ states possess the shallow well. The $a'^3\Sigma^+$, $1^3\Sigma^-$, $2^3\Pi$, $1^3\Delta$, $1^5\Pi$, $2^5\Pi$, $3^5\Pi$, and $1^7\Sigma^+$ states are found to be the inverted ones with the spin–orbit coupling effect taken into account. The PECs are calculated using the CASSCF method, which is followed by the internally contracted MRCI approach with Davidson correction. Core–valence correlation and scalar relativistic corrections are included. The vibrational properties are evaluated for the $2^5\Sigma^+$, $3^5\Sigma^+$, and $3^5\Pi$ states and the second well of the $3^3\Pi$ state. The spin–orbit coupling effect is accounted for by the state interaction method with the Breit–Pauli Hamiltonian. The PECs are extrapolated to the complete basis set limit. The spectroscopic parameters are evaluated, and compared with available measurements and other theoretical results. The Franck–Condon factors and radiative lifetimes of the transitions from the $a'^3\Sigma_1^+$, $a^3\Pi_1$, $A^1\Pi_1$, $1^3\Delta_1$ and $a^3\Pi_{0^-}$ states to the $X^1\Sigma_{0^+}^+$ state are calculated for several low vibrational levels, and some necessary discussion is performed. Analyses show that the spectroscopic parameters reported in this paper can be expected to be reliably predicted ones.

1. Introduction

The AsN is one of the most important semiconductor materials, which can be used for the light-emitting and photovoltaic devices. As a result, the AsN molecule has attracted extensive attentions of physicists, chemists and material scientists. Much experimental [1–7] and theoretical works [8–13] have been done to obtain its various physical properties. However, little spectroscopic knowledge of the AsN has been known, and spectroscopic information is available only for few Λ-S states and Ω states up to now. As we know, all the applications as the semiconductor material need the accurate spectroscopic properties. For this reason, this paper in detail investigates the potential energy curves (PECs) so that some spectroscopic knowledge of the molecule can be extended.

Early in 1934, for the first time, Spinks [1] observed nearly 30 red degraded bands of the AsN molecule in emission. In 1967 and 1968, D'incan and Fémelat made a partial analysis of the $A^1\Pi$–$X^1\Sigma^+$ transitions, and observed

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a new transition involving the same lower state [2]. In 1970, Jones [2] photographed six bands of the strongly perturbed $A^1\Pi$–$X^1\Sigma^+$ system of the molecule with a dispersion of approximately 0.4 Å/mm, and Dixit et al. [3] also photographed the 0–0 and 0–1 bands of the $A^1\Pi$–$X^1\Sigma^+$ system at a dispersion of 0.38 Å/mm. In 1974, Fémelat and Jones [4] studied several transition bands originating from the $A^1\Pi$–$X^1\Sigma^+$ system. Some spectroscopic parameters and molecular constants were evaluated from these measurements [1–4]. In 1979, Huber and Herzberg [14] summarized some accurate spectroscopic parameters and molecular constants of involved states as of that time. In 1982, Perdigon and Fémelat [5] made a detailed rotational analysis of the $A^1\Pi$–$X^1\Sigma^+$ transition of $As^{14}N$ and $As^{15}N$ molecules so as to explain the perturbations observed in the $A^1\Pi$ state, and evaluated several spectroscopic parameters of $a^3\Pi$ and $A^1\Pi$ states. In addition, they also obtained the spin–orbit (SO) constant of $a^3\Pi$ state. In 1988, Henshaw et al. [6] identified two bands of AsN molecule in the chemiluminescence from the reaction, and evaluated several spectroscopic parameters of $X^1\Sigma^+$ and $a'^3\Sigma^+$ states. In 1988, Saraswathy and Krishnamurty [7] photographed the ultraviolet bands of $A^1\Pi$–$X^1\Sigma^+$ transition of the $As^{14}N$ and $As^{15}N$ under high dispersion. In combination with previous measurements, they reanalyzed the rotational structures of several states involved there. In 1999, Kerr and Stocker [15] thought that the accurate ground-state dissociation energy of AsN molecule should be 5.03 ± 0.02 eV. Summarizing these measurements [1–7,15], we find that the spectroscopic parameters of AsN molecule were evaluated only for the $X^1\Sigma^+$, $a'^3\Sigma^+$, $a^3\Pi$, and $A^1\Pi$ states, and the SO coupling constant was determined only for the $a^3\Pi$ state.

