Vibrationally resolved resonant x-ray emission spectra of diatomic molecules

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Abstract. We report here the measurements of vibrationally resolved resonant x-ray emission spectra of core-excited N₂ and O₂ molecules in the 1s → π* resonance region. The measured spectra were compared with the simulated spectra calculated based on the lifetime-vibrational interference theory. We find that the specific excitation to the ν₀ vibrational level in the intermediate core-hole state of N₂ molecule leads to clear vibrational structure (ν₀ = 0 – 3) in both of the final electronic X¹Σ⁺ (participator band) and a ¹Πₙ (spectator band) states. In contrast to that, the excitation to higher-ν vibrational levels gives rise to the complicated structure in the resultant soft x-ray emission spectra. In the case of O₂ molecule, we have observed some structures arising from the vibrational progression, but we find that much higher resolution for the spectrometer is needed to observe distinct vibrational levels.

1. Introduction

Soft x-ray emission (SXE) spectroscopy with the aid of energy selective excitation provides an excellent tool for investigating the electronic structure and determining symmetries of occupied and unoccupied orbitals in molecules [1, 2, 3, 4, 5, 6], since the dipole nature restricts the possible symmetries of all the states involved in the absorption / emission processes. With the advent of synchrotron radiation (SR) sources, the resonant SXE spectroscopy has been successfully applied to diatomic molecules, such as N₂ [3], O₂ [4] and CO [5, 7], as they provide us with simple but excellent test systems to advance the basic understanding of the electronic structure as well as the dynamic processes concerned.

Recent advancement of the SXE spectrometer, e.g., throughput and resolution, will provide us with an opportunity to gain further knowledge of the excitation / relaxation processes in core-excited molecules. Recently, Tokushima et al developed a high performance slit-less spectrometer for SXE spectroscopy [8] which is applicable to gas-phase experiment. By taking this occasion, we have applied the resonant SXE spectroscopy to diatomic N₂ and O₂ molecules in the region of 1s → π* resonance to study the effect of nuclear motion on the excitation / relaxation processes.

In this article, we report the measurements of vibrationally resolved resonant SXE spectra of core-excited N₂ and O₂ molecules. Although these molecules have been previously studied by means of the resonant SXE spectroscopy [3, 4], we show the spectra measured with the resolving power E/ΔE of ~1,950 for N₂ and of ~2,040 for O₂, which are better than those of previous work (E/ΔE ~ 790 for N₂ [3] and ~530 for O₂ [4]), in the present study. It is obvious that the present spectra are of higher
2. Experimental

The experiments were carried out on the a-branch of the soft x-ray undulator beamline BL17SU at SPring-8, an 8 GeV SR facility in Japan. This beamline is equipped with the high-resolution varied-line-spacing-plane-grating monochromators [9], which can provide us with highly stabilized monochromatic soft x rays with resolving power of over 10,000 [10]. The direction of the polarization vector, e.g., horizontal or vertical, of the incident photon beam, generated by the multi-polarization-mode undulator [11, 12, 13], can be switched by changing the operational mode of the undulator when the photon energy is higher than 500 eV [14]. Although the degree of linear polarization is not so high, e.g., \( \rho \sim 0.82 \) (- 0.73) at 500 eV, we can perform the angle-resolved SXE spectroscopy without rotating the spectrometer. In the present study, however, we have set up the multi-polarization-mode undulator to be a helical mode, e.g., \( \rho \sim 0.98 \) (0.95) at 530 eV (400 eV), so as to achieve higher photon flux.

Energy calibration of the incident photon beam was performed by recording the total ion yield spectra of N\(_2\) and O\(_2\) molecular gases in the inner-shell excitation region, and the absolute energy scale was established using the reference energies published in the previous paper [15, 16]. The accuracy of energy scale for the incident photon beam was estimated to be about ±40 meV. Although the monochromator of BL17SU has ability to achieve the resolving power \( E/\Delta E > 15,000 \), the photon band pass, at a photon energy of 530 eV (400 eV), was set to be about 65 meV (39 meV) to achieve higher photon flux in the present study.

