Activation of Dinitrogen by Gas-Phase Species

Li-hui Mou\textsuperscript{a,b,c}, Gui-duo Jiang\textsuperscript{a,b,c}, Zi-yu Li\textsuperscript{a,c}, Sheng-gui He\textsuperscript{a,b,c}\textsuperscript{*}

\textit{a. State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China}
\textit{b. University of Chinese Academy of Sciences, Beijing 100049, China}
\textit{c. Beijing National Laboratory for Molecular Sciences and CAS Research/Education Center of Excellence in Molecular Sciences, Beijing 100190, China}

(Dated: Received on August 12, 2020; Accepted on September 8, 2020)

Reactions of gas-phase species with small molecules are being actively studied to understand the elementary steps and mechanistic details of related condensed-phase processes. Activation of the very inert N≡N triple bond of dinitrogen molecule by isolated gas-phase species has attracted considerable interest in the past few decades. Apart from molecular adsorption and dissociative adsorption, interesting processes such as C−N coupling and degenerate ligand exchange were discovered. The present review focuses on the recent progress on adsorption, activation, and functionalization of N\textsubscript{2} by gas-phase species (particularly metal cluster ions) using mass spectrometry, infrared photo-dissociation spectroscopy, anion photoelectron spectroscopy, and quantum chemical calculations including density functional theory and high-level \textit{ab initio} calculations. Recent advances including characterization of adsorption products, dependence of clusters’ reactivity on their sizes and structures, and mechanisms of N≡N weakening and splitting have been emphasized and prospects have been discussed.

Key words: Dinitrogen activation, Atomic cluster, Reaction mechanisms

I. INTRODUCTION

Gas-phase reactions can be studied under isolated and well-controlled conditions. Gas-phase species, particularly the atomic clusters with limited number of atoms and well-defined structures, are often used as ideal models of active sites in complex catalytic processes. The investigations on the reactions of gas-phase species with small molecules are thus of great importance and are being actively studied to understand the mechanisms of activation and transformation of chemical bonds, particularly the very inert bonds such as RC−H \cite{1−10}, OC−O \cite{11−17}, H−H \cite{18−23}, and N≡N \cite{24−35}. The gas-phase reactions involving organic (such as CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, CH\textsubscript{3}OH, etc.) and inorganic (such as H\textsubscript{2}, H\textsubscript{2}O, SO\textsubscript{2}, CO, CO\textsubscript{2}, etc.) molecules have been extensively investigated and reviewed in literatures \cite{36−52}. In recent years, activation of small molecules related to energy and environment, such as N\textsubscript{2} \cite{24−35}, has heightened concerns in this field.

N\textsubscript{2} activation is important in view of its abundance in atmosphere and versatility in many fields, such as fertilizers, biomolecules, and medicines \cite{53}. However, the high bond energy (941.7 kJ/mol) and negative electron affinity \cite{54} render its activation a persistent challenge to synthetic as well as theoretical chemistry. The large-scale Haber-Bosch process in industry requires high temperature (~400 °C) and pressure (~25 MPa) to synthesize ammonia and produces large amounts of greenhouse gases \cite{55}. In contrast, the natural nitrogenase can activate and convert N\textsubscript{2} under ambient conditions \cite{56}, which draws extensive attentions to searching for mild and effective systems for N\textsubscript{2} fixation and activation. Though impressive progress has been made in many areas \cite{57−61}, designing a catalyst to produce ammonia under mild conditions on an industrial scale is still a long-term goal. One of the obstacles might lie in the lack of in-depth mechanism analysis due to the complexity of condensed-phase systems \cite{62, 63}. To drive this field forward, therefore, it would be essential to understand the intrinsic mechanisms at the molecular level.

To the best of our knowledge, experimental studies of the reactions between gas-phase species and N\textsubscript{2} were firstly reported in 1985 using a fast-flow reaction device \cite{64} for Co\textsubscript{0} and Nb\textsubscript{n} clusters with N\textsubscript{2}. Since then, a lot of transition metal species including neutral and ionic species (Ta\textsubscript{n} \cite{65}, Mo\textsubscript{n} \cite{66}, W\textsubscript{n} \cite{67}, V\textsubscript{n}Co\textsubscript{0.1} \cite{68}, V\textsubscript{n}O\textsubscript{0.1} \cite{68}, Co\textsubscript{n} \textsuperscript{+/−} \cite{69−71}, Nb\textsubscript{n} \textsuperscript{+/−} \cite{70, 72}, Ag\textsubscript{n} \textsuperscript{+/−} \cite{73}, Ni\textsubscript{n} \textsuperscript{−} \cite{74}, Pt\textsubscript{n} \textsuperscript{−} \cite{74}, Pd\textsubscript{n} \textsuperscript{−} \cite{74}, etc.) have been
prepared and their interactions with N2 have been studied by using the fast flow reactors. Important findings including metal-, size-, and charge-dependent reactivity as well as ligand effects have been demonstrated. However, N2 adsorption modes (molecularly or dissociatively, binding sites, etc.) and the activation mechanisms were still unclear due to the lack of characterization techniques and theoretical analysis. These results have been briefly mentioned in a review article by Zhao et al. [52]. The improvement of reaction devices [75–78], the emergence of infrared photo-dissociation (IRPD) spectroscopy [79, 80] and anion photoelectron spectroscopy (PES) [81, 82], and the application of state-of-the-art quantum chemistry calculations have recently led to further understanding of N2 activation [28–35]. Considering these recent research progresses and the fact that there are very few reviews focusing on the topic of N2 activation by gas-phase species, we will go through the related publications and try to provide a complete outline.

