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# Theoretical study of Van der Waals complexes of Al atom with N<sub>2</sub>

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# Theoretical study of Van der Waals complexes of Al atom with N<sub>2</sub>

## Abstract

Al-N<sub>2</sub> Van der Waals complexes have recently been produced in molecular beam experiments and studied with threshold laser photoionization. The ionization potential measured for the Al-N<sub>2</sub> complex (46821 cm<sup>-1</sup>), combined with Al atom ionization potential (48279 cm<sup>-1</sup>) and Al-N<sub>2</sub> dissociation energy measured by Bouchard and McMahon (19246175 cm<sup>-1</sup>) leads to the estimation of the Al-N<sub>2</sub> complex binding energy at 4666175 cm<sup>-1</sup> (Ref. 1). The purpose of our study is to estimate the Al-N<sub>2</sub> and Al-N<sub>2</sub> binding energies using theoretical calculations and to compare them with the experimental results.

## Disciplines

Chemistry

## Comments

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Galina Chaban and Mark S. Gordon

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# LETTERS TO THE EDITOR

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## NOTES

### Theoretical study of Van der Waals complexes of Al atom with N<sub>2</sub>

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Al-(N<sub>2</sub>)<sub>x</sub> Van der Waals complexes have recently been produced in molecular beam experiments and studied with threshold laser photoionization.<sup>1</sup> The ionization potential measured for the Al-N<sub>2</sub> complex (46 821 cm<sup>-1</sup>), combined with Al atom ionization potential (48 279 cm<sup>-1</sup>) and Al<sup>+</sup>-N<sub>2</sub> dissociation energy measured by Bouchard and McMahon (1924 ± 175 cm<sup>-1</sup>)<sup>2</sup> leads to the estimation of the Al-N<sub>2</sub> complex binding energy at 466 ± 175 cm<sup>-1</sup> (Ref. 1). The purpose of our study is to estimate the Al-N<sub>2</sub> and Al<sup>+</sup>-N<sub>2</sub> binding energies using theoretical calculations and to compare them with the experimental results.

In this paper we present *ab initio* calculations of potential energy surfaces for the lowest electronic states of Al-N<sub>2</sub> and Al<sup>+</sup>-N<sub>2</sub>, including structural parameters and dissociation energies for van der Waals complexes found on these potential energy surfaces.

The calculations of Al-N<sub>2</sub> and Al<sup>+</sup>-N<sub>2</sub> ground state energetics were performed using the quadratic configuration interaction method QCISD(T)<sup>3</sup> and the GAUSSIAN92 program.<sup>4</sup> The potential energy curves were obtained by calculating single-point energies at different values of the Al-N<sub>2</sub> distance, keeping the N-N distance at its equilibrium value obtained at the same QCISD(T) level. In order to estimate zero point energies, second order perturbation theory (MP2)<sup>5</sup> was used to calculate analytic Hessians for structures that were found to be minima on the potential energy surfaces.

Four types of correlation consistent basis sets were used: valence-triple-zeta (cc-pVTZ),<sup>6</sup> augmented valence-triple-zeta (aug-cc-pVTZ),<sup>7</sup> core-valence-triple-zeta (cc-pCVTZ),<sup>8</sup> and augmented core-valence-triple-zeta (aug-cc-pCVTZ). The latter basis set used the same diffuse function exponents as the aug-cc-pVTZ basis set. The pVTZ types of basis sets were used with frozen core calculations denoted QCISD(T,fc) and MP2(fc). The pCVTZ type basis sets were used with QCISD(T) and MP2 with the core electrons included in the correlation. Calculations that include all core electrons are denoted QCISD(T,full) and MP2(full), while calculations that include only the second shell core electrons of Al are denoted QCISD(T) and MP2. Our previous calculations of van der Waals complexes of second and third period metal atoms with H<sub>2</sub> (Ref. 9) showed that basis sets of triple-zeta quality give satisfactory results for binding energies of weakly bound complexes. Also, it has been shown<sup>10-14</sup> that the augmented correlation consistent pVTZ basis sets are converged with respect to basis set superposition errors. Binding

energies may be slightly improved by correlating core orbitals, with the corresponding use of core-valence basis sets.