The x-ray spectra emitted from the core-excited molecules were recorded by using the high performance slit-less spectrometer equipped with the compact flange-mounted liquid flow-cell [8, 17]. Although this spectrometer was originally aimed at performing the spectroscopic studies on the liquid target [18, 19], in the present study we have introduced the target molecular gas into the flow-cell instead of the liquid. The flow-cell utilizes a 150 nm thick Au-coated SiC membrane window to separate the flowing gas at atmospheric pressure from the high vacuum. Calibration of the SXE spectrometer was performed by measuring the normal fluorescence emitted from the core-ionized molecules and also the photons elastically scattered from the target gas. The estimated energy resolution of the SXE spectrometer was 258 meV (203 meV) for the experiment on the O\(_2\) (N\(_2\)) molecule.

3. Results and discussion

3.1. Total ion yield spectra

Figure 1 shows the total ion yield spectra of molecular (a) N\(_2\) and (b) O\(_2\) in the region of 1s \( \rightarrow \pi^* \) excited states. Both spectra were fitted by means of a least squares fitting procedure employing Voigt functions for the vibrational progression, where thin solid curves indicate the individual components of the vibrational progression and thick curves are the sum of them. Lorentzian width (\( \omega_L \)) and Gaussian width (\( \omega_G \)) were assumed to be the same for the individual components in the fitting procedure.

For the N\(_2\) molecule, shown in Fig.1(a), we have tried to fit the observed spectrum by adopting the spectroscopic constants reported by Feifel et al [20] for the vibrational energy levels of the N\(_2\) (N 1s, \( \nu = 0 \) \( \rightarrow \) (\( \pi^* \), \( \nu' = 0 \rightarrow 6 \)) transitions. We obtained \( \omega_L = 109 \text{ meV} \) and \( \omega_G = 39 \text{ meV} \) from the present fitting procedure. The obtained value of 109 meV for \( \omega_L \) is slightly smaller than the recently reported values, which are ranging from 113 meV to 116 meV [16, 21, 22, 23], but identical to the value reported by Ohashi et al [24] where the fitting was applied to the total ion yield spectrum. For the O\(_2\) molecule, shown in Fig.1(b), we have adopted the actual lifetime width of the core-excited state (\( \Gamma = 149 \text{ meV} \)) for \( \omega_L \) and the spectroscopic constants \( \omega_L \) and \( \omega_G \) [25] for the vibrational energy levels of the O\(_2\) (O 1s, \( \nu = 0 \) \( \rightarrow \) (\( \pi^* \), \( \nu' = 0 \rightarrow n \)) transitions. In the present analysis, we have assumed the vibrational progressions up to \( n = 15 \). As shown in Fig.1, the results of these fitting demonstrate to be good enough to validate the employed spectroscopic constants for the intermediate core-hole state.
3.2. Soft x-ray emission spectra

Figures 2 and 3 show the SXE spectra of N\textsubscript{2} and O\textsubscript{2} molecules, respectively. All the SXE spectra shown in Figs 2 and 3 are raw spectra, i.e., no correction is made for self-absorption and absorption by the Au-coated SiC membrane window. All the spectra have exhibited a participator band as well as a spectator band. In the case of the participator decay, the excited electron fills the core-hole giving rise to the final electronic state identical to the ground state of the molecule. In the case of the spectator decay, on the other hand, one of the valence electrons, i.e., 3\sigma_{g} orbital, fills the inner-shell vacancy while the excited electron remains in the \pi_{g} orbital. Electrons in the inner-valence 2\sigma_{u} and 1\pi_{u} orbitals are not allowed to fill the core-hole owing to the parity selection rule. For both spectra of N\textsubscript{2} and O\textsubscript{2} molecules, we could clearly recognize the fine structure, i.e., vibrational structure. This fine structure has not been clearly observed in the previous experiments [3, 4].