It should be mentioned that matrix isolation infrared spectroscopy is also an effective way to study the bonding and reactivity of simple metal dinitrogen complexes. A lot of studies based on matrix isolation spectroscopy have been published since 1970s [83–92], and a thorough review by Himmel and Reiher covering most of the important progresses by 2006 has been conducted [62]. This short review will emphasize the recent research advances on N2 activation by gas-phase species. The details of the experimental and computational methods can be found in the original contributions.

II. RESULTS AND DISCUSSION

Table I lists the experimentally and theoretically studied reactions between N2 and gas-phase species including the atomic and diatomic ions, bare metal clusters, and some doped clusters since 1985. Most of the clusters adsorb N2 in a molecular way and only a few of them can cleave the N≡N bond for further functionalization. Some selected studies below will emphasize the new mechanisms of N2 adsorption, activation, and functionalization revealed recently by using state-of-the-art experimental and theoretical methods.

A. Molecular adsorption

Scheme 1 shows four modes by which N2 can coordinate to transition metal (M) centers of gas-phase species. The end-on (η1-N2) coordination (Scheme 1(a)) is the most prevalent binding mode for N2 and has been identified in the final adsorption products [28, 33, 110, 115, 116, 128]. The side-on (η2-N2) (Scheme 1(b)) and side-on-side-on (μ-η2-μη2-N2) (Scheme 1(c)) N2 complexes are uncommon and only reported as the theoretical intermediates in the gas-phase reactions [30–32]. The side-on-end-on (μ-η2-η1-N2) binding (Scheme 1(c)) is also uncommon, and the only characterized example is the adduct product V5N7− formed in the reaction of V5N5+ + N2 [34]. Details are depicted below.

1. End-on coordination

This is the most prevalent coordination mode observed for N2 adsorption by gas-phase transition metal species [129]. Such coordination can be characterized by virtue of IRPD spectroscopy. A representative example in this field is shown in FIG. 1 [27] and the result was reported by Niedner-Schatteburg group. A customized Fourier transform-ion cyclotron resonance (FT-ICR) mass spectrometer was employed to perform the processes of cluster production, isolation, N2 condensation, infrared photon dissociation and mass analysis. The IRPD spectra of the [Co9(N2)]1+ (n=8–17) cluster complexes formed in the cryogenic hexapole ion trap have single or multiple IR active bands within the range of 2180–2290 cm−1, which are significantly red-shifted with respect to the IR inactive stretching mode of free N2 (at 2359 cm−1) [130]. This indicates a weakening of the N≡N bond. Molecular adsorption of N2 on naked Co9+ clusters can be confirmed considering dissociative [N−Co9−N]+ adsorption would lead to much lower Co−N stretching frequency (∼600 cm−1). The red-shifts have been also observed in other studies using IRPD method, and can be interpreted by the Blyholder model [131] which explains the σ-donor/π-acceptor synergistic bonding scheme. In this study, [Co9(N2)]1+ and [Co9(N2)]1+ (both at 2285 cm−1) have significant less red-shifts than those of all other complexes studied, which reveals remarkable cluster size dependent features. The [Co10−13(N2)]1+ complexes show only one strong band, while multiple bands for larger clusters (n=14–17) occur and might be due to the complexity of the corresponding geometric and electronic structures. Though the observed spectral features (e.g. the “jump” from n=9 to n=10 or the presence of multiple bands) cannot be assigned perfectly, the density functional theory (DFT) calculations predicted a possible icosahedral Co13+ core and the end-on coordinated N2 in [Co13(N2)]1+ has a stretching frequency of 2221 cm−1 which is close to the experimental result.

