Neutral decay of double-holed doubly excited resonances of N_2

Masatoshi Ukai, Kosei Kameta, Noriyuki Kouchi, and Yoshihiko Hatano
Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

Kenichiro Tanaka
Photon Factory, National Laboratory for High Energy Physics, Oho, Tsukuba, Ibaraki 305, Japan
(Received 26 May 1992)

The neutral decay of doubly excited resonances (DER's) of N_2 has been observed by measuring the excitation spectrum of vacuum ultraviolet fluorescence emitted from photodissociation fragments in the 20–38-eV region. A number of DER's with the $[(1\pi_u)^{-1}(3\sigma_g)^{-1}(\pi_g)^1{:}C\,^2\Sigma_u^+]ns\sigma_g$ Rydberg series ($n=3$–10) have been revealed. Rydberg progressions onto the $N_2{}^+(D\,^2\Pi_g)$ state have also been observed. Strongly dissociative DER's correlating with satellites have been shown as broad peaks in the 23–33-eV region, which have appeared to have a correlation with the single-holed $(X\,^2\Sigma_g^+)\sigma_u$ shape resonance.

PACS number(s): 33.20.Ni, 33.80.Gj, 33.90.+h

I. INTRODUCTION

It has generally been believed that high-lying resonances above about 25 eV dissociate or autoionize so rapidly that they do not give rise to observable resonances. This has caused considerable difficulty in studying electron correlation in double-holed doubly excited resonances (DER's) even of well-known simple molecules such as N_2 [1]. Many-body effects [2] in DER, where multiple correlations among each two of core holes and exited electrons are involved, contribute to the complicated nature of decay processes. This is also the case for shape resonances in final two-hole one-particle ionization channels [3] leading interchannel coupling to yield different partial ionization channels. These resonances, induced by the breakdown of the single-particle excitation, result in ionic satellites and also DER as a result of final-state correlation [2]. Photoabsorption [4,5] and photoionization [7–11] studies have been the only chances to examine resonance states, which presented DER Rydberg states of N_2 and CO two decades ago [1,12]. However, high-lying resonances such as DER's become invisible due to their smaller intensities of oscillator strength and a greater majority of continuum ionization even in partial ionization channels, which, in their threshold region, preserve information of energetic locations of resonance state [8] because of the less important contribution of single-continuum ionization. Dadouch *et al.* revealed rich DER Rydberg structures of CO in the 25–40-eV region by detecting negatively charged fragments [13]. However, the unstable N^- nature prevented the observation. Hence, we remark that almost nothing is known about the DER of N_2 above 22-eV excitation energy.

We also remark that much is not known about the neutral dissociation of DER, the alternative decay channel of autoionization. Fluorescences from photodissociation fragments are originated from initially induced resonances being their minor decay channel but free from continuum ionization [14,15]. This can overcome the spectroscopic difficulty according to continuum ionization. We stress an importance of measuring the fluorescence excitation spectrum (FES) emitted from neutral fragments, which can provide a sensitive tool in the spectroscopy of DER in N_2,

$$N_2 + h\nu \rightarrow N_2{}^{**}(n\lambda)^{-1}(n'\lambda')^{-1}(n^*\lambda^*)^1(n^{*\prime}\lambda^{*\prime})^1$$
$$\rightarrow N^* + N^*$$
$$\rightarrow N + h\nu' ,$$

where $n\lambda$ denotes a quantum state of an electronic orbital.

In this paper, the observation of the neutral decay of DER's of N_2 is presented by the vacuum ultraviolet (vuv)–FES measurement from photodissociation fragments. The purpose of the present work is to reveal the energetic locations of the doubly excited N_2 resonances in the 20–38-eV region. We present DER Rydberg series converging on the $N_2{}^+(C\,^2\Sigma_u^+)$ state and valence excited DER correlating with other ionic satellites. Also the dissociation of the lowest $(C\,^2\Sigma_u^+)3s\sigma_g$ Rydberg state is revealed. The single previous effort of measuring vuv FES from excited N by Lee *et al.* [16] in the 20–62-eV region, which revealed no information on DER, might have forced one to regard the FES measurement as an inferior spectroscopy. However, the progress of synchrotron radiation (SR) sources has enabled us to look at this minor but, therefore, quite informative process. We thus underline the importance of the neutral decay path of DER's in competition with autoionization not only as an aspect of the decay dynamics but also as a sensitive tool in the spectroscopy of DER's.

II. EXPERIMENT

The experiment was performed using an extreme-uv SR from a 2.5-GeV positron storage ring at the Photon

Factory. The experimental arrangement was described previously [14, 15, 17].