The SXE spectrum of N\textsubscript{2} molecule measured at 401.32 eV is represented together with the results of Gaussian profile fitting. Short vertical bars in Figs 2 and 3 indicate calculated vibrational energies for the final electronic X \textsuperscript{1}Σ\textsubscript{g}\textsuperscript{+} (participator band) and a \textsuperscript{1}Π\textsubscript{g} (spectator band) states using the spectroscopic constants available from the literature [26, 28]. It is unfortunate that no reliable spectroscopic constants...
Figure 2. Soft x-ray emission (SXE) spectra of N₂ molecule recorded for four different excitation energies. No correction was made for self-absorption and absorption by the Au-coated SiC membrane window. The SXE spectrum measured at 401.32 eV is represented together with the results of Gaussian profile fitting. Short vertical bars in the figure indicate calculated vibrational energies for the final electronic X $^1\Sigma_g^+$ (participator band) and a $^1\Pi_g$ (spectator band) states using the spectroscopic constants [28].

for the O₂ spectator band are available from the literature. For the N₂ spectrum, especially for the participator band, we can recognize that the calculated energy positions agree well with the center positions of each Gaussian profile. As can be seen in these figures, the observed fine structure can be explained as the vibrational progressions. Again we can notice that the vibrational structure for N₂ molecule is more obvious than that of O₂ molecule. Thus the SXE spectrometer with much higher resolution is indispensable to study the vibrational structure more clearer for O₂ molecule.

3.3. Absorption corrections
In order to interpret the observed SXE spectra correctly, we stress here that the corrections for the spectrum, especially due to the self-absorption correction, is indispensable, since the target gas in the
Figure 3. Soft x-ray emission (SXE) spectra of O₂ molecule (left panel) recorded by tuning the excitation energies to the energy points indicated by arrows in Fig.1(b). The corresponding energies are also shown as solid lines in the total ion yield spectrum (right panel). In the SXE spectra, no correction was made for self-absorption and absorption by the Au-coated SiC membrane window. Short vertical bars in the figure depict calculated vibrational energies for the final electronic X³Σ⁺ (participator band) states using the spectroscopic constants [26].

Flow-cell is in atmospheric pressure and the energy region of interest overlays with the π resonance. For the proper absorption corrections, the following steps are needed to proceed:

(i) absorption correction for the incoming SR beam by the Au-coated SiC membrane window and the target gas itself,
(ii) self-absorption correction for the outgoing SXE spectrum by the target gas,
(iii) absorption correction for the outgoing SXE spectrum by the Au-coated SiC membrane window.

For the correction (ii), the volume of gas-cell along the incoming and outgoing paths were divided into thin layers, and we corrected the intensity distribution of the SXE spectrum in each thin layer. Now let us consider, for example, the correction for 4th thin layer. The intensities I(E,E) of the incident, absorbed and measured flux for 4th thin layer can be described as:
on the same emission energy scale:

\[ I_s(E_x) = I_0 \exp\left\{ -\mu_x(E_x) \rho_x \csc \theta \right\} \times \prod_{i=1}^{4} \exp\left\{ -\mu_i(E_x) \rho_i \csc \theta \right\}, \]

\[ I_{s}^{\text{abs}}(E_x) = I_s(E_x) (1 - \exp\{-\mu_x(E_x) \rho_x \csc \theta \}), \]

\[ I_{s}^{\text{cor}}(E_x, E) \propto I_{s}^{\text{abs}}(E_x) S(E_x, E) \exp\{-\mu_x(E) \rho_x \csc \theta \} \times \prod_{i=1}^{4} \exp\{-\mu_i(E) \rho_i \csc \theta \}, \]

where \( E_x \) is the excitation energy of in-coming radiation, \( I_0 \) the primary photon flux incident on the gas-cell, \( \mu_x \) and \( \mu_i \) the mass attenuation coefficients of the gas-cell window and the target [29, 16], \( \rho_x \) and \( \rho_i \) the densities of the gas-cell window and the target, \( x_x \) and \( x_i \) the thicknesses of the gas-cell window and the target thin layer, \( \theta \) the angles of the in-coming and out-going radiations with respect to the layer surface, \( E \) the energy of the out-going radiation to be measured, \( S(E_x, E) \) the spectral function excited by the in-coming radiation, respectively. We assumed that the spectral function and the angular distributions of the photon-in−−−photon-out process for each thin layer are identical with each other.