Parts of the C<sub>∞v</sub> potential energy surfaces for the two lowest Al-N<sub>2</sub> states (<sup>2</sup>Π and <sup>2</sup>Σ) are shown in Fig. 1(a). The single-point energies are calculated at different distances *R* between Al and the closest N atom at the QCISD(T,fc)/aug-cc-pVTZ level of theory. The N-N distance was fixed at 1.104 Å, the N<sub>2</sub> equilibrium distance. The <sup>2</sup>Π state has a weakly bound complex (the one observed experimentally<sup>1</sup>), while the <sup>2</sup>Σ state is entirely repulsive. The absence of a complex for the <sup>2</sup>Σ state can be explained by the repulsion of a singly occupied *p* orbital of Al and a nitrogen lone pair. The dissociation energy (*D<sub>e</sub>*) of the <sup>2</sup>Π complex is 343 cm<sup>-1</sup>, and the equilibrium distance (*R<sub>e</sub>*) between Al and the N-N bond (*R<sub>Al-N</sub>*) is 3.43 Å at the QCISD(T,fc)/aug-cc-pVTZ level of theory. The <sup>1</sup>Σ ground state for Al<sup>+</sup>-N<sub>2</sub> is shown in Fig. 1(b). It has a very deep minimum with *R<sub>e</sub>* = 2.86 Å and *D<sub>e</sub>* = 1789 cm<sup>-1</sup>.

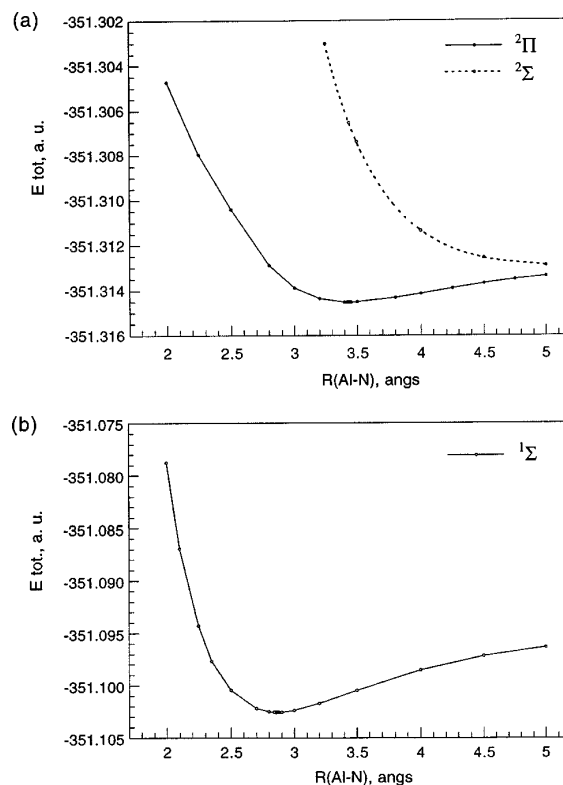


FIG. 1. Potential energy curves for (a) Al-N<sub>2</sub> and (b) Al<sup>+</sup>-N<sub>2</sub> lowest electronic states.

TABLE I. Structural parameters (Å) and dissociation energies ( $\text{cm}^{-1}$ ) for  $\text{Al}-\text{N}_2$  and  $\text{Al}^+-\text{N}_2$  van der Waals complexes.

Method/basis set	$\text{Al}-\text{N}-\text{N}$					$\text{Al}^+-\text{N}-\text{N}$					Differences	
	$R$ , Å	$r$ , Å	$D_e$	$\Delta$ ZPE	$D_0$	$R$ , Å	$r$ , Å	$D_e$	$\Delta$ ZPE	$D_0$	$\Delta D_e$	$\Delta D_0$
MP2(fc)/cc-pVTZ	3.39	1.114	398	100	298	2.84	1.114	1999	165	1833	1601	1535
MP2(fc)/aug-cc-pVTZ	3.39	1.114	398	88	310	2.85	1.114	1852	154	1698	1454	1388
MP2/cc-pCVTZ	3.35	1.110	424	74	350	2.82	1.110	2058	162	1897	1634	1547
MP2/aug-cc-pCVTZ	3.35	1.111	413	98	315	2.83	1.111	1901	165	1736	1488	1421
MP2(full)/cc-pCVTZ	3.35	1.110	425	75	350	2.81	1.110	2062	163	1899	1637	1549
MP2(full)/aug-cc-pCVTZ	3.35	1.111	417	98	319	2.83	1.111	1960	164	1796	1543	1477
QCISD(T,fc)/cc-pVTZ	3.45	1.104	328	(93)	(235)	2.84	1.104	1923	(153)	(1770)	1595	(1535)
QCISD(T,fc)/aug-cc-pVTZ	3.43	1.104	343	(82)	(261)	2.86	1.104	1789	(143)	(1646)	1446	(1385)
QCISD(T)/cc-pCVTZ	3.42	1.101	344	(69)	(275)	2.83	1.101	1957	(151)	(1806)	1613	(1531)
QCISD(T)/aug-cc-pCVTZ	3.40	1.101	345	(91)	(254)	2.84	1.101	1812	(153)	(1659)	1467	(1405)
QCISD(T,full)/cc-pCVTZ	3.42	1.101	345	(70)	(275)	2.82	1.101	1961	(152)	(1809)	1616	(1534)
QCISD(T,full)/aug-cc-pCVTZ	3.40	1.101	349	(91)	(258)	2.84	1.101	1862	(153)	(1709)	1513	(1451)

<sup>a</sup> $R$  is the equilibrium distance between the Al atom and the closest N atom;  $r$  is the equilibrium N–N distance.