Molecular orbital (MO) analysis can be performed to understand the mechanistic details of N2 adsorption by metal clusters. The TaC4− cluster anion was observed to adsorb N2 while TaC1−3− anions were inert under 298 K in a linear ion trap reactor [28]. The DFT calculations predicted that there is a negligible barrier when N2 molecule approaches to TaC4− while insurmountable barriers will be encountered along the reaction pathways of TaC1−3− with N2. The MO analysis for the separate reactants [TaCn− (n=1–4) and N2] and the adsorption complexes (TaCnN2−) gave valuable insights into the adsorption mechanisms. The frontier orbitals
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To be continued.
and corresponding orbital compositions are shown in FIG. 2. It is known that the lowest unoccupied molecular orbital (LUMO) of \( N_2 \) is \( \pi^\star \) antibonding molecular orbital. The \( \alpha \)-highest occupied molecular orbital (\( \alpha \)-HOMO) of \( TaC_4^- \) is mainly composed of \( \pi \)-type \( Ta 5d_{xz, yz} \) orbital (68.91\%), which has matched symmetry with the \( \pi^\star \) orbital of \( N_2 \), thus resulting in a favorable orbital overlap (FIG. 2(b)). During \( N_2 \) adsorption, the electrons are transferred from \( Ta \) to \( N_2 \) (\( \pi \) back-donation) to weaken the \( N\equiv N \) bond, where the \( N_2 \) molecule serves as a \( \pi \) acceptor. In contrast, the \( \pi \)-type \( Ta 5d \) orbitals of \( TaC_1\cdots \) that have matched symmetry with the \( \pi^\star \) orbital of \( N_2 \) are below the corresponding \( \alpha \)-HOMO orbitals, which leads to more \( \sigma \) repulsion and an unfavorable energy barrier in the initial \( N_2 \) adsorption. This study sizes the \( C_n \) ligand effect on the electronic structure and \( N_2 \) adsorption reactivity of the transition metal center.

2. Side-on-end-on coordination

This very uncommon coordination mode to trap \( N_2 \) in a reaction product has been recently characterized for the \( V_5N_7^- \) anion that was produced through the reaction of \( V_5N_5^- \) with \( N_2 \) \((V_5N_5^-+N_2\rightarrow V_5N_7^-)\) in a linear ion trap reactor and studied by the photoelectron imaging spectroscopy (PEIS) and the DFT calculations [34]. The pseudo-first-order rate constant \( (k_1) \) for the reaction of \( V_5N_5^- \) with \( N_2 \) was determined to

\[ \text{Rate} = k_1 \times [V_5N_5^-] \times [N_2] \]

Table I continue.

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<tr>
<td>( Ta_{3}N_{3}H_{0,1}^- )</td>
<td>( Ta_{3}N_{3}H_{0,1}N_{2}^- )</td>
<td>( (6.4\pm 1.3) \times 10^{-13} )</td>
<td>( \text{C, H, theory} )</td>
<td>( \text{ligand effect} )</td>
<td>2019 [32]</td>
</tr>
</tbody>
</table>

\(^{a}\) The rate constants \( k_1 \) are in unit of \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}.
\(^{b}\) The experimental methods are labelled as \( A−I \): \( A \): fast flow reactor-mass spectrometry (MS), \( B \): collision cell-MS, \( C \): linear ion trap reactor-MS, \( D \): FT-ICR cell-MS, \( E \): thermal desorption spectrometry, \( F \): IR-PD spectroscopy, \( G \): guided ion beam-MS, \( H \): photoelectron spectroscopy, and \( I \): photodissociation spectroscopy.

(Fig. 2). It is known that the lowest unoccupied molecular orbital (LUMO) of \( N_2 \) is \( \pi^\star \) antibonding molecular orbital. The \( \alpha \)-highest occupied molecular orbital (\( \alpha \)-HOMO) of \( TaC_4^- \) is mainly composed of \( \pi \)-type \( Ta 5d_{xz, yz} \) orbital (68.91\%), which has matched symmetry with the \( \pi^\star \) orbital of \( N_2 \), thus resulting in a favorable orbital overlap (FIG. 2(b)). During \( N_2 \) adsorption, the electrons are transferred from \( Ta \) to \( N_2 \) (\( \pi \) back-donation) to weaken the \( N\equiv N \) bond, where the \( N_2 \) molecule serves as a \( \pi \) acceptor. In contrast, the \( \pi \)-type \( Ta 5d \) orbitals of \( TaC_1\cdots \) that have matched symmetry with the \( \pi^\star \) orbital of \( N_2 \) are below the corresponding \( \alpha \)-HOMO orbitals, which leads to more \( \sigma \) repulsion and an unfavorable energy barrier in the initial \( N_2 \) adsorption. This study sizes the \( C_n \) ligand effect on the electronic structure and \( N_2 \) adsorption reactivity of the transition metal center.