A negligibly small amount of higher-order components of dispersed SR from the 1-m Seya-Namioka monochromator with a right-angle-reflecting prefocusing system has enabled us to perform this reliable and informative study. A typical SR flux of 1×10^9 photons/s at 24 eV was monitored by a photocurrent from a Au mesh and using a photomultiplier through a sodium salicylate-coated window. FES measurements were performed by a 0.01-nm step with a 0.03-nm bandpass (14-meV resolution at 24 eV). An absolute wavelength of the monochromatized SR was calibrated for the neutral levels of N_2 in the 86–98-nm region [4] and the narrow DER levels of Xe [17]. A research grade N_2 gas admitted without further purification into a sample cell was monitored using a capacitance manometer to maintain 10 mTorr achieving a linear pressure dependence region. Undispersed vuv fluorescences in the spectral 105–180-nm region from a sample gas were detected by a CsI-coated microchannel plate (MCP) through a LiF window. The present MCP can respond to the $N_2{}^+(C\,{}^2\Sigma_u^+ \rightarrow X\,{}^2\Pi_g)$ fluorescence [18]. However, the present FES has been ascribed to excited neutral N fragments via initially induced DER, because (1) predissociation is the major decay channel for the $N_2{}^+(C\,{}^2\Sigma_u^+, v'>3)$ states [10], (2) less than 10% of the Franck-Condon population [19] for $N_2{}^+(C\,{}^2\Sigma_u^+, v'\leq 3)$ among the total vibrational levels gives negligible contribution of $N_2{}^+(C\,{}^2\Sigma_u^+ \rightarrow X\,{}^2\Pi_g)$ to the total vuv cross section [5,17], and (3) the dipole $(e,e+\text{ion})$ cross section for N^+ production [11] is identical to the $N_2{}^+(C\,{}^2\Sigma_u^+)$ cross section [9]. The FES involves dissociative ionization above the lowest dissociative ionization limit at 34.6 eV to give vuv fluorescent fragments.

III. RESULTS AND DISCUSSION

Figure 1 presents the FES of N_2 in the incident 20–38-eV region. The FES shows the first rise at 20.1 eV where the lowest dissociation limit $N(3s\,{}^4P)+N({}^4S^\circ)$ for the vuv fluorescent products lies. Some other dissociation limits and the lowest dissociative-ionization-excitation limit $N(3s\,{}^4P)+N^+({}^3P)$ at 34.6 eV are also indicated in Fig. 1. The vuv FES is far from identical to the result by Lee and co-workers [5,16]. This is not simply caused by the spectral resolution but due to considerable experimental problems such as higher orders of SR. This forces us to regard their result as a preliminary FES and not informative at all about DER. The FES presents several broad peak structures centered at around 23.5, 26.5, 28.5, and 31 eV (numbered as 1, 2, 3, and 4 in Fig. 1, respectively). The peaks appear to be based on an extremely broad enhancement in the 25–33-eV region. An increase of FES at around 35 eV should correspond to the fluorescence originated from ionic satellites.

Figure 2 expands the vuv FES in the 20–26-eV region. In the region just above the threshold at 20.1 eV, several sharp peaks are shown, which were not observed in the previous FES [5,16] but were shown weakly in the photoabsorption [4,5] and electron-energy-loss spectra [20]

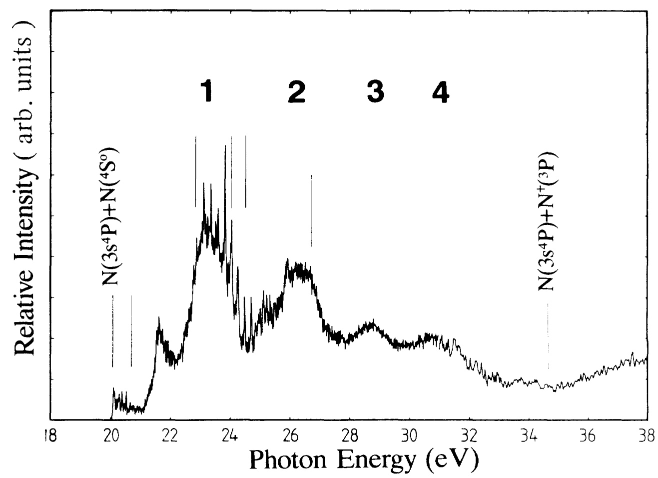

FIG. 1. Vacuum ultraviolet fluoresence (105–180 nm) excitation spectrum of N_2 in the 20–38-eV region obtained with 14-meV incident photon resolution at 24 eV. The vertical lines indicate the lowest dissociation limit $N(3s\,{}^4P)+N({}^4S^\circ)$, other dissociative excitation limits, and the lowest dissociative-ionization-excitation limit $N(3s\,{}^4P)+N^+({}^3P)$ to give vuv fluorescent fragments. The broad peaks centered at around 23.5, 26.5, 28.5, and 31 eV are numbered as 1, 2, 3, and 4, respectively. Notice the peaks 2–4 are based on a broad enhancement in 25–33 eV.

