High-resolution photoelectron spectroscopy using multibunch synchrotron radiation: rotational-resolved photoelectron bands of $\text{O}_2^+ (b^4\Sigma_g^-, \nu')$

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Abstract

We report rotational-resolved single-photon threshold photoelectron and pulsed field ionization zero kinetic energy (PFI–ZEKE) photoelectron (PE) spectra of $\text{O}_2^+$ in the energy range of 18.1–20.2 eV measured using high-resolution monochromatized multibunch undulator synchrotron radiation. The PFI–ZEKE PE bands for $\text{O}_2^+ (b^4\Sigma_g^-, \nu' = 0–9)$ have been simulated using the Buckingham–Orr–Sichel model derived for rotationally resolved single-photon ionization cross-sections. Only the $D\Sigma^+_N (2, 0)$ and $Q\Sigma^+_O (2, 2)$ or $O, Q$ and $S$ rotational branches are observed for these PFI–ZEKE PE bands, indicating that the outgoing electron continuum channels with angular momenta $l = 1$ and 3 dominate in the threshold ionization transitions $\text{O}_2^+ (b^4\Sigma_g^-, \nu' = 0–9, N'') \rightarrow \text{O}_2^+ (X^2\Sigma_g^+, \nu'' = 0, N'')$. The relative rotational branch intensities for $O_2^+ (b^4\Sigma_g^-, \nu' = 4$ and 5) are found to be drastically different from those for $O_2^+ (b^4\Sigma_g^-, \nu' = 0–3, 6$ and 7). Considering that the energies of $O_2^+ (b^4\Sigma_g^-, \nu' = 4$ and 5) are close to the dissociation limit of $O^+(4\Sigma^+) + O(3P)$ and that the crossing location of the $O_2^+ (b^4\Sigma_g^-, \nu' = 4$ and 5) potential curves is shown to be in the vicinity of $O_2^+ (b^4\Sigma_g^-, \nu' = 4$ and 5), we suggest that the latter observation is the result of predissociative perturbations by the $d^4\Sigma_g^+$ state. Within the uncertainties of this experiment, the ionization energies for the formation of $O_2^+ (b^4\Sigma_g^-, \nu' = 0–9, N'') = 1$ can be satisfactorily characterized using a Morse potential. The effective lifetimes for high-$n$ Rydberg states converging to $O_2^+ (b^4\Sigma_g^-, \nu' = 0, 2–5)$ prepared in the present experiment are nearly constant with values in the range of 1.8–2.0 $\mu$s. The observation that the effective lifetimes for high-$n$ Rydberg states converging to $O_2^+ (b^4\Sigma_g^-, \nu' = 4$ and 5) are significantly longer than the known dissociative lifetimes of the corresponding ionic states is in accordance with the expectation that the couplings between the $O_2^+$ ion core and the high-$n$ Rydberg electron involved are negligibly small. © 1998 Elsevier Science B.V. All rights reserved.
1. Introduction

As an important atmospheric gas [1], the solar vacuum ultraviolet (VUV) photoionization mechanism of \( \text{O}_2 \) to form \( \text{O}_2^+ \) in the Earth’s ionosphere has been the subject of intense investigations by photoionization mass spectrometry [2] and photoelectron (PE) spectroscopy [3–14] for several decades. The photoionization efficiency (PIE) spectrum of \( \text{O}_2 \) in the photon energy range below 25 eV is dominated by complex, strong autoionizing Rydberg structures [2]. A complete assignment of these autoionizing Rydberg states is still unavailable. These autoionizing Rydberg states are known to have a significant effect on the threshold photoelectron (TPE) spectrum of \( \text{O}_2 \) via near-resonance autoionization mechanisms [13,15], i.e. if an ionization limit coincides with a sufficiently strong autoionization state, the TPE signal may be observed even though the Franck–Condon factor (FCF) is unfavorable. Here, we refer to TPEs as PEs formed slightly above the ionization threshold in an electric field-free region. Deviation from the Franck–Condon behavior in the TPE spectrum can also be caused by shape resonance [11,16–18], which is a direct result of the internuclear distance dependence of the electronic transition moment. The detailed interpretation of the PIE and TPE spectra of \( \text{O}_2 \) requires the measurements of both spectra to a rotationally resolved level. In addition to yielding accurate spectroscopic information, a rotationally resolved PE study would also reveal the partial wave character of the outgoing PE, and thus is a detailed probe of molecular photodissociation dynamics [19].