2. Side-on-end-on coordination

This very uncommon coordination mode to trap \( N_2 \) in a reaction product has been recently characterized for the \( V_5N_7^- \) anion that was produced through the reaction of \( V_5N_5^- \) with \( N_2 \) \((V_5N_5^-+N_2\rightarrow V_5N_7^-)\) in a linear ion trap reactor and studied by the photoelectron imaging spectroscopy (PEIS) and the DFT calculations [34]. The pseudo-first-order rate constant \( (k_1) \) for the reaction of \( V_5N_5^- \) with \( N_2 \) was determined to

\[ \text{Rate} = k_1 \times [V_5N_5^-] \times [N_2] \]

 DOI:10.1063/1674-0068/cjcp2008141 ©2020 Chinese Physical Society
The DFT calculations predicted a large N−4 reactant and product clusters generated in the experiment, which can interpret the experimental results. The table able energy barrier for the following N−4−4 and mental value. Therefore, the DFT calculated 4.26 eV, which is in good agreement with the experimental result. For V5N3H−, the vertical detachment energy (VDE) of 1.74 eV, which is very close to the experimental result. For V5N3−, the ground state has a non-dissociative N2 unit (V5N7−) based on the structure of 4V5N5−. The theoretical VDE value of 4V5N7− is 2.26 eV, which is in good agreement with the experimental value. Therefore, the DFT calculated 4V5N5− and 4V5N7− are the most probable structures of the reactant and product clusters generated in the experiments. The DFT calculations predicted a large N2 binding energy of 1.95 eV for 4V5N7− and an insurmountable energy barrier for the following N−N cleavage process, which can interpret the experimental results. The MO analysis (FIG. 3(c)) reveals that this very stable coordination mode results from an efficient orbital overlap between the d-d bonding orbital of the dual metal sites (V1−V2) and π* orbital of N2.

B. N≡N cleavage and functionalization

1. Hydrogen-assisted N≡N cleavage

It is significant to study the role of hydrogen in N2 activation because hydrogen is related to both Haber-Bosch process and biological nitrogen fixation. A study on the reactivities of Co3Dn− (n=0–4) with N2 reveals that the deuterium atoms can lead to less negatively charged Co centers and lift the HOMO energies of Co3H2−4−, thus facilitating N2 approaching and π back-donation [33]. The important role of hydrogen atom has also been recently demonstrated by dissociative N2 adsorption onto Ta3N3H0.1− [32]. The reactions of Ta3N3H0.1− cluster anions with N2 in a linear ion trap reactor resulted in the adsorption products assigned as Ta3N3H0.1−:

Ta3N3− + N2 → Ta3N5− (1)
Ta3N3H+ + N2 → Ta3N5H− (2)

The pseudo-first-order rate constant for the reaction of Ta3N3H− with N2 is (3.2±0.7)×10−12 cm3-molecule−1·s−1, which is five times faster than that of Ta3N3− with N2 (6.4±1.3)×10−13 cm3-molecule−1·s−1. The PES experiments and quantum chemical calculations were carried out to study the structures of reactants and products as well as the mechanistic details. As shown in FIG. 4, the VDE values of Ta3N3− and Ta3N3H− are 2.07 and 1.87 eV, respectively. For the N2 adduct products, the VDE values of Ta3N3− and Ta3N3H− are 2.50 and 2.69 eV, respectively. Obviously, the experimental VDE values of products are significantly blue-shifted with respect to those of reactants, and the degree of blue-shift is much higher for Ta3N3H−/Ta3N3− pair (0.82 eV) than Ta3N3−/Ta3N3− pair (0.43 eV). The quantum chemistry calculated low-lying isomers for Ta3N3− (R1, R1′) and Ta3N3H− (R2, R2′) are presented in FIGs. 4(c1) and (c2). From the relative energies and the match of the experimental and theoretical VDE values, the R1 and R2 are the most likely species generated in the experiment. The geometric structure of R2 (Ta3N3H−) differs significantly from that of R1 (Ta3N3−). The R1 has one Ta−Ta bond (269 pm) and three two-fold coordinated N atoms with the doublet state while R2 is in triplet state and has one three-fold coordinated N atom. The DFT calculated VDE values of R1 (2.08 eV) and R2 (1.83 eV) well match the experimental results (2.07 eV and 1.87 eV). It is noteworthy that additional density of states (DOS) simulations [132] indicated that several structures might coexist for Ta3N3− and Ta3N3H−.
FIG. 2 (a) A comparison on frontier orbitals of TaC−, TaC2−, TaC3−, and TaC4−. The atomic orbital compositions of Ta are given. The highlighted orbital has matched symmetry with the π* orbital of N2. (b) A favorable orbital overlap between TaC4− and N2. Adapted from Ref.[28] ©2018 American Chemical Society.

while R1 and R2 were the major components generated in the experiments.

