Title
R-matrix calculation of integral and differential cross sections for low-energy electron-impact excitations of the N$_2$ molecule

Author(s)
Tashiro, Motomichi; Morokuma, Keiji

Citation
PHYSICAL REVIEW A (2007), 75(1)

Issue Date
2007-01

URL
http://hdl.handle.net/2433/50520

Copyright 2007 American Physical Society

Type
Journal Article

Textversion
publisher
R-matrix calculation of integral and differential cross sections for low-energy electron-impact excitations of the $N_2$ molecule

Motomichi Tashiro* and Keiji Morokuma

Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, Georgia 30322, USA

(Rceived 12 July 2006; revised manuscript received 17 November 2006; published 30 January 2007)

Low-energy electron-impact excitations of $N_2$ molecules are studied using the fixed-bond R-matrix method based on state-averaged complete active-space self-consistent-field orbitals. Thirteen target electronic states of $N_2$ are included in the model within a valence configuration interaction representation of the target states. Integrated as well as differential cross sections of the $A^3\Sigma_u^+, B^3\Pi_u, W^3\Delta_u, B^1\Sigma_u^+, a^1\Sigma_g^+, a^1\Pi_g, w^1\Delta_u$, and $C^3\Pi_u$ states are calculated and compared with the previous experimental measurements. These excitations, especially of the higher four states, have not been studied enough theoretically in the previous literature. In general, good agreements are observed both in the integrated and differential cross sections. However, some discrepancies are seen in the integrated cross sections of the $A^3\Sigma_u^+$ and $C^3\Pi_u$ states, especially around a peak structure.

DOI: 10.1103/PhysRevA.75.012720

I. INTRODUCTION

Electron-impact excitation of nitrogen molecules plays an important role in atmospheric emission of planets and satellites such as the Earth, Titan, and Triton. For example, excitation of the $a^1\Pi_g$ state and subsequent transitions to the ground $X^1\Sigma_g^+$ state are responsible for the far-ultraviolet emissions of the Lyman-Birge-Hopfield system which are prominent in the airglow of the Earth’s atmosphere [1]. Recently, Khakoo et al. [2] measured differential cross sections (DCS’s) of electron-impact excitation of the $N_2$ molecule from the ground $X^1\Sigma_g^+$ state to the eight lowest excited electronic states of $A^3\Sigma_u^+, B^3\Pi_u, W^3\Delta_u, B^1\Sigma_u^+, a^1\Sigma_g^+, a^1\Pi_g, w^1\Delta_u$, and $C^3\Pi_u$ states. Based on their differential cross-section data, Johnson et al. [3] derived integral cross sections (ICS’s) for these electron-impact excitations. In general, their ICS’s are smaller than the other experimental cross sections at low impact energies below 30 eV. These deviations may have some significance for the study of atmospheric emissions, because a mean kinetic energy of electrons at high altitudes is about 10 eV [4]. To shed light on this situation from a theoretical point of view, we perform ab initio R-matrix calculations of electron-impact excitations of $N_2$ molecules in this work.

Many previous experimental measurements have been focused on excitation to a specific electronic state. For example, Ajello and Shemansky [5] and Mason and Newell [6] measured ICS’s for electron-impact excitation to the $a^1\Pi_g$ state, whereas Poparic et al. [7], Zubek [8], and Zubek and King [9] measured cross sections for the $C^3\Pi_u$ state. In addition to these works, Zetner and Trajmar [10] reported excitation cross sections to the $A^3\Sigma_u^+, B^3\Pi_u, W^3\Delta_u$, and $a^1\Pi_g$ states. So far, comprehensive measurements of the excitation to the eight lowest electronic states are limited to the three groups of Cartwright et al. [11], Brunger and Teubner [12], and Khakoo et al. [2]. The measurements of Brunger and Teubner [12] include excitation DCS’s for the $E^3\Sigma_g^+$ and $a^1\Sigma_g^+$ states in addition to the eight lowest excited states. The DCS’s of Brunger and Teubner [12] and Khakoo et al. [2] were later converted to ICS’s by Campbell et al. [13] and Johnson et al. [3], respectively. Detailed reviews of electron $N_2$ collisions can be found in Itikawa [14] and Brunger and Buckman [15].

