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Direct Determination of the Permanent Dipole Moments and Structures of Al−CH_3CN and Al−NH_3 by Using a 2-m Electrostatic Hexapole Field

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Abstract: The supersonic beams of the (1−1) metal−ligand complexes of Al−CH_3CN and Al−NH_3 were produced by a laser evaporation method. Nondestructive structure selection of the complexes and the dipole moment determination were performed by using a 2-m electrostatic hexapole field. The experimentally determined permanent dipole moments are 1.2 ± 0.1 D for Al−CH_3CN and 2.7 ± 0.2 D for Al−NH_3. We find that the dipole moment of Al−NH_3 becomes larger than that of neat NH_3, while the formation of the Al−CH_3CN complex produces a smaller dipole moment than that of neat CH_3CN on the other hand. We performed the ab initio calculations to draw out plausible complex structures and to clarify the bonding character after formation of the complex, and we made comparisons with the computational results done by several groups. The Mulliken population analysis suggests the Al→CH_3CN charge flow, but on the other hand the Natural population analysis indicates very little charge flow. For the Al−NH_3 complex, the polarization effect of NH_3 and the N→Al σ donation would enhance the dipole moment strength. However, there still remains a controversial disagreement between the theoretical predictions and the experimental results. Further experimental determination using the hexapole method for various metal−ligand complexes and clusters could reveal the basic nature of interaction in the complex systems in general, and this method would complement theoretical calculations.

Introduction

Over the past two decades, much attention has been paid to molecular clusters and metal−ligand type complexes to link the gap between the gas phase and the condensed one. Various spectroscopic techniques have been applied to newly synthesized complexes to obtain information about energetics, structure, and dynamics.[1−9] Bonding character and structure of such complexes are compared with its constituent “free” molecules.[10−13] Small size clusters can serve as a model system for observing metal−ligand interaction in an isolated form. Only recently, Jakubek and Simard have performed a ZEKE study of the $AlND_3$ complex for measuring the ionization potentials and the vibrational frequencies in the excited states.[14] Howard et al.[15] measured the three products $Al(NH_3)_4$, $HAl-NH_2$, and $Al(NH_3)_2$ from the reaction of Al + NH_3 using ESR. In theoretical computation, Davy and Jaffrey have performed the ab initio calculation on Al−NH_3 and they suggested that the insertion products of $HAl-NH_2$ and H_2Al-NH might not be likely.[16,17] They also stated that the relatively strong bond could be formed through the N→Al σ donation in the formation of the Al−NH_3 complex. They found by using a Mulliken population analysis that the slightly negative charge (−0.2 e) was located on the Al atom. However, Mulliken population analysis often gives unrealistic computational results in many systems. Besides the above-mentioned studies, little is known about interaction nature between the Al atom and simple molecules in the gas phase.[17] We demonstrate here a direct experimental application of the electrostatic hexapole to the supersonic beams of Al−CH_3CN and Al−NH_3 complexes for determining permanent dipole moments, which are a useful signature for probing metal−ligand interaction. We find that the dipole moment of Al−NH_3 becomes larger than that of neat NH_3, and the formation of the

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Al$-$CH$_3$CN complex produces a smaller dipole moment than that of neat CH$_3$CN. The ab initio calculations suggest the plausible structures of the complexes, but there remains a disagreement between the theoretical predictions and the experimental results. The present work suggests the importance of comparative studies in theory as well as in experiment to clarify the metal$-$ligand interactions.

