Neutral Dissociation of Superexcited Nitric Oxide Induced by Intense Laser Fields

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Superexcited states of NO molecule and their neutral dissociation processes have been studied both experimentally and theoretically. Neutral excited N\textsuperscript{+} and O\textsuperscript{2+} atoms are detected by fluorescence spectroscopy for the NO molecule upon interaction with 800 nm intensive laser radiation of duration 60 fs and intensity 0.2 PW/cm\textsuperscript{2}. Intense laser pulse causes neutral dissociation of superexcited NO molecule by way of multiphoton excitation, which is equivalent to single photon excitation in the extreme-ultraviolet region by synchrotron radiation. Potential energy curves (PECs) are also built using the calculated superexcited state of NO\textsuperscript{+}. In light of the PECs, direct dissociation and pre-dissociation mechanisms are proposed respectively for the neutral dissociation leading to excited fragments N\textsuperscript{+} and O\textsuperscript{2+}.

\textbf{Key words:} Superexcited state, Neutral dissociation, Intense laser

Supercered molecules and their behaviors is a subject of particular interest [1−6] for the researches of radiation chemistry, photochemistry, upper atmospheric physics, and astrophysics. Supercered state (SES) of a molecule is a highly excited state, whose internal energy exceeds the first ionization potential (IP). The statement of superexcited state of a molecule was first put forward by Platzman [7]. Afterward, Hatano and coworkers studied much on the subject and noted that most observed SESs are assigned to Rydberg states which are vibrationally (or/and rotationally), doubly, or inner core exited and converge to each of ion states [1]. SES occurs widely when a molecule is impacted by high energy particles like vacuum-ultraviolet (VUV) photons, X-ray photons, energetic electrons, and so on. SES possesses rich internal energy and thus unstable, undergoing decay instantly. Auto-ionization, dissociative ionization, ion pair dissociation, and neutral dissociation are the most common decay ways of SESs. The dissociation mechanism is obscure since the dissociative potential energy surface (PES) of the SES is absent in the literature. Dissociation of the superexcited molecules CH\textsubscript{4} and O\textsubscript{2} has been studied in the recent years. The dissociation mechanisms are revealed [8, 9]. In this work, the dissociation of another important molecule, nitric oxide NO\textsubscript{2}, is studied. The superexcited state of NO is produced by the excitation of ultrashort intense laser pulse. Fluorescent emission after the laser pulse is detected. From the recorded spectral lines we found dissociation products of N and O atoms. The dissociation can be interpreted by our calculated PESs with a spectator model.

García et al. measured the near-infrared dispersed fluorescence of neutral atomic fragments using narrow band synchrotron of the energy 17.2−25.8 eV [10]. Thirteen atomic O or N species dissociated from the SES of NO are recorded. In order to interpret the dissociation mechanism, they tried to calculate the \textit{ab initio} PECs for the SESs. At least 29 roots for a certain symmetry of a NO molecule was calculated. However, the PECs and their crossings were too complicated in the highly energy region. The dissociation mechanism is thus obscure yet.

In this paper, we report our theoretical study on the dissociation of NO also. We obtain the PECs for the SESs of NO by another approach. Based on the PECs, we propose direct and predissociation mechanism to interpret the dissociation processes of SESs leading to excited N and O atoms respectively. The emissions of products thus could be well explained. These theoretical results can provide a better insight into the essence of SESs than before. Through the above studies, the concept of the SES of NO molecule and the mechanism of the dissociation are better clarified. Considering the Rydberg character of the SESs, we properly build the PECs for the SESs using the calculated PECs of NO\textsuperscript{+} which the Rydberg states converge to.