Finally, we summed up the contribution from each thin layer to plausibly establish the absorption-corrected intensity distribution as a function of the SXE energy. Actually, the correction was performed to extract the spectral function \( S(E_x, E) \) by using the spreadsheet. Although this simple procedure does not give us the absolute correction, it is good enough to overlook the relative energy dependence of the self-absorption correction factor. Figure 4 shows the typical example of absorption corrections made for the SXE spectrum of \( \text{N}_2 \) molecule measured at 401.66 eV excitation energy. In order to facilitate the comparison, the intensity of the corrected spectrum was normalized to that of the uncorrected one for the energy region of the spectator band. As we can recognize from the figure, the effect of the self-absorption correction is remarkable at the SXE energy region of 400.5 ~ 401.7 eV, i.e., the energy of \( \text{N}_2 \) 1s \( \rightarrow \pi^* \) resonance region.

### 3.4 Spectral shape analysis

For the analysis of the spectral shape, we need to treat the problem beyond the ordinary Franck-Condon theory, because the coherently excited levels can cause interference effects where the levels can decay to the same final vibronic states. In such case, a conventional Franck-Condon analysis, in which the excitation and relaxation are treated as two independent processes, is no longer valid and a one-step formalism taking account of the lifetime-vibrational interference effects [30] is suitable to analyze the resonantly excited SXE spectrum. Similar spectral analyses have been made for the resonant Auger spectra of \( \text{N}_2 [31, 32] \) and \( \text{O}_2 [33] \) molecules and the resonant SXE spectra of \( \text{N}_2 [3] \) and \( \text{CO} [7] \) molecules. Accordingly, our simulation is based on the method similar to these previous studies.

The intensity distribution \( I_f(E_x) \) of the SXE spectrum can be described as the summation of the population probability \( I_f(E_x) \) on the same emission energy scale:

\[ I_f(E_x) \propto \sum_n I_f(E_n). \]

In the present analysis, we calculated the \( I_f(E_x) \) within the framework of the one-step formalism and also the two-step formalism. In the case of the one-step formalism, the \( I_f(E_x) \) was calculated based on the lifetime-vibrational interference theory as

\[ I_f(E_x) \propto G(E_x) \sqrt{\sum_n \frac{<f|n><n|0>}{E_x - (E_n - E_0) + i\Gamma/2}}^2, \]

where \( E_x, E_n \) and \( E_0 \) are the excitation energy, the vibrational energy of the intermediate core-hole state and of the ground state. \( G(E_x) \) is the monochromator function and \( \Gamma \) is the lifetime width of the
Figure 4. Soft x-ray emission (SXE) spectra of N₂ molecule measured at 401.66 eV. The thick solid line shows the spectrum with absorption corrections, whereas the dashed line represents the spectrum without any corrections.

intermediate core-hole state. By combining the above two formulae, we get the intensity distribution as:

\[ I(E_x) \propto G(E_x) \sum_n \frac{\langle f | n > | n \rangle \langle n | 0 \rangle}{E_x - (E_n - E_0) + i\Gamma/2}^2 + G(E_x) \sum_n \frac{\langle f | n > | n \rangle \langle n | 0 \rangle}{E_x - (E_n - E_0) + i\Gamma/2} \frac{\langle f | n > | n \rangle \langle n | 0 \rangle}{E_x - (E_n - E_0) + i\Gamma/2} \]  