Experimental Section

The apparatus consists of four differentially pumped chambers for a laser evaporation beam source, a buffer pumping, a 2-m electrostatic hexapole field, and finally a time-of-flight mass spectrometer. Typical base pressures are $\sim 3 \times 10^{-7}$ Torr. The (1$-$1) complexes of Al$-$CH$_3$CN or Al$-$NH$_3$ were synthesized by the laser evaporation using the 532-nm second harmonic of a pulsed Nd^{3+}:YAG laser of 5$-$10 mJ/pulse fluence, which was focused on a rotating Al rod (4 mm ϕ). The evaporated Al atoms were cooled by collisions with either Ne or He carrier gas at 600 Torr, and they were sent to the 15-mm long reaction channel where they were mixed with CH$_3$CN or NH$_3$ vapor of 70 Torr. Because of many collisions with the carrier gas, it is reasonable to assume that synthesized complexes are relaxed down to the ground state electronically and internally. Thus the rotational state distribution can be described as a Boltzmann type. The cluster beam is skimmed and collimated and then state-selected in the hexapole field. This electrostatic field selectively transmits and focuses a cluster (or complex), which is a symmetric-top structure with a nonzero permanent dipole moment.[18] Complexes in the beam are then ionized in the mass spectrometer chamber by a gently focused ArF excimer laser to avoid multiphoton ionization. The ionized complexes were accelerated for TOF detection. The mass resolution was $\Delta m = 1$. Typically, 6000 TOF profiles were averaged by a digital oscilloscope (LeCroy 9320) for measured hexapole rod voltages scanned in stepwise from 0 to 12 kV to get the focusing curves, namely the dependence of the beam intensity on the hexapole rod voltage, V_0. The delay time of the ionizing laser was adjusted to the center of the pulse beam in the case of the focusing curve measurement. We then carried out the trajectory simulation of the hexapole field for fitting the experimental focusing curves, in which the first- and second-order Stark effects were taken into account. Other necessary parameters for the simulation, i.e., the apparatus function of the complex beam line, the velocity, and the angular distribution of the beam, were measured. The rotational temperature of the beam was approximated to be equal to its translational temperature.[19] Consequently, the magnitude of the dipole moment is left as the only one adjustable parameter in the computer simulation.

Calculations

To estimate structures and charge distributions of the synthesized complexes, ab initio MP2 calculation was performed as implemented in the Gaussian 94 program.[20] The Al-complexe structures were optimized using the 6-311++G** basis set without any symmetry constrains. It is found that the optimized structure of the Al$-$NH$_3$ complex was slightly distorted from C_{3v} symmetry owing to the Jahn$-$Teller effect. But practical distortion should be even smaller than the estimation because of the spin$-$orbit interaction as already suggested by Jakubek and Simard. In the present ab initio calculation, we neglected the spin$-$orbit interaction, while the effect of this interaction would cancel out the Jahn$-$Teller interaction. For this reason, we optimized the Al$-$NH$_3$ complex again by imposing C_{3v} symmetry. We then performed the natural population analysis (NPA) for the optimized structure in addition to the Mulliken population analysis to get detailed insight into the roles of the charge transfer within the complexes, namely the partial electron transfer from the Al atom to the ligand molecule.

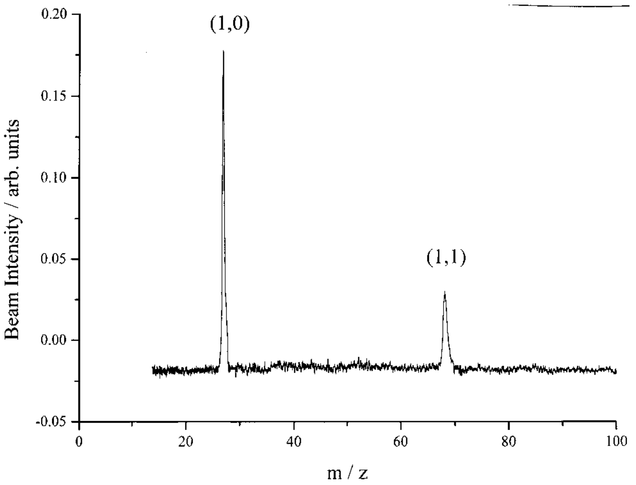

Figure 1. Time-of-flight mass spectrum of the Al$-$CH$_3$CN (1$-$1) complex.

Results

Figure 1 shows the TOF mass spectrum of the Al$-$CH$_3$CN (1$-$1) complex (the second peak) obtained under the experimental conditions mentioned in the previous section, where we optimized the formation of the (1$-$1) complex. The first peak labeled as (1$-$0) corresponds to neat aluminum and the complexes larger than (1$-$1) combinations could not be seen. The stream velocity of the beam and its velocity spread were $V_s = 1540$ ms^{-1} and $\alpha_s = 110$ ms^{-1}, respectively. The latter value of the velocity spread corresponds to a translational temperature of 50 K.