The experiments were carried out at Center for Optics, Photonics and Laser (COPL), Université Laval, Québec, Canada. The spectrometer used in this work has been described in detail elsewhere [8]. Briefly, the

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experimental setup comprised three parts: first a femtosecond (fs) Ti:sapphire oscillator (Spectra Physics Tsunami™) seeded Chirp Pulse Amplification (CPA) module (Spectra Physics Spitfire™), which generate pulse possessing of a duration of about 60 fs at FWHM (full width at half maximum), 800 nm wavelength, 1 kHz repetition rate, maximum energy of 2 mJ/pulse with a diameter of about 5 mm (1/e² level of intensity); second, a stainless steel source chamber of pure NO pumped to a base pressure of 5.3 Pa; and third the fluorescence detecting spectrometer (Acton research Corporation, SpectraPro 500i™).

The neutral dissociation of the superexcited diatomic molecule, NO, is investigated. The SESs of the molecule NO are produced by the intense Ti:sapphire laser pulses. Products of the neutral dissociation are detected by fragmentation spectroscopy. Figure 1 shows the wide range fluorescence spectrum recorded between the wavelengths of 200 and 900 nm. The spectral lines in the spectrum are attributed to the transitions of the oxygen or nitrogen atoms, which are the dissociation products of superexcited NO**.

The spectral lines in the emission spectrum are assigned as the transitions of excited oxygen atoms or nitrogen atoms. Eight transitions of O* and three transitions of N* in the fluorescence spectrum have been assigned (Fig.1). The observed transitions and their assignments are listed in Table I.

We measured the fluorescence intensity of the O or N atoms as a function of the laser intensity. Five slopes are obtained as 5.9, 5.9, 8.9, 9.5, and 7.6 in a lg-lg plot for the wavelengths of 615.6, 744.2, 777.4, 844.6, and 868.3 nm, respectively. The strong laser intensity dependence indicates that a multiphoton excitation absorbing 6 to 9 photons takes place. The NO molecule can be excited to a highly excited state, whose energy is beyond the first ionization potential of 9.264 eV. The highly excited state, or the superexcited state, then undergoes dissociation leading to the product of N and O atoms which we observed.

To interpret the dissociation process we use ionic core model, which has been successfully applied to explain the dissociation of CH₄ and O₂ molecules [8, 9]. Most superexcited states are Rydberg states consisting of an excited ion core and a Rydberg electron. In the ionic core model, the Rydberg electron can be treated as a spectator, not participating in the dissociation directly. The whole dissociation process involves two steps, dissociation of the ion core into two fragments and recombination of the ionic fragment with the Rydberg electron. The principle quantum number n and angular quantum number ℓ are supposed to be unchanged during the dissociation [8].

To understand the dissociative process, it is necessary to know the related potential energy curve. However, accurate calculation for the high-lying states of molecules is extremely difficult. To obtain the PESs

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<tr>
<td>532.9</td>
<td>O</td>
<td>2s²2p⁹(S²)5d→2s²2p⁹(S²)3p</td>
<td>⁴D⁰→⁴P</td>
<td>19.56</td>
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<tr>
<td>595.8</td>
<td>O</td>
<td>2s²2p³(S²)5d→2s²2p³(S²)3p</td>
<td>⁴D⁰→⁴P</td>
<td>19.32</td>
</tr>
<tr>
<td>615.6</td>
<td>O</td>
<td>2s²2p⁹(S²)4d→2s²2p⁹(S²)3p</td>
<td>⁴D⁰→⁴P</td>
<td>19.25</td>
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<tr>
<td>645.4</td>
<td>O</td>
<td>2s²2p³(S²)5s→2s²2p³(S²)3p</td>
<td>⁴S⁰→³P</td>
<td>19.16</td>
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<tr>
<td>700.2</td>
<td>O</td>
<td>2s²2p³(S²)4d→2s²2p³(S²)3p</td>
<td>⁴D⁰→³P</td>
<td>19.26</td>
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<tr>
<td>725.4</td>
<td>O</td>
<td>2s²2p³(S²)5s→2s²2p³(S²)3p</td>
<td>⁴S⁰→³P</td>
<td>18.95</td>
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<tr>
<td>746.9</td>
<td>N</td>
<td>2s²2p³⁴(P)3p→2s²2p³⁴(P)3s</td>
<td>⁵S⁰→³P</td>
<td>18.50</td>
</tr>
<tr>
<td>777.4</td>
<td>O</td>
<td>2s²2p³⁴(S)3p→2s²2p³⁴(S)3s</td>
<td>⁵P⁰→³S⁰</td>
<td>17.24</td>
</tr>
<tr>
<td>818–824</td>
<td>N</td>
<td>2s²2p³⁴(P)3p→2s²2p³⁴(P)3s</td>
<td>⁴P⁰→³P</td>
<td>18.34</td>
</tr>
<tr>
<td>844.6</td>
<td>O</td>
<td>2s²2p³⁴(S)3p→2s²2p³⁴(S)3s</td>
<td>³P⁰→³S⁰</td>
<td>17.49</td>
</tr>
<tr>
<td>868.3</td>
<td>N</td>
<td>2s²2p³⁴(P)3p→2s²2p³⁴(P)3s</td>
<td>⁴D⁰→³P</td>
<td>18.33</td>
</tr>
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a The wavelength band contains seven spectral lines for the transition ⁴P⁰→³P of different spectroscopic branched terms.
of high-lying Rydberg states, we first investigate the PESs of the excited states of NO\(^+\), to which the Rydberg states converging. Two ionic states leading to the products of O\(^+\)+N and N\(^+\)+O, respectively are calculated. The calculations are performed with the MOLPRO software package [11] at CASCCF/avz level.