<sup>b</sup>Values in parentheses are estimations of QCISD(T),  $\Delta$  ZPE, and  $D_0$  obtained from scaled MP2  $\Delta$  ZPE.

These results suggest that the dissociation energy  $D_0$  ( $\text{Al}^+-\text{N}_2$ ) may be somewhat smaller than the reported experimental value ( $1924 \pm 175 \text{ cm}^{-1}$ ).<sup>2</sup> To find more accurate values for dissociation energies, we performed calculations for the  $\text{Al}-\text{N}_2$  ( $^2\Pi$ ) and  $\text{Al}^+-\text{N}_2$  ( $^1\Sigma$ ) complexes in which the core electrons are correlated, as well as the valence electrons. All results are presented in Table I. The table also includes zero point energies ( $\Delta$ ZPE) for the same two complexes obtained at the MP2 level with the various basis sets. The  $\Delta$ ZPE correspond to the differences between the zero point energy of  $\text{Al}-\text{N}_2$  or  $\text{Al}^+-\text{N}_2$  and the zero point energy of  $\text{N}_2$ . The QCISD(T) estimates for  $D_0$  are given in parentheses, because they are obtained using  $D_e$  from QCISD(T) and  $\Delta$ ZPE from corresponding MP2 calculations with the same basis set, scaled by a factor of 0.93. To assess this procedure, the  $\text{Al}-\text{N}_2$  and  $\text{Al}^+-\text{N}_2$  QCISD(T,fc) potential energy curves were fitted by means of the distributed approximating functional (DAF) method.<sup>15</sup> The second derivatives calculated at the fitted minima give  $\text{Al}-\text{N}_2$  vibrational stretching frequencies of 44 and  $97 \text{ cm}^{-1}$  for  $\text{Al}-\text{N}_2$  and  $\text{Al}^+-\text{N}_2$ , respectively. These are slightly less than the MP2 frequencies: 52 and  $110 \text{ cm}^{-1}$ , in accordance with the smaller QCISD(T)  $D_e$  relative to MP2. So, the use of scaled MP2 zero point corrections seems reasonable.

Our best estimate for the dissociation energy of neutral  $\text{Al}-\text{N}_2$  ( $^2\Pi$ ) is in the region of  $D_e=345-349$ , and  $D_0=254-258 \text{ cm}^{-1}$ . For the positive ion complex our calculations give dissociation energies between  $D_e=1812-1862$  and  $D_0=1659-1709 \text{ cm}^{-1}$ . The estimate for  $\Delta D_0 = D_0(\text{Al}^+-\text{N}_2) - D_0(\text{Al}-\text{N}_2)$  is in the region of  $1405-1451 \text{ cm}^{-1}$ , which is quite close to the  $\text{AlIP}=\text{IP}(\text{Al})-\text{IP}(\text{AlN}_2)=1458 \text{ cm}^{-1}$ , measured by Brock and Duncan.<sup>1</sup> The remaining difference may be due to relativistic corrections that we have not taken into account. This correction should be close to that estimated by Partridge, Bauschlicher, and Visscher for the  $\text{AlAr}$  complex,<sup>16</sup> for which it was found to reduce the binding energy by about  $34 \text{ cm}^{-1}$ .

**Conclusions.** Equilibrium geometries and dissociation energies are estimated for ground state  $\text{Al}-\text{N}_2$  and  $\text{Al}^+-\text{N}_2$  van der Waals complexes at the QCISD(T) level of theory with correlation consistent basis sets. Zero point energies for these complexes are calculated at the MP2 level and scaled to obtain estimates for QCISD(T). The resulting  $\Delta D_0$

$=D_0(\text{Al}^+-\text{N}_2)-D_0(\text{Al}-\text{N}_2)$  is  $1400-1450 \text{ cm}^{-1}$ , which is close to that measured in laser photoionization experiments by Brock and Duncan.<sup>1</sup> However, we find that  $D_0(\text{Al}^+-\text{N}_2)$  is in the region  $1650-1710 \text{ cm}^{-1}$ , somewhat less than that found by Bouchard and McMahon ( $1924 \pm 175 \text{ cm}^{-1}$ ). Correspondingly, our estimate for  $D_0(\text{Al}-\text{N}_2) \approx 250-260 \text{ cm}^{-1}$  is also less than that suggested previously. This energy may decrease by  $35-40 \text{ cm}^{-1}$  due to the spin-orbit correction.<sup>16</sup>

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