Several groups have performed theoretical calculation of low-energy electron collisions with $N_2$ molecules. For example, Chung and Lin [16] employed the Born approximation to calculate excitation cross sections for the 11 target states including the $A^3\Sigma_u^+, B^3\Pi_u, W^3\Delta_u, a^1\Pi_g, w^1\Delta_u$, and $C^3\Pi_u$ states. Later, the same group of Holley et al. [17] calculated excitation ICS’s for the $a^1\Pi_g$ state using a two-state close-coupling method. Fliflet et al. [18] and Mu-Tao and McCoy [19] reported distorted-wave cross sections for excitation of the $A^3\Sigma_u^+, B^3\Pi_u, W^3\Delta_u, a^1\Pi_g$, $C^3\Pi_u$, $E^3\Sigma_g^+$, $b^1\Sigma_g^+$, and $c^1\Pi_g$ states. In general, these approximate methods are expected to be accurate at high impact energies above 30 eV. However, a more elaborate method is required for precise comparison with experiments at low energies.

Gillan et al. [20] calculated excitation ICS’s for the $A^3\Sigma_u^+$, $B^3\Pi_u$, and $W^3\Delta_u$ states using the fixed-nucleus R-matrix method. They included the four lowest target states in their R-matrix model, with target configuration interaction (CI) wave functions containing 2–13 Configuration State Function (CSF’s). Their cross sections for the $A^3\Sigma_u^+$ and $W^3\Delta_u$ states agree well with the experimental results of Cartwright et al. [11]. However, ICS’s for the $B^3\Pi_u$ state deviate considerably from the experimental cross sections. Subsequently, they extended their R-matrix model to include the eight lowest valence states [21]. Their target CI wave functions were much improved from their previous work by employing valence active space description, resulting in 68–120 CSF’s per target state. In their paper, the ICS’s were shown for the $A^3\Sigma_u^+$, $B^3\Pi_u$, $W^3\Delta_u$, and $B^1\Sigma_u^+$ states, while the DCS’s were presented for only the $A^3\Sigma_u^+$ state. Agreement with the ICS’s of Cartwright et al. [11] is good for these four excited states. However, agreement is marginal at DCS level.
In this work, we study electron impact excitation of \( \text{N}_2 \) molecules by the fixed-nucleus \( R \)-matrix method as in our previous work on electron \( \text{O}_2 \) scatterings [22,23]. Although our theoretical treatment is similar to the previous work of Gillan et al. [21], more target states and partial waves of a scattering electron are included in the present work. The main purpose of this work is a comparison of ICS’s as well as DCS’s for the eight lowest excited states with the experimental results of Cartwright et al. [11], Brunger and Teubner [12], Campbell et al. [13], Khakoo et al. [2], and Johnson et al. [3]. This is because previous theoretical works have covered only a part of these eight excitations.

In this paper, details of the calculation are presented in Sec. II, and we discuss the results in Sec. III comparing our ICS’s and DCS’s with the previous theoretical and available experimental data. Then summary is given in Sec. IV.

II. THEORETICAL METHODS

The \( R \)-matrix method itself has been described extensively in the literature [24–26] as well as in our previous paper [22]. Thus we do not repeat general explanation of the method here. We used a modified version of the polyatomic programs in the UK molecular \( R \)-matrix codes [24]. These programs utilize Gaussian-type orbitals (GTO’s) to represent target electronic states as well as a scattering electron. Although most of the previous \( R \)-matrix works on electron \( \text{N}_2 \) collisions have employed Slater-type orbitals (STO’s), we select GTO’s mainly because of simplicity of the input and availability of basis functions. In the \( R \)-matrix calculations, we have included 13 target states: \( \Sigma^+_1 \), \( \Sigma^-_1 \), \( \Pi^+_1 \), \( \Delta^-_1 \), \( \Delta^+_1 \), \( \Delta^-_2 \), \( \Delta^+_2 \), \( \Pi^-_2 \), \( \Pi^+_2 \), \( \Sigma^-_3 \), \( \Sigma^+_3 \), \( \Pi^-_3 \), \( \Pi^+_3 \). The potential energy curves of these target electronic states are shown in Fig. 1 for reference. These target states were represented by valence configuration interaction wave functions constructed by state-averaged complete active-space self-consistent-field (SA-CASSCF) orbitals. Note that some target states, \( 3\Sigma^+_1 \), \( 3\Sigma^-_1 \), and \( 1\Sigma^-_1 \), are Rydberg states and cannot be described adequately in the present valence active space. Inclusion of these states is intended to improve the quality of the \( R \)-matrix calculations by adding more target states in the model, as in our previous works [22,23] as well as other \( R \)-matrix works [27,28]. A test calculation was performed with an extra \( 4a_g \) orbital in the target orbital set. However, the target excitation energies as well as the excitation cross sections did not change much compared to the results with the valence orbital set described above. Also, removal of the \( 3b_{1u} \) orbital from the target active space did not affect the result much in our calculation. In this study, the SA-CASSCF orbitals were obtained by calculations with MOLPRO suites of programs [29]. The target orbitals were constructed from the \([5\sigma 3\pi 1\delta]\) level of basis set taken from Sarpa et al. [30]. In our fixed-bond \( R \)-matrix calculations, the target states were evaluated at the equilibrium bond length \( R=2.068a_0 \) of the \( \text{N}_2 \) \( X^1\Sigma^+_g \) ground electronic state. Although we also performed calculations with \( R=2.100a_0 \) as in the previous \( R \)-matrix calculation of Gillan et al. [21], the cross sections with \( R=2.068a_0 \) and \( R=2.100a_0 \) are almost the same. Thus, we will only show results with the equilibrium bond length of \( \text{N}_2 \) in the next section. The radius of the \( R \)-matrix sphere was chosen to be \( 10a_0 \) in our calculations. In order to represent the scattering electron, we included diffuse Gaussian functions up to \( l=5 \), with nine functions for \( l=0 \), seven functions for \( l=1–3 \), and six functions for \( l=4 \) and 5. Exponents of these diffuse Gaussians were fitted using the GTOBAS program [31] in the UK \( R \)-matrix codes. In addition to these continuum orbitals, we included eight extra virtual orbitals, one for each symmetry.