The DFT calculated reaction pathways for Ta3N3H0.1− with N2 are shown in FIG. 5. For the Ta3N3H+ + N2 reaction system (FIG. 5(a)), N2 molecule is initially trapped by a Ta atom in a side-on mode (η2) to form I1 (−1.10 eV). Via TS1, N2 is anchored by two Ta atoms to form I2, where the N−N bond is elongated from 110 pm in free N2 to 134 pm. The N−N bond is completely broken by surmounting TS2 (−0.87 eV) to produce P1 (−3.11 eV) with a terminal nitrogen atom. In the reaction of Ta3N3− with N2 (FIG. 5(b)), the initial complex I3 (−1.42 eV) also has a η2-coordinated N2, which transforms to I4 in a side-on-end-on mode (η2:η1) through TS3. Then, a critical structure I5 with a three-fold coordinated N atom shows up by overcoming TS4, and finally, N−N is cleaved to form the product P2 (−2.97 eV) via TS5 (−0.66 eV). Therefore, the strong N≡N bond can be cleaved by both Ta3N3H− and Ta3N3− clusters, and the former is more favorable kinetically and thermodynamically than the latter, which is consistent with the experimental results that Ta3N3H− is more reactive toward N2 than Ta3N3−. Further analysis reveals that this hydrogen-assisted reactivity is ascribed to the different geometric structure and charge distribution as well as the higher HOMO energy of Ta3N3H− caused by the presence of H atom, which results in more electron storage in Ta−Ta bond of Ta3N3H−, and more favorable π-back donation to N2.

2. C−N coupling

Functionalization of N2 after breaking N≡N bond is a persistent pursuit in gas-phase studies, but so far, has been rarely reported. A ditantalum carbide cluster anion (Ta2C4−) has been recently found to couple the cleavage of N≡N bond with the formation of a C−N bond under mild conditions using mass spectrometry, PEIS, and quantum chemistry calculations [29]. As shown in FIG. 6, the reaction of Ta2C4− with N2 in a linear ion trap reactor resulted in the formation of Ta2C4N2−:

$$\text{Ta}_2\text{C}_4^{−} + \text{N}_2 \rightarrow \text{Ta}_2\text{C}_4\text{N}_2^{−} \quad (3)$$

The pseudo-first-order rate constant of reaction (3) was estimated to be \((2.0±0.3) \times 10^{-11} \text{ cm}^3\text{-molecule}^{-1}\text{-s}^{-1}\). Collision-induced dissociation (CID) experiments using Xe (FIGs. 6 (c−g)) as collision gas suggested that the losses of N2 and CN− units would occur when the center-of-mass collisional energies \((E_c)\) were greater
FIG. 3 The experimental photoelectron spectra and DFT calculated lowest-lying structures of (a) V$_5$N$_5^-$ and (b) V$_5$N$_7^-$. (c) The molecular orbital interaction between V$_5$N$_5^-$ and the side-on-end-on coordinated N$_2$ unit. The experimental VDE values in eV are given. Adapted from Ref.[34] ©2019 Wiley-VCH.

than 3.3 and 4.6 eV, respectively:

$$\text{Ta}_2\text{C}_4\text{N}_2^- + \text{Xe} \rightarrow \text{Ta}_2\text{C}_4^- + \text{N}_2 + \text{Xe}$$

$$E_c \geq 3.3 \text{ eV} \tag{4}$$

$$\text{Ta}_2\text{C}_4\text{N}_2^- + \text{Xe} \rightarrow \text{Ta}_2\text{C}_3\text{N} + \text{CN}^- + \text{Xe}$$

$$E_c \geq 4.6 \text{ eV} \tag{5}$$

The CN$^-$ fragment observed experimentally suggests the formation of a C–N bond, which is supported by the quantum chemistry calculated reaction pathway shown in FIG. 7.

In the most favorable reaction pathway of Ta$_2$C$_4$-N$_2$ (FIG. 7), the N$_2$ molecule is initially trapped by the Ta atom with a binding energy of 0.53 eV ($\Delta H_0$) to form an end-on coordinated complex I6. A side-on-bridging complex (I7) with larger binding energy (1.24 eV) occurs by overcoming TS6. Subsequently, by surmounting a barrier of 0.69 eV (TS7), the N–N bond is cleaved to form I8. After that, the formation of C–N bond takes place via TS8 to generate a more stable intermediate I9. The subsequent cleavage of the C–CN bond (TS9) leads to the formation of end-on bonded CN unit, which has the character of a triple bond and the bond length (118 pm) is quite close to that of the cyanide anion (CN$^-$, 117 pm). The energy required for dissociation from I10 to Ta$_2$C$_4$-N$_2$ and Ta$_2$C$_3$N+CN$^-$ is calculated to be 3.23 and 3.86 eV, respectively, which is generally consistent with the CID experiments. The PEIS experiments were carried out to characterize the structure of the adsorption product. It turns out that the intermediate I10 with an end-on bonded CN unit is the most probable product in the experiment. The natural population analysis reveals that the Ta–Ta bond is the major electron donor to weaken and eventually cleave the N≡N bond, and the two crucial C$_2$ ligands make the Ta atoms more positively charged. The MO analysis verifies the role of Ta–Ta center as an electron reservoir that consecutively provides the requisite electrons to break the N≡N bond.