Figure 2 shows the focusing curves of the Al$-$CH$_3$CN (1$-$1) complex measured with two kinds of carrier gases to change the stream velocity and the rotational temperature: Al seeded in He(A) and Ne(B). It is ideal for determining the dipole moment but it is sometimes difficult to isolate individual $|JKM\rangle$ peaks of the focusing curve if a molecule possesses only a small dipole moment because of the overlap of adjacent peaks. Nonetheless it was sufficient for determination of the dipole moment and structure of complexes to measure the threshold voltage and its V_0-dependence on the beam intensity. Using the 2-m hexapole field, we were able to measure the threshold at $V_0 = 5$ kV and the beam intensity enhancement for the Al$-$CH$_3$CN (1$-$1) complex. This result on the focusing curve indicates clearly to us that the Al$-$CH$_3$CN complex possesses "nonzero" permanent dipole moment and its structure satisfies the symmetric-top. The solid lines in Figure 2 (A for the He carrier gas and B for the Ne one) represent the best-fit simulations. The best agreement between the experiment and the simulation with the single adjustable parameter for both curves in two independent experimental conditions confirms that 1.2 ± 0.1 D is reliable as the permanent dipole moment of Al$-$CH$_3$CN. This result concludes that the structure of the Al$-$CH$_3$CN (1$-$1) complex should be the symmetric-top and it possesses 1.2 ± 0.1 D permanent dipole moment. It is not possible to determine from only the experimental data whether the Al atom is bound to the N-end or the methyl end of CH$_3$-

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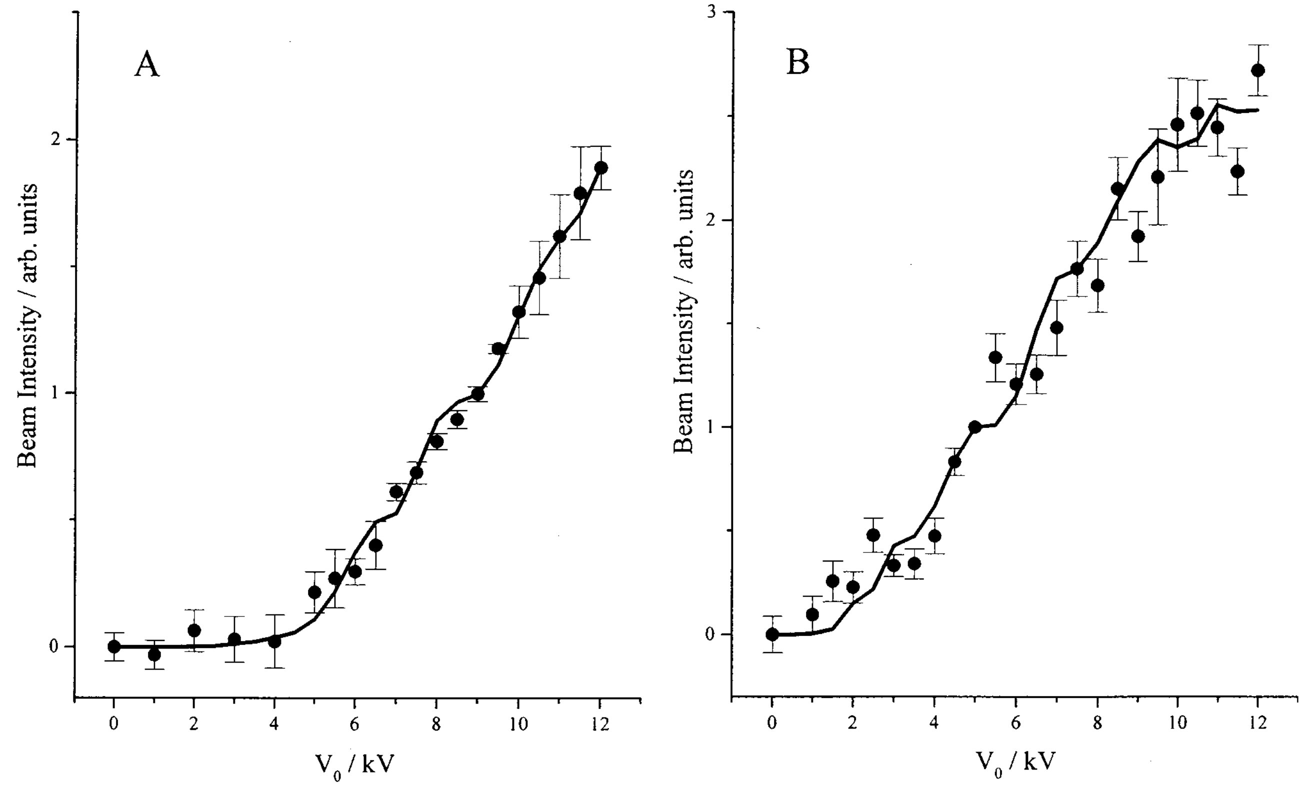

Figure 2. Focusing curves of the Al−CH_3CN (1−1) complex with the carrier gas of He (A) and Ne (B). The solid circles with experimental error bars give the data points. The mass peak is tuned to *m*/*e* 68. The simulated curves are shown with the solid lines.