Recent synchrotron-based experiments using TPE spectroscopic techniques [6–9] and VUV laser-based studies using pulsed field ionization zero kinetic energy (PFI–ZEKE) PE spectroscopic schemes [10–14] have provided much spectroscopic and dynamical information about the photoionization of \( \text{O}_2 \) in the energy range of 12–30 eV. The VUV laser PFI–ZEKE PE experiments have measured rotationally resolved PE bands for selected vibrational levels of \( \text{O}_2^+(\chi^2 \Pi_g) \) and \( \text{O}_2^+(\alpha^4 \Pi_u) \) [10–14]. These studies have revealed valuable insight into the role of near-resonance autoionization [13] and shape resonance [11] in \( \text{O}_2 \) photoionization. Due to the tediousness of tuning VUV laser radiation in a broad energy range [20–24], the single-photon PFI–ZEKE PE study of \( \text{O}_2 \) performed by the Hepburn group [12–14], covering much of the region from the ionization threshold of \( \text{O}_2 \) to 17 eV, must be considered a heroic effort. The studies of higher excited \( \text{O}_2^+ (b^4 \Sigma_g^- , B^3 \Sigma_g^- , c^4 \Sigma_u^+ ) \) states have only been made using HeI–PE [3–5] and synchrotron-based TPE [6–9] spectroscopic techniques. The previous PE experiments at energies higher than 18 eV achieved an energy resolution of \( \geq 5 \) meV (full-width-at-half-maximum, FWHM) [6,7,9], and thus are limited to measurements at the rotationally resolved level.

The first experiment that clearly demonstrated the formation of PFI–ZEKE PEs using synchrotron radiation was reported by Weitzel and Guther [25] in a recent single-bunch synchrotron electron time-of-flight (TOF) study. By applying a pulsed electron extraction scheme, they have separated TPEs from delayed PFI–ZEKE PEs of the Ar\(^+ (\,^5 \Pi_{1/2}) \) state. However, this experiment was not designed for PFI–ZEKE PE spectroscopic measurements, but only to demonstrate the ability to eliminate the effect of PFI–ZEKE PEs in a TPE–photoion coincidence study.

We have recently developed a new scheme for performing PFI–ZEKE PE measurements using the high-resolution monochromatized multibunch (488 MHz) undulator synchrotron radiation at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) [26–30]. By employing an electron spectrometer, we have shown in a recent experiment that PFI–ZEKE PE spectra for gaseous molecules can be obtained in the multibunch synchrotron operation with essentially complete suppression of prompt background electrons [26,27]. A resolution of 0.5 meV (FWHM), comparable to that achieved in VUV

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\( \text{Dedicated to Prof. Ikuzo Tanaka on the occasion of his 70th birthday.} \)
laser PFI–ZEKE PE studies, is now routinely obtainable in experiments using the high-resolution PFI–ZEKE PE spectrometer of the Chemical Dynamics Beamline. Most importantly, this new PFI–ZEKE PE scheme overcomes the difficulty caused by the high-energy tail of the electron transmission function associated with the conventional TPE method [31,32]. The latter technique was the method of choice in previous synchrotron-based PE studies. This new synchrotron-based PFI–ZEKE PE approach promises not only to extend PFI–ZEKE PE measurements to beyond the current high-energy tuning limit of ≈ 18 eV for VUV lasers but also to significantly increase the productivity in high-resolution PE spectroscopic studies of gaseous molecules.

Using this new detection scheme, we have obtained the rotationally resolved PFI–ZEKE PE spectrum of O$_3$ in the full energy range of 12–25 eV, corresponding to the formation of O$_3^+$ ($X^2I'$, $a^4I'$, $A^3I''$, $b^4Σ^+_g$, $B^3Σ^+_g^-$, and $c^4Σ^+_g^-$) states. In this paper, we present a comprehensive analysis of the PFI–ZEKE PE and TPE spectra for O$_3$ in the energy region of 18.1–20.0 eV, covering the formation of O$_3^+$ ($b^4Σ^+_g^-$, $v^+$). A preliminary analysis of selected PFI–ZEKE PE vibronic bands of O$_3^+$ ($b^4Σ^+_g^-$, $v^+$) has been reported [27].