3. Degenerate ligand exchange

This unprecedented thermal reaction between Ta$_2$N$_2$ and N$_2$ has been recently reported by using FT-ICR mass spectrometry in conjunction with quantum chemical calculations [31]. The FT-ICR mass spectra are shown in FIG. 8. The mass-selected and thermalized Ta$_2$N$^+$ could react with trace amounts of background gases like oxygen or water, to generate Ta$_2$NO$^+$ and Ta$_2$NOH$_2^+$ (FIG. 8(a)). Upon introducing $^{15}$N$_2$ into the ICR cell, a new signal assigned as Ta$_2$N$_2$ was observed (FIG. 8(b)) while no additional signal appeared when leaking the unlabeled N$_2$, suggesting the following channel:

$$\text{Ta}_2^{14}\text{N}^+ + ^{15}\text{N}_2 \rightarrow \text{Ta}_2^{15}\text{N}^+ + ^{14}\text{N}^{15}\text{N} \tag{6}$$

The rate constant for this reaction amounts to $1.9 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$, which corresponds to a collision efficiency ($\phi$) of 3.0%.
Quantum chemical calculations revealed that Ta$_2$NO$^+$ and Ta$_2$NOH$_2^+$ are impossible to involve in the formation of Ta$_2$N$^{15}$N$^+$ because the following channels are heavily endothermic:

$$\text{Ta}_2\text{NO}^+ + 15\text{N}_2 \rightarrow \text{Ta}_2\text{N}^{15}\text{N}^+ + 15\text{NO}$$  (7)
$$\text{Ta}_2\text{NOH}_2^+ + 15\text{N}_2 \rightarrow \text{Ta}_2\text{N}^{15}\text{N}^+ + \text{H}_2\text{N}^{15}\text{NO}$$  (8)

Therefore, the Ta$_2$N$^{15}$N$^+$ must stem from a degenerate ligand exchange reaction in which the active species Ta$_2$N$^{14}$N$^+$ firstly breaks the triple bond of N$^2$ and then reassembles the N atoms to form Ta$_2$N$^{15}$N$^+$ and N$_2$.

The DFT calculated most favorable potential energy profile is presented in FIG. 9. The N$_2$ molecule is firstly captured by two Ta atoms in a side-on-end-on mode ($\mu$-\text{$\eta$}$^2$-$\eta$-$\text{N}_2$) to form I1, where the N–N bond is stretched from 109 pm to 133 pm. Further elongation of N–N bond (150 pm) proceeds over TS10 and the formed I12 contains a doubly side-on bonded N$_2$ unit ($\mu$-\text{$\eta$}$^2$-$\eta$-$\text{N}_2$). The final and complete rupture of N–N bond takes place easily by surmounting a minor barrier (TS11) and generates a global minimum (I13) that has two structurally equivalent, symmetry-related N atoms (i.e., N and N$_a$). After that, the reverse processes from I13 to the final products including I13$\rightarrow$TS11$\rightarrow$I12$\rightarrow$TS10$\rightarrow$I11$\rightarrow$Ta$_2$N$^{15}$N$^+$ $+ \text{N}^{14}\text{N}_{2}$ ensue under the same potential energies. It is found that the oscillation of Ta–Ta bond length plays a vital role in the whole process, namely, the elongation and shrinkage of Ta–Ta bond occur alternately, which has resemblance with that in the Ta$_2^+/\text{N}_2$ system reported earlier [30]. The MO analysis provides a better understanding on the roles of Ta–Ta bond in the N≡N triple bond cleavage process. That is, the donation of d-electrons from Ta–Ta centers to $\pi^*$ antibonding orbitals of N$_2$, and the concurrent electron transfer from the bonding $\pi$ and $\sigma$ orbitals of N$_2$ to empty d-orbitals of the Ta atoms synergistically weaken and break the N≡N bond. Note that the donation of d-electrons from Ta–Ta centers to $\pi^*$ antibonding orbitals of N$_2$ plays a dominant role in the N$_2$ activation. This degenerate ligand exchange involving dis- and re-assembly of N$_2$, which can also be regarded as the scope of N$_2$ functionalization ($\text{N}^{14}\text{N}^{15}$ coupling), constitutes a catalytic cycle in view of the...
FIG. 7 The quantum chemistry calculated potential energy profile for Ta$_2$C$_4^-$+$N_2$→Ta$_2$C$_3$N$^-$+CN$^-$. The relative energies ($\Delta H_0$ in eV) with respect to the separate reactants (Ta$_2$C$_4^-$+$N_2$) are given. Adapted from Ref.[29] ©2019 American Chemical Society.