We constructed the 15-electron configurations from the orbitals listed in Table I. The CI target wave functions are composed of the valence orbitals in Table I with the \( 1a_g \) and \( 1b_{1u} \) orbitals kept doubly occupied. We have included three types of configurations in the calculation. The first type of configurations has the form

\[
\begin{align*}
\text{Singlet states} & \quad \text{Triplet states} \\
\text{Single states} & \quad \text{Triplet states} \\
\text{Continuum} & \quad \text{Continuum}
\end{align*}
\]

FIG. 1. Potential energy curves of the \( \text{N}_2 \) electronic states. The equilibrium distance of the \( X^1\Sigma^+_g \) state, \( R=2.068a_0 \), is used in our \( R \)-matrix calculations.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>( A_g )</th>
<th>( B_{2u} )</th>
<th>( B_{2u} )</th>
<th>( B_{1u} )</th>
<th>( B_{1u} )</th>
<th>( B_{1u} )</th>
<th>( A_u )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence</td>
<td>( 1-3a_g )</td>
<td>( 1b_{2u} )</td>
<td>( 1b_{3u} )</td>
<td>( 1-3b_{1u} )</td>
<td>( 1b_{3g} )</td>
<td>( 1b_{2g} )</td>
<td>( 1b_{1u} )</td>
</tr>
<tr>
<td>Extra virtual</td>
<td>( 4a_g )</td>
<td>( 2b_{2u} )</td>
<td>( 2b_{3u} )</td>
<td>( 1b_{1g} )</td>
<td>( 4b_{1u} )</td>
<td>( 2b_{3g} )</td>
<td>( 2b_{2g} )</td>
</tr>
<tr>
<td>Continuum</td>
<td>( 5-39a_g )</td>
<td>( 3-35b_{2u} )</td>
<td>( 3-35b_{3u} )</td>
<td>( 2-17b_{1u} )</td>
<td>( 5-37b_{2u} )</td>
<td>( 3-18b_{3g} )</td>
<td>( 3-18b_{2g} )</td>
</tr>
</tbody>
</table>
1a_e^2 b_1^2 (2a_e 3a_e 1b_2a 1b_3 1b_13 1b_2f 110^1(2A_e)
\times (4a_e^3)(2A_e),
\end{equation}

where the scattering electron occupies a bound 4a_e virtual orbital, instead of the diffuse continuum orbitals in expression (1). As in Table I, we included one extra virtual orbital for each symmetry. The third type of configurations has the form

\begin{equation}
1a_e^2 b_1^2 (2a_e 3a_e 1b_2a 1b_3 2b_13 3b_1a 1b_3 a 1b_2 f 110^1(2A_e)
\times (5a_e ... 39a_e)(2A_e).
\end{equation}

Here we assume that the total symmetry of this 15 electrons system is 2A_e. The first 4 electrons are always kept in the 1a_e and 1b_1 orbitals; then, the next 10 electrons are distributed over the valence orbitals with the restriction of target-state symmetry, 1A_e symmetry of the N2 ground state in this case. The last electron, the scattering electron, occupies one of the diffuse orbitals, of a_e symmetry in this example. To complete the wave function with the total symmetry 2A_e, we also have to include configurations with the other target states combined with diffuse orbitals having appropriate symmetry in the same way as in the example. The second type of configurations has the form

\begin{equation}
1a_e^2 b_1^2 (2a_e 3a_e 1b_2a 1b_3 2b_13 3b_1a 1b_3 a 1b_2 f 110^1(2A_e)
\times (4a_e^3)(2A_e),
\end{equation}

The R-matrix calculations were performed for all eight irreducible representations of the D_{2h} symmetry, 1A_e, 2B_e, 3B_e, 1B_1g, 2B_1g, 3B_1g, and A_g, in doublet-spin multiplicity of the electron plus target system. DCS’s were evaluated in the same way as in our previous paper [23].