Here, the first term is called as direct term and the second term the interference term. In the case of the two-step formalism, on the other hand, the \[ I_f(E_x) \] was simply calculated by adopting the probability to produce the intermediate core-hole state \[ k_{\text{IXAS}}(E_x) \] and the Franck-Condon factors between the intermediate state and the final state as

\[ I_f(E_x) \propto |\langle f | n > | n \rangle|^2 \times k_{\text{IXAS}}(E_x). \]

In the spectral shape analysis, we have used the well-established parameters listed in Table 1 for the potential curves of the ground, intermediate core-excited and final states [3, 20, 25, 27, 28]. We have confirmed the validities for some parameters as shown in Figs 1 and 2. The Franck-Condon factors, i.e., the squares of overlap integrals of the vibrational wave functions, were calculated using the Morse potentials. The intensity distribution of the SXE spectra were simulated by employing the one-step formalism based on the lifetime-vibrational interference theory [30]. For comparison, we also calculated the SXE spectra by means of the two-step formalism.

Figures 5 and 6 depict the results of the simulations for N₂ and O₂ molecules, respectively. In these figures, the solid circles represent the measured SXE spectra and the solid curves show the simulated
Table 1. Spectroscopic parameters of \( \text{N}_2 \) and \( \text{O}_2 \) molecules used for calculations of the Morse potential curves and the Franck-Condon Factors.

| Configuration | state | \( \tilde{T}_{00} \) /eV | \( \omega_{\nu_0} \) /cm\(^{-1} \) | \( \omega_{\nu_0 \omega_{\nu_0}} \) /cm\(^{-1} \) | \( r_e \) /\( \text{\AA} \) |
|---------------|-------|-----------------|-----------------|-----------------|-----------------|
| \( \text{N}_2 \) G.S. | \( X^1\Sigma_g^+ \) | 0.0 | 2358.57\(^b\) | 14.324\(^a\) | 1.09768\(^a\) |
| \( \text{NN}^* \) 1\( \sigma_g^1 \) 1\( \pi_g \) | 1\( \Pi_u \) | 400.88\(^b\) | 1904.1\(^c\) | 17.235\(^c\) | 1.1645\(^d\) |
| \( \text{N}_2 \) 3\( \sigma_u^1 \) 1\( \pi_u \) | a 1\( \Pi_g \) | 8.55\(^e\) | 1694.2\(^e\) | 13.949\(^e\) | 1.2203\(^\#\) |
| \( \text{O}_2 \) G.S. | \( X^3\Sigma_g^+ \) | 0.0 | 1580.361\(^f\) | 12.073\(^e\) | 1.2079\(^\#\) |
| \( \text{OO}^* \) 1\( \sigma_u^1 \) 1\( \pi_u \) | 3\( \Pi_g \) | 530.24\(^f\) | 1116.271\(^g\) | 12.905\(^g\) | 1.3427\(^\#\) |

\( \tilde{T}_{00} \) is the excitation energy from the G.S. to the lowest (\( \nu^\prime = 0 \)) vibrational level of the excited state, \( \omega_{\nu_0} \) the vibrational energy, \( \omega_{\nu_0 \omega_{\nu_0}} \) the anharmonicity constant, and \( r_e \) the equilibrium internuclear distance.

\(^a\) [3].
\(^b\) [20].
\(^c\) [27].
\(^d\) [28].
\(^e\) Parameter determined by the present fitting procedure.
\(^f\) [25].