(EELS). They correspond to the level positions of the Rydberg series converging on the $N_2{}^+(D\,{}^2\Pi_g)$ state as tentatively proposed by Wu, Lee, and Judge [5] (WLJ). However, WLJ's levels do not fit the present peak positions. It is natural that their peak top positions of asymmetric profiles [5] fail to explain the present peak levels which are free from a continuum channel. Furthermore, some other peaks are also shown in the present FES. We suggest that at least two Rydberg progressions which preserve the $N_2{}^+(D\,{}^2\Pi_g)$ vibrational structure are required to explain the peak structures in the 20–21 eV region.

Figures 1 and 2 also present rich sharp spike structures in the 22–26-eV region. Some of these spikes were also presented in the previous FES [5,16], the photoabsorption [4,5] and partial photoionization [8] cross sections and the EELS spectrum [20]. Codling [1] proposed tentative assignments of the $(C\,{}^2\Sigma_u^+)4s\sigma_g$ and $5s\sigma_g$ Rydberg series converging on the $N_2{}^+(C\,{}^2\Sigma_u^+)$ state. Further-revealed sharp spikes are presently assigned by the vibrational Rydberg series of the principal quantum numbers of 5, 6, 7, 8, 9, and 10 with an almost common value of 0.95 for the quantum defect which predicts the majority of the $ns\sigma_g$ character. A detailed analysis is in progress to reduce precise quantum defects for each of vibrational Rydberg states.

It has been discussed that the lowest $(C\,{}^2\Sigma_u^+)3s\sigma_g$ Rydberg state was not observed spectroscopically [1,8]. We call the reader's attention to the unexpected sharp rise at around 21.5 eV, which does not correspond to any dissociation limit, as evidence of the lowest Rydberg state. This unexpected rise in comparison with a small intensity just above the first dissociation limit at 20.1 eV

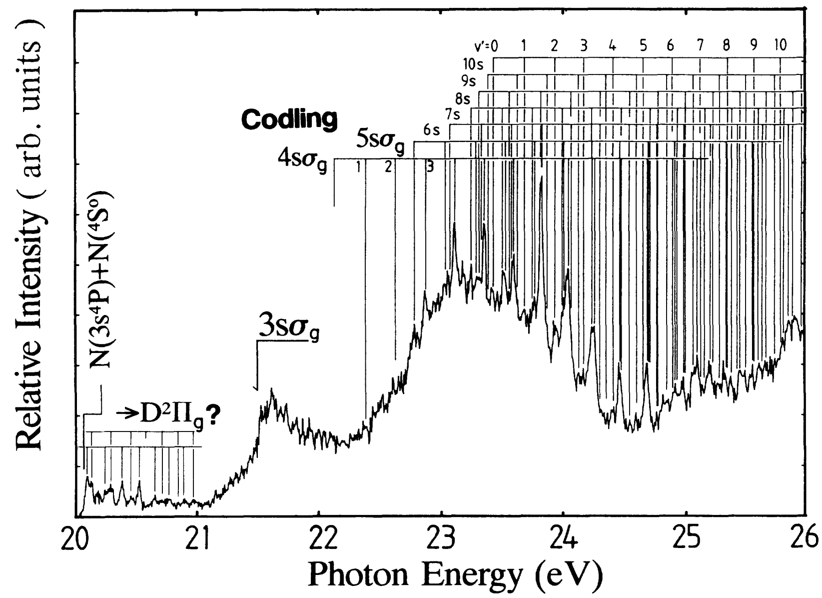

FIG. 2. Expanded presentation of vuv FES of N_2 in the 20–26-eV region with 14-meV incident-photon resolution at 24 eV. Tentative level positions of the Rydberg series in the 20–21-eV and 22–26-eV regions are indicated. The level positions of the vibrational $(C\,^2\Sigma_u^+)4s\sigma_g$ and $5s\sigma_g$ progressions are obtained from Ref. [1]. Notice that the intense rise at 21.5 eV as indicated by an arrow corresponds to the neutral dissociation of the lowest $(C\,^2\Sigma_u^+)3s\sigma_g$ state.

reminds us of the small barrier of the $N_2{}^+(C\,^2\Sigma_u^+)$ potential curve [1]. We remark that the sharp rise in the FES at 21.5 eV reflects the strongly dissociative nature of the free $(C\,^2\Sigma_u^+)3s\sigma_g$ Rydberg state which opens on exceeding the potential barrier. A somewhat lower potential location than the estimate with $m=2.04$ appears to be a general case of larger quantum defects for the lowest DER $ns\sigma_g$ Rydberg states.