III. RESULTS AND DISCUSSION

A. Excitation energies

Figure 1 shows the potential energy curves of all N2 target states included in the present R-matrix model. These curves were obtained by the same SA-CASSCF method employed in our R-matrix calculation. Table II compares the excitation energies of the N2 target states from the present calculation with the previous R-matrix results of Gillan et al. [21], multireference coupled-cluster results of Ben-Shlomo and Kaldor [33] as well as experimental values. Since these energies are evaluated at different internuclear distance, 2.068a_0 in our case, 2.100a_0 in Gillan et al. [21], and 2.074a_0 in Ben-Shlomo and Kaldor [33], precise comparison is not so meaningful. However, deviations of excitation energies from the experimental values are less than 0.8 eV in our calculation, which is good considering the level of calculation. In terms of excitation energies, our calculation and the previous R-matrix calculation of Gillan et al. [21] have similar quality.

In addition to this good agreement of target energies with experimental results, N2^+ energies are also well described in our SA-CASSCF calculation. In our calculation, N2^+ X 2Σ^+_g and A 3Π_u states are located at 15.63 and 17.21 eV above N2 X 2Σ^+_g state, respectively. Compared to the experimental values of 15.61 and 17.08 eV, our SA-CASSCF calculation gives good results. Note that the energy ordering of N2^+ X 2Σ^+_g and A 3Π_u states is not well described in the Hartree-Fock level calculation; see Ermir and McLean [34], for example.

B. Integral cross sections

Figure 2 shows integral cross sections for electron impact excitation from the N2 X 2Σ^+_g state to the A 3Π_u, B 3Π_u, W 3Δ_u, and C 3Π_u states. In this figure, present results are compared with the previous R-matrix calculations of Gillan et al. [21], recent calculations of da Costa and Lima [35], experimental results of Cartwright et al. [11], Campbell et al. [13], and recent measurements of Johnson et al. [3]. Renormalized values of Cartwright et al. [11] are used as recommended by Trajmar et al. [36]. Figure 3 compares the present excitation cross sections of the a′ 3Σ_u, a 3Π_u, w 3Δ_u, and C 3Π_u states with the previous experimental results of Cartwright et al. [11], Campbell et al. [13], and Johnson et al. [3]. For the a 3Π_u-state cross sections, the recent calculations of da Costa and Lima [35] and other experimental values of Ajello and Shemansky [5], Zetner and Trajmar [10], and Mason and Newell [6] are included. For the C 3Π_u–state cross sections, the experimental results of Zubek [8], Zubek and King [9], and Poparic et al. [7] are included.

Our excitation cross sections for the A 3Σ_u state have a resonance feature at approximately 12 eV as in the previous R-matrix results of Gillan et al. [21]. The N2 X 2Σ^+_g resonance state is responsible for this peak structure. The
main configuration of this resonance state is $1\pi_{1g}^2\pi_{2u}^2$. Other than the $^2\Pi_u$ symmetry partial cross sections, the $^2\Pi_u$ symmetry contributes to the ICS’s as a smooth background component (not shown in the figure). Compared to the previous $R$-matrix cross sections, the peak at 12 eV is more pronounced in our case. Our results are slightly larger than theirs at 12–17.5 eV. Compared to the recent experimental results of Johnson et al. [3], our cross sections are about 50% larger at 12.5–20 eV, though 50% smaller at 10 eV. Also our calculation overestimates the results of Campbell et al. [13]; however, the results of Cartwright et al. [11] agree well with our results except at 12.5 eV. The position of the resonance peak depends rather strongly on the internuclear distance of N$_2$ molecule, which is 12.2 eV for 2.068$a_0$ and 11.75 eV for 2.100$a_0$ in our calculations. Thus, inclusion of vibrational motion may be necessary to resolve this discrepancy of the resonance peak.