FIG. 8 Mass spectra for the reaction of Ta$_2$N$^+$ with (a) Ar at 5.0×10$^{-3}$ mPa and (b) $^{15}$N$_2$ at 5.0×10$^{-3}$ mPa after a reaction time of 8 s at ambient temperature. Adapted from Ref.[31] ©2019 National Academy of Sciences.

unchanged catalytically active species Ta$_2$N$^+$ after the thermal reaction.

4. N≡N cleavage by trinuclear metal centers

Investigation on the mechanism of N≡N bond dissociation is of great importance for designing efficient catalysts. Three kinds of intermediates for N$_2$ cleavage are shown in Scheme 2. The dinuclear side-on-end-on ($\mu$-$\eta^2$-$\eta^1$-N$_2$) and side-on-side-on ($\mu$-$\eta^2$-$\eta^2$-N$_2$) modes shown in Scheme 2(a) and 2(b) prevail in most of the reported examples of N≡N bond cleavage [30−32, 89, 90]. Recently, a key intermediate with N$_2$ binding to three metal atoms in the end-on/side-on/side-on ($\mu_3$-$\eta^1$-$\eta^2$-$\eta^2$-N$_2$) mode (Scheme 2(c)), has been identified in the facile N≡N cleavage by V$_3$C$_4^-$ anions [35].

Upon the reactions of V$_3$C$_4^-$ cluster anion with N$_2$ in a linear ion trap reactor, an adsorption product assigned as V$_3$C$_4$N$_2^-$ was observed, suggesting the following reaction channel:

$$V_3C_4^- + N_2 \rightarrow V_3C_4N_2^- \quad (9)$$

The pseudo-first-order rate constant for the reaction of V$_3$C$_4^-$ with N$_2$ is $(8.7\pm1.8)\times10^{-12}$
cm$^3$-molecule$^{-1}$-s$^{-1}$. The CID experiments using Xe as collision gas showed that the losses of the V atom and CN$^-$ anion occurred at threshold energies near 3.8 and 4.8 eV, respectively, corresponding to the following dissociation channels:

\[
V_3C_4N_2^- + Xe \rightarrow V_2C_4N_2^- + V + Xe, \quad E_c \geq 3.8 \text{ eV} \quad (10)
\]

\[
V_3C_4N_2^- + Xe \rightarrow V_3C_3N + CN^- + Xe, \quad E_c \geq 4.8 \text{ eV} \quad (11)
\]

The loss of V and CN$^-$ rather than N$_2$ from V$_3$C$_4$N$_2^-$ in the CID experiment indicated that the N$_2$ unit is dissociatively adsorbed onto V$_3$C$_4$ cluster, and a CN unit is formed in the product V$_2$C$_4$N$_2^-$. This is supported by the PEIS experiments and quantum chemistry calculations. Structure characterization by the PEIS experiments revealed that the V$_3$C$_4$$^-$ anion has a V$_2$ core coordinated by two C$_2$ ligands (labeled as $^1R3$), and the low-lying isomers with dissociated N$_2$ unit and a C$-$N bond are the most probable structures of V$_3$C$_4$N$_2^-$ (labeled as P3 and P4).

FIG. 10 shows the most favorable reaction pathway for the formation of P3 and P4 from $^1$R3+N$_2$ calculated by quantum chemistry calculations. The reaction starts with N$_2$ adsorption on one V atom (marked as V1) to form the end-on coordinated I14. Via TS12, N$_2$ is trapped by two V atoms (V1 and V2) in the side-on-end-on mode, and the N$-$N bond is reduced to the double bond in I15 (bond length of 121 pm). After that, the structural rearrangement of the cleavage of a V$-$C bond (I15$\rightarrow$TS13$\rightarrow$I16) and the formation of a V$-$N bond (I16$\rightarrow$TS14$\rightarrow$I17) take place. A key intermediate I17 with the N$_2$ unit bonded with three metal atoms in the end-on-side-on-side-on (ESS) mode is formed. In I17, the N$-$N bond is elongated to 136 pm, which is the typical value of a N$-$N single bond. Subsequently, by overcoming a surmountable barrier of 0.60 eV (TS15), the N$-$N bond splitting to generate I18 containing two bridging N atoms is achieved. In contrast, the direct N$-$N cleavage from I15 via the dinuclear metal center encounters a high energy barrier of 2.18 eV (TS19). After the N$-$N bond cleavage, the C$-$N coupling takes place (I18$\rightarrow$TS16$\rightarrow$I19), and the consecutive cleavage of the C$-$CN bond leads to the formation of the low-lying isomer P3 (I19$\rightarrow$TS17$\rightarrow$P3), which can be isomerized to P4 by overcoming a small energy barrier of 0.51 eV (TS18).