Origins of these broad peaks are discussed in the following. Peak 1 around 23.5 eV is superposed with the above-mentioned sharp spikes. Wendin [2] proposed a strongly repulsive valence excited DER of $(1\pi_u)^{-1}(3\sigma_g)^{-1}(\pi_g)^2$ with the $C\,^2\Sigma_u^+$ core configuration in this region, with which Langhoff predicted a small amount of mixing from $(2\sigma_u)^{-1}(\pi_g)^1$ with the $B\,^2\Sigma_u^+$ core configuration [3,8]. This provided the observation of the peak structure in the $B\,^2\Sigma_u^+$ partial ionization cross section [6,8,9] as a result of the $^2\Sigma_u^+$ final states correlation [21]. It is clear, however, that the appearance of a neutral decay in the present FES is driven from the strongly repulsive $(1\pi_u)^{-1}(3\sigma_g)^{-1}(\pi_g)^1(n\lambda)^1$ character [2,8] of double-holed DER.

Nothing is obtained of potential curves for N_2 DER's which can explain peaks 2–4. It is natural that these peak profiles represent the strongly repulsive nature of the DER's whose cores correspond to the correlation satellites [22] in the binding-energy region of 23–45 eV as investigated by Krummacher, Schmidt, and Wuilleumier [7]. Some of these satellites were shown to have a vibrational spectrum [7]. A correlation interaction between the excited two-electron orbitals may cause a different potential structure from that of the satellite. Anyway these DER's have a strongly dissociative nature due to the two-holes in bonding orbitals and the antibonding nature of the excited orbitals giving the present revelation in the vuv FES.

DER Rydberg states converging on the $N_2{}^+(C\,^2\Sigma_u^+)$ state has a strongly dissociative nature owing to the loss of two bonding outer-valence electrons in the core and to the occupation on the antibonding orbitals. The latter is also the case for the single-holed shape resonance [22,23]. The extremely broad enhancement in the 25–33-eV region reminds us of the $N_2{}^+(X\,^2\Sigma_g^+)\sigma_u$ shape resonance [22,23]. An antibonding property of this shape resonance which induced non-Franck-Condon $N_2{}^+(X\,^2\Sigma_g^+)$ vibrational populations [23] also drives the outgoing nuclear motion toward the dissociation limit. An intense decay frequency of the shape-resonantly trapped electron wave [23] does not allow us to extract such a large vuv intensity. This implies that a kind of correlation also drives predissociation. We predict that a complicated channel-coupling behavior of the $(X\,^2\Sigma_g^+)\sigma_u$ shape resonance presenting wide structures in the experimental $A\,^2\Pi_u$ and $B\,^2\Sigma_u^+$ partial cross sections [8] also gives rise to an evidence in the present FES.

We finally remark that the $C\,^2\Sigma_u^+$ partial cross section has not been examined well [3]. The $N_2{}^+(C\,^2\Sigma_u^+)$ state has the nature of an ionic satellite and would show a similarity to the inner-shell-holed $N_2{}^+(B\,^2\Sigma_u^+)$ state in the intensity borrowing [22]. The broken single-particle excitation in the shape resonance requires the rearranging correlation to provide interchannel coupling to other partial channels. This implies that this DER shape resonance induces a strongly preferential neutral dissociation. However, as far as we know, almost nothing [22] is available for shape resonances correlating with satellites. Peaks 2–4 should be examined further from this view point.

In summary, the observation of the neutral decay of N_2 DER's has been presented by measuring the vuv FES in the 20–38-eV region from photodissociation fragments. Rich DER Rydberg series converging on the $N_2{}^+(C\,{}^2\Sigma_u^+)$ state as well as the lowest $(C\,{}^2\Sigma_u^+)3s\sigma_g$ state have been revealed. We have also obtained Rydberg progressions converging on the $N_2{}^+(D\,{}^2\Pi_g)$ state. Broad peaks have been ascribed to the strongly dissociative DER, the DER correlating with ionic satellites, and also the single-holed $(X\,{}^2\Sigma_g^+)\sigma_u$ shape resonance. The DER states are optically forbidden in a single-particle excitation model but, therefore, are so much more discernible in the neutral decay channel rather than in the single-holed partial channels that, as we remark, FES measurements from neutral fragments can provide a sensitive tool in the spectroscopy of DER's. Also, absence of continuum channels in most cases can enable us to perform detailed straightforward determinations of the above DER Rydberg levels of which analysis is in progress.

ACKNOWLEDGMENTS

This work has been performed under an approval of the Photon Factory Programme Advisory Committee for Proposal No. 90-133. The authors would like to thank the staff of the Photon Factory for support. Financial support for a part of this work from the Photon Factory and the Grant-in-Aid of the Ministry of Education, Science and Culture of Japan are acknowledged.

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