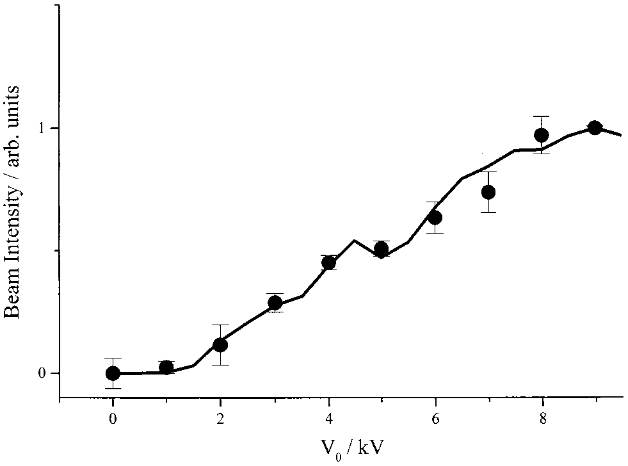

Figure 3. Focusing curve of the Al−NH_3 (1−1) complex represented by the solid circles with error bars. The simulated curve is shown with the solid line.

CN. The ab initio calculations are therefore necessary to answer the question. We carried out the calculation and obtained the recommended structure that the Al atom is bound to the N-end of the molecule.

The same procedures of measurement and calculation were carried out for the Al−NH_3 (1−1) complex. The focusing curve of Al−NH_3 is shown in Figure 3 where the beam intensity was measured at the parent ion peak (*m*/*e* 44). The dipole moment of Al−NH_3 was determined to be 2.7 ± 0.2 D. The complex structure was simulated by the calculation, and it was found to be symmetric-top again. The ±0.2 error of the dipole moment was estimated from the deviation between the experimental data and the simulated ones near the threshold voltage of the focusing curve.

Table 1. Calculated Energetics and Dipole Moments of Complexes and Molecules

	D_e/eV	μ_{calc}	μ_{exp}	$\Delta\mu_{exp}$
CH_3CN	-	4.30	3.92[a]	-
Al−CH_3CN	0.236	7.09	1.2 ± 0.1	−2.7 ± 0.1
NH_3	-	1.78	1.468[a]	-
Al−NH_3	0.453	5.21	2.7 ± 0.2	+1.2 ± 0.2

[a] Reference 32.

It is worth noting that the dipole moment of Al−NH_3 (i.e. 2.7 D) is enhanced after the metal−ligand formation. (Note that the dipole moment of neat NH_3 is 1.5 D.) On the other hand, the dipole moment of Al−CH_3CN (1.2 D) becomes smaller than that of the composite CH_3CN molecule (3.9 D) after theformation of the complex. This dual behavior on the dipole moment change after the formation of the complex indicates that the charge transfer and polarization effects between the Al atom and the ligand molecule such as NH_3 and CH_3CN are not as simple as usually discussed. We will discuss this point in more detail later.

Table 1 summarizes the theoretical (μ_{calc}) and experimental (μ_{exp}) dipole moments of the Al−CH_3CN and Al−NH_3 complexes. The dipole moments of their composite molecules, CH_3CN and NH_3, and the calculated binding energies are also listed. $\Delta\mu_{exp}$ stands for the difference in magnitude between the dipole moment of a complex and its composite molecule.

Figure 4 shows the optimized structures of the neural Al−CH_3CN (1−1) and Al−NH_3 (1−1) complexes that we obtained by ab initio calculation with MP2/6-311++G**. The bond lengths are given in angstroms and the angles in degrees. The structures of acetonitrile (CH_3CN) and ammonia (NH_3) molecules are also shown (referenced from a book on microwave spectroscopy).[30] The values in parentheses stand for the natural charges. We have investigated by the present calculation that there are no other optimized structures. It is generally regarded