In 1985, Ohanessian et al. [8] made the first *ab initio* calculations of this molecule. They calculated the PECs of eight states by the configuration interaction (CI) method with the basis set of double-zeta quality. In 1992, Toscano and Russo [9] obtained the PECs of six states by the linear combination of Gaussian type orbitals-model potential-local spin density (LCGTO-MP-LSD) approach. In 1995, Katsuki [10] determined the ground-state PEC using the model potential. They [8–10] evaluated some spectroscopic parameters of the involved states. In 2001, Martin and Sundermann [11] proposed a group of correlation-consistent valence basis sets with the Stuttgart–Dresden–Bonn (SDB) relativistic effective core potentials. In 2003, Peterson [12] developed a group of convergent basis sets with the relativistic pseudopotentials. With the basis sets, they [11,12] evaluated the ground-state spectroscopic parameters. In 2010, Wang and Sun [13] computed the ground-state PEC, and evaluated the spectroscopic parameters. Summarizing the theoretical spectroscopic results available in the literature [9–13], we find the following. Firstly, most calculations are focused on the ground state, and few results achieve high quality. Secondly, no core–valence correlation correction has been included into the PEC calculations, though it can bring about the important effect on the accurate prediction of spectroscopic parameters. And thirdly, very few transition properties (such as Franck–Condon factors and radiative lifetimes of transitions) are calculated, though the transition properties are very useful in observing the excited states. Therefore, to improve the quality of spectroscopic parameters of the AsN molecule, more accurate calculations should be done.

The aim of this work is to extend the spectroscopic knowledge of AsN molecule. Firstly, extensive *ab initio* calculations of the PECs will be made, in which both the core–valence correlation and scalar relativistic corrections are included so that the spectroscopic properties will be evaluated as accurately as possible. Secondly, the effect of SO coupling on the PECs will be introduced into the calculations since no PECs have been determined for any Ω states up to now. And thirdly, the Franck–Condon factors and radiative lifetimes of the transitions from several low-lying states to the ground state are calculated for several low vibrational levels since the theoretical transition properties are very few in the literature, though they are very useful in observing the AsN molecule in experiment.

In the next section, we will briefly describe the theory and method used in this paper. In Section 3, the PECs of 21 states, $X^1\Sigma^+$, $a'^3\Sigma^+$ ($1'^3\Sigma^+$), $1^5\Sigma^+$, $1^3\Delta$, $1^3\Sigma^-$, $a^3\Pi$ ($1^3\Pi$), $1^5\Pi$, $2^5\Sigma^+$, $3^5\Sigma^+$, $2^3\Delta$, $2^3\Pi$, $3^3\Pi$, $3^5\Pi$, $A^1\Pi$, $1^5\Sigma^-$, $2^3\Sigma^+$, $3^3\Sigma^+$, $1^7\Sigma^+$, $1^5\Delta$, $2^5\Delta$, and $2^5\Pi$, of the AsN molecule are calculated using the complete active space self-consistent field (CASSCF) method, which is followed by the internally contracted multireference CI (icMRCI) approach [16,17] with Davidson correction (icMRCI+Q) [18,19]. The effect of core–valence correlation and scalar relativistic corrections on the PECs is taken into account. All the PECs are extrapolated to the complete basis set (CBS) limit. The spectroscopic parameters are evaluated, and compared with those available in the literature. The Franck–Condon factors and radiative lifetimes of transitions from the $a'^3\Sigma_1^+$, $a^3\Pi_1$, $A^1\Pi_1$, $1^3\Delta_1$ and $a^3\Pi_{0-}$ states to the $X^1\Sigma_{0+}^+$ ground state are calculated, and some necessary discussion is performed. And finally, some concluding remarks are given in Section 4.

Table 1
Dissociation relationships of a few states of the AsN molecule.

Dissociation channel	Electronic state	Relative energy/cm^{-1}
$As(^4S_u)+N(^4S_u)$	$X^1\Sigma^+$, $a'^3\Sigma^+$, $1^5\Sigma^+$, $1^7\Sigma^+$	0.0
$As(^2D_u)+N(^4S_u)$	$1^3\Delta$, $1^5\Delta$, $a^3\Pi$, $1^5\Pi$, $2^3\Sigma^+$, $2^5\Sigma^+$	$10{,}590.7 \pm 223.3$
$As(^2P_u)+N(^4S_u)$	$1^3\Sigma^-$, $1^5\Sigma^-$, $2^3\Pi$, $2^5\Pi$	$17{,}899.5 \pm 224.7$
$As(^4S_u)+N(^2D_u)$	$2^3\Delta$, $2^5\Delta$, $3^3\Pi$, $3^5\Pi$, $3^3\Sigma^+$, $3^5\Sigma^+$	$19{,}181.5 \pm 143.9$
$As(^2D_u)+N(^2D_u)$	$A^1\Pi$, ($2^1\Sigma^+$, $3^1\Sigma^+$, $4^1\Sigma^+$, $4^3\Sigma^+$, $5^3\Sigma^+$, $6^3\Sigma^+$, $1^1\Sigma^-$, $2^1\Sigma^-$, $1^3\Sigma^-$, $2^3\Sigma^-$, $1^1\Pi$, $2^1\Pi$, $3^1\Pi$, $4^1\Pi$, $3^3\Pi$, $4^3\Pi$, $5^3\Pi$, $6^3\Pi$, $1^1\Delta$, $2^1\Delta$, $3^1\Delta$, $3^3\Delta$, $4^3\Delta$, $5^3\Delta$, $1^1\Phi$, $2^1\Phi$, $1^3\Phi$, $2^3\Phi$, $1^1\Gamma$, $1^3\Gamma$)	29,953.9