Our excitation cross sections for the $B^3\Pi_u$ state have a small bump at 12.8 eV, which is not evident in the previous $R$-matrix cross sections. The origin of this bump is the N$_2^-$ $1\Delta_g$ state, with main configuration of $3\sigma_g^11\pi_u^2$. Other than this bump, the ICS’s are mostly composed of the $^3\Pi_u$ symmetry contribution and have a shape similar to the previous $R$-matrix results. The magnitude of our ICS’s is about 50% larger than the previous results of Gillan et al. [21]. Recently, da Costa and Lima [35] calculated ICS’s for the $B^3\Pi_u$ state using the Schwinger multichannel method with the minimal orbital basis for the single-configuration interaction (MOBSCI) approach. There cross sections are much larger than our results above 12 eV. Also, there is a prominent peak around 10 eV in their ICS’s, which does not exist in the $R$-matrix calculations. Compared to the experimental ICS’s, our results agree well with the cross sections of Cartwright et al. [11], especially above 15 eV. However, the results of Campbell et al. [13] are much larger than ours. Recent measurements of Johnson et al. [3] agree better with the previous $R$-matrix calculation of Gillan et al. [21].

For the excitation cross sections for the $W^3\Delta_u$ state, our results have a shape and magnitude similar to the previous $R$-matrix results. Most of our ICS’s are composed of the $^3\Pi_u$ symmetry partial cross sections. Agreement with the experimental cross sections of Johnson et al. [3] is good in this case. The cross sections of Campbell et al. [13] agree well with our results at 15 and 17.5 eV, but their value is about half as much as our result at 20 eV. The results of Cartwright et al. [11] are about 2 times larger than our cross sections.

Our excitation cross sections for the $B^3\Sigma_u^-$ state are about half of the previous $R$-matrix cross sections of Gillan et al. [21]. Apart from this difference in magnitude, the shape of the cross sections is similar. Dominant component in these ICS’s is the $^3\Pi_u$ symmetry partial cross sections, although the $^3\Pi_u$ symmetry also has certain contribution around 18–20 eV. Among three different experimental measurements, our results agree well with the results of Johnson et al. [3]. The experimental cross sections of other two groups are much larger than our results at 15 and 17.5 eV, and have a different energy dependence compared to the present calculation.

The situation of the excitation cross sections for the $a^1\Sigma_u^+$ state is similar to the case of the $B^3\Sigma_u^-$ state. The $^3\Pi_u$ and $^3\Pi_u$ symmetry partial cross sections contribute almost equally to the ICS’s. Our cross sections roughly agree with the results of Johnson et al. [3], while the cross sections of Cartwright et al. [11], and Campbell et al. [13] at 15 eV are much larger than our result. The results of Cartwright et al. [11] and Campbell et al. [13] decrease as the impact energy increases from 15 to 20 eV; however, our cross sections increase mildly in this energy region.

In case of excitation to the $a^3\Pi_u$ state, several other experimental results are available in addition to the measurements of Cartwright et al. [11], Campbell et al. [13], and Johnson et al. [3]. The cross-section profiles of Johnson et al.
Figure 4. Differential cross sections for electron-impact excitation from the N$_2$ X $^1\Sigma_g^+$ state to the A $^3\Sigma_u^+$ state. Electron-impact energy of (a) 12.5 eV, (b) 15 eV, and (c) 17.5 eV. The solid line represents our result. For comparison, we include the previous theoretical cross sections of Gillan et al. [21] and experimental results of Khakoo et al. [2], Brunger and Teubner [12], Cartwright et al. [11], Zetner and Trajmar [10], and LeClair and Trajmar [37].

This work
Gillan et al [21]
Khakoo et al [2]
Brunger and Teubner [12]
Cartwright et al [11]
Zetner and Trajmar [10]
LeClair and Trajmar [37]

(a) 12.5 eV
(b) 15 eV
(c) 17.5 eV

Cross section (10$^{-19}$ cm$^2$ sr$^{-1}$)

Scattering angle(degree)

Figure 5. Differential cross sections for electron-impact excitation from the N$_2$ X $^1\Sigma_g^+$ state to the B $^3\Pi_u$ state. Electron-impact energy of (a) 12.5 eV, (b) 15 eV, and (c) 17.5 eV. The results of Schwinger multichannel calculations by da Costa and Lima [35] are also shown in the panels. Other details are the same as in Fig. 4.