In the energy diagram (Fig. 2), the dashed lines represent the ionic states at different inter-nuclear distance. The solid curves are the related Rydberg states, which are obtained by shifting down the ionic curve. The energy limit on the long-distance side is adjusted by the experimental data [12].

With these Rydberg PESs of NO, we are able to trace the dissociation pathway of the superexcited NO molecules, and to provide the possible dissociation mechanisms of superexcited NO\(^+\) molecules. In strong laser fields, NO molecules may absorb many photons immediately accompanying with a vertical excitation. The equilibrium distance of the ground state of NO is 1.15 Å. A Franck-Condon transition can create superexcited NO\(^+\) molecule as indicated by the arrow in the energy diagram.

After the laser excitation, the wave-packet produced moves on the Rydberg PESs (shown by blue color in Fig. 2) then. The moving wave packet splits into two parts in the curve crossing region around 2.0 Å. Each part of the wave packet leads to a pair of dissociation products. A direct dissociation pathway along shown by blue color in Fig. 2 produces the fragments of O\(^{3}\Pi)+N\(^+\) (2s\(^2\)2p\(^3\)3p, \(^4\)S or \(^4\)P\(^o\) or \(^4\)D\(^o\)), which emit at the wavelengths of 746.9, 818–824, and 868.3 nm, respectively. Another part of the wave packet crosses to the PESs shown in Fig. 2 by red color in the diagram. The curve-crossing results in apo-dissociation, producing the products of N(\(^4\)S\(^o\))+O* (2s\(^2\)2p\(^3\)3p, \(^3\)P or \(^3\)P).

The products fluorescence at the wavelengths of 777.4 and 844.6 nm respectively.

We have found that NO molecule undergoes neutral dissociation in strong laser fields at the intensity of 0.2 PW/cm\(^2\). Seventeen emitting lines have been recorded in the fluorescence spectroscopy. The emissions are assigned to the transition of excited N and O atoms to the ground state. The emitters are the dissociation products of NO molecules. After multiphoton excitation, the superexcited NO molecules undergo spontaneous dissociation. To understand the dissociation mechanism of the SESs of NO molecules, the ionic core model is used. The related PESs are built and shown in Fig. 2. Direct dissociation mechanism is suggested to explain the N–O bond cleavage leading to N\(^+\) and O. Pre-dissociation mechanism is suggested to explain the N–O bond cleavage leading to N and O\(^+\).

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![FIG. 2 Potential energy curves (PECs). The dashed lines are the ionic PECs which the Rydberg-type SESs converging to; the solid lines are PECs of the related SESs. The blue lines are the wave-packet produced moves on the Rydberg PESs. The red lines are the wave packet crosses to the PESs. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.](image)


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