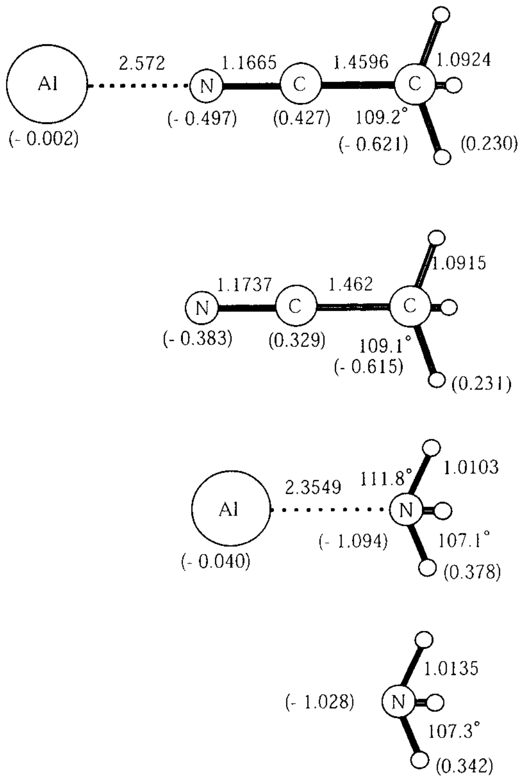

Figure 4. Optimized structures of the Al−CH_3CN and Al−NH_3 complexes calculated by MP2/6-311++G**. Bond lengths and angles are shown in Å and deg, respectively. The structure of acetonitrile and ammonia determined by microwave spectroscopy[32] are also shown. Values in parentheses are the natural charges.

that calculated results of the dipole moment strongly depend on the basis set as well as the type of computational method we choose.[21] It turns out to be a tendency that the present calculation tends to overestimate the dipole moment. It is important to point out again that the magnitude of the Al−NH_3 dipole moment is enhanced after formation of the complex both experimentally and theoretically. But it seems there is a controversy that the experimental dipole moment of the Al−CH_3CN complex, i.e., 1.2 D, is smaller than the 3.92 D of CH_3CN despite the predicted value of 7 D from the calculation.

Table 2 summarizes the natural population analysis (NPA) and the Mulliken charges for Al−CH_3CN and Al−NH_3 optimized at the MP2/6-311++G**.

Table 2. Natural Population Analysis (NPA) and Mulliken Charges in Al−CH_3CN and Al−NH_3 Complexes Optimized at the MP2/6-311++G** Level

	Mulliken	NPA	NPA(CH_3CN)
C	+0.266	+0.427	+0.329
C	−0.649	−0.621	−0.616
H	+0.190	+0.231	+0.223
H	+0.190	+0.231	+0.223
H	+0.190	+0.231	+0.232
N	−0.059	−0.498	−0.616
Al	−0.129	−0.020	

	Mulliken	NPA	NPA(NH_3)
N	−0.575	−1.113	−1.028
H	+0.269	+0.386	+0.343
H	+0.269	+0.386	+0.343
H	+0.269	+0.386	+0.343
Al	−0.235	−0.045	

Discussion

So far, there has been neither experimental nor theoretical information about the dipole moment or structure of the Al−CH_3CN complex except for calculations about the species it resembles; such as ionic clusters of the Al^+ ion with CH_3CN[22] and Li^+ and Na^+ ions with CH_3CN.[23] They estimate that the metal ions are likely to be bound to the N-end of the molecule. Recently, the complex structures of neutral alkaline metal atoms with CH_3CN have been reported.[24] This calculation indicates that the alkaline atom preferentially makes a bond with the N-end of the molecule again. It is therefore expected that the polarization effect of CH_3CN would increase the magnitude of the complex dipole moment because of the high polarizability of acetonitrile. This expectation was confirmed by the present calculation that the natural charge distribution of CH_3CN is drastically changed after formation of the complex.

In classical mechanics, the dipole moment of the molecule or complex can be represented by the sum of the point charges in a molecule, namely $\mu = \sum_i q_i \mathbf{r}_i$, where q_i is a point charge at a position $\boldsymbol{r}_i$ in the molecule. We calculated the dipole moments based on this vector summation with the aid of the natural charges computed by the NPA shown in Table 2, and the obtained values are 4.5 D for Al−CH_3CN and 3.7 D for CH_3CN, respectively. The same increasing trend can be seen in the calculated values of the dipole moment in Table 1. This dipole increase due to formation of the Al−CH_3CN complex from CH_3CN could be understood usually as a polarization effect of the CH_3CN molecule. However, the above theoretical expectation turns out to be controversial against the experimental finding that we have measured the smaller dipole moment after the formation of complex Al−CH_3CN.