In this work, the intermediate with the N$_2$ unit bound to three V atoms in the ESS coordination mode (I17) accounts for the facile dissociation of N$_2$ triple bond. To gain a comprehensive understanding of the bonding character between the metal center (V$_3$) and the N$_2$ unit, the molecular orbital analysis on the orbital interactions in the ESS-coordinated V$_3$C$_4$N$_2^-$ and V$_3$N$_2^-$ was performed (FIG. 11). It turns out that the strong orbital interactions in V$_3$C$_4$N$_2^-$ derive from the $\pi$ backdonation from the metal core V$_3$ to the N$_2$ unit. One molecular orbital (denoted as $\psi_y$) in V$_3$C$_4$N$_2^-$ composed of three d atomic orbitals (d$_{xz}$ of V1, d$_{yz}$ of V2, and d$_{xy}$ of V3) has the proper symmetry to match well with the empty antibonding orbital ($\pi^*_x$) of N$_2$. The other molecular orbital (denoted as $\psi_z$) composed of three other d atomic orbitals (d$_{xz}$ of V1, d$_{x^2}$ of V2, and d$_{z^2}$ of V3) can also overlap efficiently with the other
FIG. 10 Potential-energy profile for $\text{V}_3\text{C}_4^-$ (R3) + $\text{N}_2$ → $\text{V}_3\text{C}_4\text{N}_2^-$ (P3/P4) in the restricted closed-shell singlet state. Energies in eV and selected bond lengths in pm are given. Adapted from Ref.[35] ©2020 American Chemical Society.

FIG. 11 Molecular orbital interactions between the occupied orbitals ($\psi_y$ and $\psi_{xz}$) of (a) $\text{V}_3\text{C}_4^-$ and (b) $\text{V}_3^-$ with the unoccupied orbitals ($\pi_x^*$ and $\pi_y^*$) of the $\text{N}_2$ unit. Adapted from Ref.[35] ©2020 American Chemical Society.

empty antibonding orbital ($\pi_y^*$) of $\text{N}_2$. As a result, the two $\pi^*$ orbitals of $\text{N}_2$ are highly occupied (27% in $\psi_y^*\rightarrow\pi_x^*$ and 22% in $\psi_{xz}\rightarrow\pi_y^*$), which leads to the high activation degree of N−N bond in I17 and the following feasible N−N bond cleavage. This study reveals a new mechanism of N≡N bond cleavage by gas-phase polynuclear metal clusters.

III. CONCLUSION AND OUTLOOK

In this review, $\text{N}_2$ activation by gas-phase species investigated using experimental and theoretical methods has been discussed. Compared to the earlier investigations, the application of characterization techniques including anion photoelectron spectroscopy (PES) and its extension of photoelectron imaging spectroscopy...
ing an early transition metal which has higher d-based on the current knowledge. Note that combin-
monia and N-containing organic compounds are still of the intact or broken N
nels like A+N
2
activation by gas-phase species, while new reaction chan-
even reaction channels.
of reactant clusters, thus changing the reactivities and
factors: (i) The electrons in the filled d orbitals of metal
 TCHAR
The introduction of Blyholder model interprets that the
activation were demonstrated under a molecular level. The detailed activation mechanisms and key factors
governing the kinetics and thermodynamics of N
2
structures, charge distributions, and
π-donor. In most cases, N2 is a better
-pi donor. The ancillary lig-
ands such as H, C, and N atoms can alter the geometric
structures, charge distributions, and d orbital energies of reactant clusters, thus changing the reactivities and
even reaction channels.

These remarkable progresses have shed light on N2 ac-
tivation by gas-phase species, while new reaction chan-
nels like A+N2→C+D (C, D≠N2) and hydrogenation of the intact or broken N2 as well as synthesis of
ammonia and N-containing organic compounds are still a pursuit. To achieve this, on the one hand, species with higher reactivities need to be tactfully designed based on the current knowledge. Note that combining an early transition metal which has higher d orbital energies with a late transition metal that owns more d electrons might be a promising approach. On the other hand, the enhance of the cluster reactors working at high gas pressure and long reaction time, and the design of a multi-stage tandem reactor may be indis-

dispensable to detect new reaction channels. Meanwhile, the improvement of characterization techniques (better resolution and sensitivity of PES/PEIS/IRPD) and the development of theoretical methods are also helpful. It is hopeful to synthesize ammonia or N-containing organ-
compounds in gas-phase studies with the develop-
ment of the experimental and theoretical methods.

IV. ACKNOWLEDGMENTS

This work was supported by the National Natu-
ral Science Foundation of China (No.21833011 and No.21973101), the Youth Innovation Promotion Asso-
ciation CAS (No.2020034), and the K. C. Wong Educa-
tion Foundation.

Activation of Dinitrogen by Gas-Phase Species