This work
Khakoo et al [2]
Brunger and Teubner [12]
Cartwright et al [11]
Zetner and Trajmar [10]
Zetner and Trajmar [10]
LeClair and Trajmar [37]

(a) 12.5 eV
(b) 15 eV
(c) 17.5 eV

Cross section (10$^{-19}$ cm$^2$ sr$^{-1}$)

Scattering angle(degree)

In this case, agreement with the results of Johnson et al. [3] is not so good compared to the excitations of the $^1\Pi_u$ and $^1\Sigma_u^-$ states. Our cross sections are about 50% larger than their values at 17.5 and 20 eV. At 15 eV, our results agree well with the cross section of Johnson et al. [3]; however, they are about 50% lower than the results of Cartwright et al. [11] and Campbell et al. [13]. In the calculated ICS’s, the $^3\Pi_u$ symmetry partial cross section is a major component, with a minor contribution from the $^3\Pi_d$ symmetry.

The calculated excitation cross sections for the C $^3\Pi_u$ state has a peak similar to the experimental results of Zubek [8] and Poparic et al. [7]. Although the shape of the cross sections is similar, the position of the cross-section peak is different from experimental results. In our case, it is located at about 17 eV, whereas corresponding peaks are located at 14 eV in the experimental cross sections. The height of the peak in our ICS’s is lower than the experimental values of Zubek [8] and Poparic et al. [7]. It is unclear whether there is a cross-section peak in the experimental cross sections of Cartwright et al. [11], Campbell et al. [13], and Johnson et al. [3]. At least, it appears that they do not have a peak around 17 eV. The origin of this discrepancy in the cross section peak is uncertain, but may be related to the employment of the fixed-nucleus approximation or insufficiency of higher excited target states in the R-matrix model. The calculated ICS’s are composed of the $^2\Sigma_u^+$ and $^2\Sigma_u^-$ symmetry.
partial cross sections near the peak structure at 17 eV. The contribution of the $^2\Sigma_u^+$ symmetry is about 50% larger than the $^2\Sigma_u$ component. Other than these two symmetries, the $^2\Pi_u$ symmetry partial cross section contributes to the ICSs as a smooth background component.

C. Differential cross sections

Figure 4 shows calculated DCS’s for excitation of the $A^3\Sigma_u^+$ state with the experimental results of Khakoo et al. [2], Brunger and Teubner [12], Cartwright et al. [11], Zetner and Trajmar [10], LeClair and Trajmar [37] and the previous $R$-matrix DCS’s of Gillan et al. [21]. Our DCS’s at 12.5, 15, and 17.5 eV have a similar shape in common. They are enhanced in the backward direction and have a small dimple at 120° with a bump at 75°. At 17.5 eV, our cross sections are increased in the backward direction and have a small dimple at 100°, which agree better with the experimental results of Brunger and Teubner [12]. In our calculation, these dimples and bumps are shifted toward the backward direction by 20°, and agreement with the results of Brunger and Teubner [12] is not so good. At 12.5 eV, our calculation overestimates the experimental results by a factor of 2. As seen in panel (a) of Fig. 2, this discrepancy is related to the existence of a resonance peak around 12.5 eV.

Figure 5 compares calculated excitation DCS’s for the $B^1\Pi_u$ state with the experimental and recent theoretical results. Our DCS’s at 12.5, 15, and 17.5 eV have backward-enhanced feature with a broad peak at 130°. At 15 and 17.5 eV, our DCS’s agree well with the results of Khakoo et al. [2] at forward direction below 80°. However, their DCS’s are much larger than our DCS’s at 12.5 and 15 eV. Agreement with the results of Cartwright et al. [11] at 15 eV is good at 20°−130°, although their DCS’s are twice as large as our DCS’s at 17.5 eV for low scattering angles. Because of a resonancelike feature at 12.5 eV as seen in panel (b) of Fig. 2, our results are larger than the experimental results at 12.5 eV. Recent Schwinger multichannel results of da Costa and Lima [35] are much larger than our DCS’s at 12.5 and 15 eV. The deviation is especially large at 12.5 eV, which is possibly related to the difference in the excitation energies of the target state.

Figure 6 shows the excitation DCS’s for the $W^3\Delta_u$ state with the experimental cross sections. At 15 and 17.5 eV, our cross section gradually increases as a function of scattering angle, without noticeable bump or dip. At 12.5 eV, the shape of DCS’s is nearly symmetric around 90°. Agreement with

FIG. 6. Differential cross sections for electron-impact excitation from the $N_2^1\Sigma_g^+$ state to the $W^3\Delta_u$ state. Electron-impact energy of (a) 12.5 eV, (b) 15 eV, and (c) 17.5 eV. Other details are the same as in Fig. 4.