Usually, the σ^* type of the lowest unoccupied molecular orbital (LUMO) of CH_3CN is likely to accept negative charge from the Al atom, therefore this Al → CH_3CN charge flow of the opposite direction with respect to CH_3CN would reduce the dipole moment of the complex. Despite the above argument, the natural population analysis (NPA) on this complex that we have performed indicates very little charge flow between Al and CH_3CN. It is therefore noteworthy at this point that the disagreement between NPA and Mulliken population analysis is meaningful in understanding what is happening in the formation of the complex. It is also suggestive for us to understand the difficulty in predicting charge distribution of the characteristic Al−CH_3CN system in which the molecule is highly polarizable.

It is well recognized that the variation method gives us a wave function with the lowest energy in principle. But this criterion is not applicable if one wants to calculate physical properties other than total energy. The electron density in valence regions essentially determines the magnitude of the

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electric dipole moment and it contributes little to total energy. Thus there is no guarantee for holding the linear relationship between the electric dipole moment and the energy especially for the open-shell molecules with small dipole moment such as CO. Calculations with a larger basis set often predict the wrong direction for the dipole moment giving 100% inaccuracy.[25] It would even be much larger for the present system.

Several researchers have studied the Al−NH_3 complex. Howard et al. investigated the reaction of Al + NH_3 using ESR with a rotating cryostat and measured three products containing one Al atom, namely $Al(NH_3)_4$, HAl−NH_2, and $Al(NH_3)_2$. Davy and Jaffrey have recently performed the ab initio calculation on three structural isomers, i.e., Al−NH_3 and two Al insertion products of HAl−NH_2 and H_2Al−NH. Their calculation suggests that the insertion products might be unlikely because the barrier height for the Al insertion into NH_3 should be as high as ∼1.4 eV even if the HAl−NH_2 shows a global minimum stability. Our present work supports that the noninsertion type of Al−NH_3 (1−1) complex should be plausible as a major product out of the laser evaporation synthesis. This conclusion also accords with the recent work done by Di Palma et al.[17] Davy and Jaffrey have also suggested that the relatively strong bond can be formed through the N→Al σ donation in the formation of the Al−NH_3 complex.[16] One expects that the dipole moment increases when the complex is formed because the $H_3^{\delta+}$−$N^{\delta-}$ charge distribution of ammonia would leads to the $H_3^{\delta+}$−N−$Al^{\delta-}$ charge separation. They found by using the Mulliken population analysis that the slightly negative charge (−0.2 e) was located on the Al atom. We also obtain almost the same amount of natural charges localized on the Al atom based on the Mulliken population analysis. Care must be taken, however, for Mulliken population analysis often gives unphysical results in many systems. Recently, NPA has been widely applied to many systems and this method has been recognized to provide physically reasonable results.[28−31] Table 2 summarizes our results on the charge distribution of the Al−NH_3 complex calculated by the NPA, indicating that there is no evidence for the charge flow between the Al atom and ammonia. It appears that the population analysis of the Al−NH_3 complex is more reliable than that of the Al−CH_3CN complex; the latter gives very different population. It is temporarily concluded that the observed increment of the dipole moment for Al−NH_3 can be partly explainable by the polarization effect, since the natural charge distribution of ammonia is only slightly changed due to formation of the complex.

Conclusion

The supersonic beams of the (1−1) metal−ligand complexes of Al−CH_3CN and Al−NH_3 were produced by a laser evaporation method. The dipole moments of Al−CH_3CN and Al−NH_3 complexes have been experimentally determined for the first time by using the 2-m electrostatic hexapole field: 1.2 ± 0.1 D for Al−CH_3CN and 2.7 ± 0.2 D for Al−NH_3. We find that the dipole moment of Al−NH_3 becomes larger than that of neat NH_3, while the formation of the Al−CH_3CN complex produces a smaller dipole moment than that of neat CH_3CN. We performed the ab initio calculations, where the Mulliken population analysis suggests the Al→CH_3CN charge flow but the Natural population analysis indicates very little charge flow on the contrary. For the Al−NH_3 complex, the polarization effect of NH_3 and the N→Al σ donation would enhance the dipole moment strength. However, there still remains a disagreement between theory and experiment. Further experimental determination using the hexapole method would complement theoretical calculations and could reveal the basic nature of interaction in the complex systems in general.

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