**Figure 5.** Comparison of the measured and simulated soft x-ray emission (SXE) spectra of \( \text{N}_2 \) molecule. Excitation energies for each spectrum are indicated near the spectra. Intensities in the spectator bands ranged between 390 and 394 eV are magnified for ease of comparison. The solid circles represent the measured spectra, while solid lines depict the simulated spectra.
Figure 6. Comparison of the measured and simulated soft x-ray emission (SXE) spectra of O$_2$ molecule. The solid circles represent the measured spectrum, while the solid lines depict the simulated spectra.

ones, where red curve indicates the total intensity calculated by the one-step formalism, green curve the intensity of interference term in the one-step formalism and blue curve the intensity calculated by the two-step formalism. In the case of N$_2$ molecule, the resonant excitation to the $\nu = 0$ component ($E_x = 400.87$ eV) leads to relatively simple structure. Both of the measured and simulated spectra are showing distinct vibrational structure which can readily be assigned to the $\nu = 0 - 4$ vibrational structure. In the meantime for the valley excitation at 400.98 eV, i.e., the excitation between two resonances, the simulated spectra indicate that the vibrational components are implying to be split into fine structure, although the measured spectra do not clearly show such multiplication. This is probably due to the lack of resolving power of the SXE spectrometer. For the higher excitation energies ($E_x = 401.32, 401.66$ eV), both of the measured and simulated spectra show much complicated spectra. From the comparison between the one-step and two-step formalisms shown in Fig.5, it seems to be difficult to say which formalism is suitable, but by looking at the high-energy end of the spectra of valley excitation the one-step formalism seems to explain better than the two-step formalism. Although the present simulations could explain a gross feature of the complicated spectra, further refinement, such as account of the relative intensity for vibrational progression, for the simulation may be needed to be done. Detailed measurements and further discussions will be given elsewhere [34].

In the case of O$_2$ molecule, on the other hand, we did not simulate the SXE spectra in the spectator band because no reliable parameters for the potential energy curve are available for the $3\sigma_g^{-1} 1\pi_u 3\Pi_g$ final electronic state. Figure 6 indicates the measured and simulated spectra for the excitation energy of 530.62 eV, which corresponds to the resonance excitation to the $\nu = 3$ component. As is shown in Fig.1(b), the lifetime width, i.e., 149 meV, of the intermediate core-hole state is larger than the energy spacing of the vibrational progression ($\sim 128$ meV), the resultant SXE spectra may be affected by the coherent excitation to more than one vibrational level because of stronger overlap between neighboring
vibrational levels for the intermediate core-hole states. Thus the \( \nu = 2 \) or 4 components will contribute to and several \( \nu' \) components will participate in the process, therefore the resultant spectrum will consist of a complex but unresolved structure. It is unfortunate that the resolution of the spectrometer, e.g., 258 meV for the \( \text{O}_2 \) measurement, was not good enough to resolve such vibrational progression even if we observe the participator band, where the spectroscopic constant \( \omega \) is about 196 meV [26]. According to the fact that the present spectrum has been excited by narrow bandpass radiation (\( \sim 65 \text{ meV} \)), the width of the resultant spectral feature is not limited by the natural width (\( \sim 149 \text{ meV} \)) of the intermediate core-hole state [35]. Apart from the width of the final state, the spectral feature is apparently governed by only the resolving power of the spectrometer. Thus in order to study the resonant SXE processes on \( \text{O}_2 \) molecule using narrow bandpass radiation, updating of the spectrometer to improve the resolving power is expected. As for the simulation, one-step formalism could not succeed to explain the structure around 529.2 eV but it accounts for the main peak (\( \sim 530.6 \text{ eV} \)) better than two-step formalism. As in the case of the simulation for \( \text{N}_2 \) molecule, a refinement for the simulation is called for.

4. Conclusions

We have presented the results of measured and simulated vibrationally resolved resonant x-ray emission spectra of \( \text{N}_2 \) and \( \text{O}_2 \) molecules in the \( 1s \to \pi^* \) resonance region. The simulations based on the lifetime-vibrational interference theory could somewhat explain the gross feature of the fine structure observed in the \( \text{N}_2 \) spectrum. We find that the resolving power \( E/\Delta E \sim 2,000 \) for the spectrometer is not sufficient for studying the vibrational structure in the SXE spectrum of \( \text{O}_2 \) molecule.

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