FIG. 7. Differential cross sections for electron-impact excitation from the $N_2^1\Sigma_g^+$ state to the $B^1\Pi_u$ state. Electron-impact energy of (a) 12.5 eV, (b) 15 eV, and (c) 17.5 eV. Other details are the same as in Fig. 4.
the experimental DCS’s of Khakoo et al. [2] is good, although their results at 15 and 17.5 eV have more complex structure such as a small peak at 80°. Our DCS’s are generally smaller than the other experimental results of Brunger and Teubner [12], Cartwright et al. [11], Zetner and Trajmar [10].

Excitation cross sections for the $B'$ $1\Sigma_u^+$ state are shown in Fig. 7. Calculated DCS’s decrease to be zero toward 0 and 180°, because of a selection rule associated with $\Sigma^+$$-\Sigma^-$ transition [38,39]. Our DCS’s have a broad single peak near 90° at 12.5 and 15 eV, whereas there are two broad peaks at 17.5 eV. The position of the right peak at 17.5 eV coincides with that of the experimental DCS’s of Khakoo et al. [2] and Cartwright et al. [11], although the peak of Cartwright et al. [11] is much higher than ours. Our results agree well with the DCS’s of Khakoo et al. [2] at 15 and 17.5 eV. However, their cross sections at 15 eV have a small dip at 100° and a small bump 60°, which do not exist in our results. At 12.5 eV, our cross sections are slightly larger than the results of Khakoo et al. [2]. On the whole, agreement with the other experimental results of Bragner and Teubner [12] and Cartwright et al. [11] is not good.

Figure 8 shows the excitation DCS’s for the $a'$ $1\Sigma_u^-$ state. Because of the $\Sigma^-$$-\Sigma^-$ selection rule, DCS’s at 0 and 180° become zero as in the case of the $B'$ $1\Sigma_u^+$-state DCS’s. Calculated DCSs have a broad single peak near 60° at 12.5 and 15 eV. At 17.5 eV, there are two broad peaks at 50° and 120°. Although there is slight overestimation of DCS’s near 50°–60°, our DCS’s agree marginally with the results of Khakoo et al. [2]. Agreement with the other experimental results is not good except low scattering angles at 17.5 eV.

Figure 9 compares our excitation DCS’s for the $a'$ $1\Pi_u$ state with the experimental cross sections. Because of large variation of the DCS’s, the cross sections are shown in logarithmic scale. Calculated DCS’s are strongly forward enhanced, which is consistent with all experimental results shown in the figure. Our DCS’s at 12.5 eV have a small dip around 100°, which moves forward to 85° at 15 eV and 75° at 17.5 eV. This behavior roughly agrees with the results of Cartwright et al. [11] and Khakoo et al. [2]. At 15 eV, our DCS’s agree better with the results of Khakoo et al. [2] than the other experimental DCS’s. At 17.5 eV, the results of Cartwright et al. [11] are closer to our DCS’s at scattering angles above 40°. Below 40°, our calculation significantly underestimates the experimental DCS’s. Our results at 12.5 eV are located between the DCS’s of Cartwright et al. [11] and Khakoo et al. [2]; however, the shape of the DCS’s is similar to their results. The shapes of DCS’s calculated by da Costa and Lima [35] are similar to our results. However, their cross sections are larger than our results at low scattering angles below 80°, where their results agree better with the experimental DCS’s of Bragner and Teubner [12] and Zetner and Trajmar [10].

Figure 10 shows calculated excitation DCS’s for the $w$ $1\Delta_u$ state with the experimental cross sections. Our DCS’s
are enhanced in the forward direction as in the case of the \( ^{1}\Pi_g \) state. However, magnitude of the enhancement is much smaller than that of the \( ^{1}\Pi_u \) state. Agreement with the DCS's of Cartwright et al. [11] is good at 17.5 eV except at low scattering angles below 20°. At 12.5 and 15 eV, their results are much larger than our DCS's. At 15 eV, our DCS's agree marginally with the results of Khakoo et al. [2], although details of the DCS profile are different. Their results are smaller than ours at 17.5 and 12.5 eV. The discrepancy is especially large for forward scattering at 12.5 eV.

Figure 11 shows excitation DCS's for the \( ^{3}\Pi_g \) state with the experimental cross sections of Khakoo et al. [2], Brunger and Teubner [12], Zubek and King [9], and Cartwright et al. [11]. Calculated DCS profiles are almost flat at 12.5 and 15 eV, whereas they are enhanced in the backward direction at 17.5 eV. Below 90°, the slope of the calculated DCS's at 17.5 eV is similar to the results of Khakoo et al. [2], Zubek and King [9], and Cartwright et al. [11], though our results are about 50% larger than their DCS's. In general, our results do not agree well with the experimental DCS's. Although the experimental results of Khakoo et al. [2] at 15 eV agrees well with our result as shown in panel (d) of Fig. 3, the angular dependence of the cross sections appears to be different.

**D. Discussion**

The excitation ICS's of the \( ^{3}\Pi_g \) state, shown in panel (b) of Fig. 2, have a small bump around 13 eV. However, there is no such structure in the previous \( R \)-matrix ICS's of Gillan et al. [21]. The origin of this bump in our calculation is the \( ^{3}\Pi_g \) state with a main configuration of \( 3\sigma_u^1\pi_g^1 \). The existence of the \( ^{3}\Pi_g \) state is not evident in the previous \( R \)-matrix cross sections of Gillan et al. [21]. Some details of the \( R \)-matrix calculations are different in their calculation and ours; e.g., they used hybrid orbitals with Slater-type functions, whereas we employed SA-CASSCF orbitals with Gaussian-type functions. These differences may contribute to the difference in magnitude of the \( ^{3}\Pi_g \) partial cross section.

In this study, we employed the fixed-nucleus (FN) approximation. As we can see in Fig. 1, equilibrium bond lengths of the excited \( \text{N}_2 \) states are longer than that of the ground state. Thus, in principle, it would be desirable to...
include the effect of nuclear motion in the \( R \)-matrix calculation. Use of the FN approximation may be responsible for several discrepancies between our calculation and experiments, including bumps in the ICS's of the \( A^3\Sigma_u^+ \) and \( B^3\Pi_u \) states and the position of the peak in the ICS's of the \( C^3\Pi_u \) state. Although the calculated DCS's agree very well with experimental results in general, our DCS's of the \( A^3\Sigma_u^+ \), \( B^3\Pi_u \), \( w^1\Delta_u \), and \( C^3\Pi_u \) states at 12.5 eV are 2–4 times larger than experimental results. These deviations in the near-threshold DCS's can also be related to the FN approximation. In spite of these discrepancies, good agreements are observed between our calculation and experiments in most ICS and DCS cases as we can see in the figures. Agreements with the recent experimental results of Khakoo et al. [2] and Johnson et al. [3] are especially impressive. It is possible to include nuclear motion in the \( R \)-matrix formalism through vibrational averaging of \( T \)-matrix elements or the nonadiabatic \( R \)-matrix method, though application of these methods will be a difficult task in the presence of many target electronic states. In the future, we plan to perform the \( R \)-matrix calculation with these methods including nuclear motion.

IV. SUMMARY

We have investigated electron impact excitations of \( \text{N}_2 \) molecules using the fixed-bond \( R \)-matrix method which includes 13 target electronic states: \( X^1\Sigma_g^+, A^3\Sigma_u^+, B^3\Pi_u \), \( W^3\Delta_u, B^1\Sigma_u^+, a^1\Sigma_u^+, a^1\Pi_u, w^1\Delta_u, C^3\Sigma_u^+, E^3\Sigma_g^+, a^1\Sigma_g^+, c^1\Pi_u \), and \( c^1\Sigma_u^+ \). These target states are described by CI wave functions in the valence CAS space, using SA-CASSCF orbitals. Gaussian-type orbitals were used in this work, in contrast to the STO's in the previous \( R \)-matrix works. We have obtained integral cross sections as well as differential cross sections of excitations to the \( A^3\Sigma_u^+, B^3\Pi_u \), \( W^3\Delta_u, B^1\Sigma_u^+, a^1\Sigma_u^+, a^1\Pi_u, w^1\Delta_u \), and \( C^3\Pi_u \) states, which have been studied a lot experimentally but not enough theoretically before. In general, good agreements are observed both in the integrated and differential cross sections, which is encouraging for further theoretical and experimental studies in this field. However, some discrepancies are seen in the integrated cross sections of the \( A^3\Sigma_u^+ \) and \( C^3\Pi_u \) states, especially around a peak structure. Also, our DCS's do not agree well with the experimental results at low impact energy of 12.5 eV, compared to the higher energies of 15 and 17.5 eV. These discrepancies may be related to the fixed-nucleus approximation or insufficiency of higher excited target states in the \( R \)-matrix model.

ACKNOWLEDGMENTS

The work of M.T. is supported by the Japan Society for the Promotion of Science. The present research is supported in part by a grant from the Air Force Office of Scientific Research: the Advanced High-Energy Closed-Cycle Chemical Lasers project (No. F49620-02-1-0357).

---

[29] H.-J. Werner et al., MOLPRO, version 2002.6, a package of \( \text{ab initio} \) programs.