The success of the laser-based PFI–ZEKE PE technique relies on the detection of long-lived high-$n$ Rydberg states by delayed Stark field ionization [33,34]. These high-$n$ Rydberg states have extended lifetimes, which are generally attributed to $l$- and $m_l$-mixing [35–39] induced by the presence of electric fields and ions formed in a laser ionization process. The variation of the lifetimes with these factors is complicated and depends on the experimental conditions. In laser PFI–ZEKE PE experiments, each laser pulse contains high photon flux and could generate a high ion density along with the formation of excited high-$n$ Rydberg species [35–37,39–45]. Due to the high frequency and the low photon flux of individual micro-pulses, a synchrotron radiation source is essentially a continuous light source. Thus, the ion density formed in a synchrotron study, such as the present experiment, is negligibly small. We have measured the effective lifetimes for high-$n$ Rydberg states converging to the O$_3^+$ ($b^4Σ^+_g^-$, $v^+$ = 0–5) vibronic states. Although these lifetimes are still affected by the presence of unknown stray fields, the lifetime lengthening effect due to inhomogeneous electric fields associated with the presence of static ions should be minimized.

2. Experiment

The design and performance of the Chemical Dynamics Beamline at the ALS has been described previously [26–30,46]. Briefly, the major components for the high-resolution photoionization facility at this beamline include a 10-cm-period undulator (U10), a gas harmonic filter, a 6.65 m off-plane Eagle-mounted monochromator, and a photoion–PE apparatus.

In the present experiment, helium is used in the harmonic gas filter where higher undulator harmonics with photon energies greater than 24.59 eV are suppressed. The fundamental light from the undulator is then directed into the 6.65 m monochromator and dispersed by a 4800 l mm grating before entering the experimental apparatus. The highest resolution obtainable using the 4800 l mm grating is shown to be $ΔE = 0.3$ meV (FWHM) at $E = 21.6$ eV [30], corresponding to a resolving power of $E/ΔE = 72000$. The photon flux was measured to be in $10^{10}–10^{11}$ photons/s range when the storage ring current was 400 mA and both monochromator slits are set to 50 μm ($E/ΔE = 25000$) in the photon energy range of 12–24 eV [28]. The ALS storage ring is capable of filling 328 electron buckets in a period of 656 ns. Each electron bucket emits a light pulse of 50 ps with a time separation of 2 ns between successive bunches. In each storage ring periods, a dark gap (48 ns) consisting of 24 consecutive unfilled buckets exists for the ejection of cations from the orbit. Thus, the present experiment is performed in the multibunch mode with 304 bunches in the synchrotron orbit, corresponding to a repetition rate of 464 MHz.

The multi-purpose photoion–PE apparatus associated with the Chemical Dynamics Beamline was used for the present study [26,27,29,30]. A continuous molecular beam of pure O$_3$ was produced by supersonic expansion through a stainless steel nozzle (diameter = 0.127 mm) at a stagnation pressure of 760 Torr and a nozzle temperature of 298 K. The molecular beam was then skimmed by a circular
skimmer (diameter = 1 mm) before intersecting the monochromatized VUV light beam 7 cm downstream in the photoionization region. The beam source chamber and photoionization chamber were evacuated by turbomolecular pumps with pumping speeds of 3000 and 1200 l/s, respectively. During the experiment, the respective pressures in the beam source chamber and the photoionization chamber were maintained at $\approx 1 \times 10^{-4}$ and $2 \times 10^{-6}$ Torr.

### 2.1. PFI–ZEKE PE measurements

The experimental scheme for performing PFI–ZEKE PE experiments using the high-resolution monochromatized undulator synchrotron radiation at the ALS has been described previously [26,27]. Briefly, a pulsed electric field (height = 0.67 V/cm, width = 40 ns) was applied to the repeller at the photoionization region to field ionize high-n Rydberg states and extract PEs toward the detector, and was applied every 2 (1.31 μs) or 3 (1.97 μs) ring periods. An electron energy spectrometer, which consists of a steradiancy analyzer [31,32] and a hemispherical energy analyzer arranged in tandem, is used to filter prompt electrons. All components involving electron detection were enclosed by two layers of μ-metal. The application of the electric field pulse is delayed by 8 ns with respect to the beginning of the 48 ns dark gap. It has been demonstrated that prompt electrons are sufficiently dispersed in $\approx 8$ ns to escape detection by the electron energy spectrometer. The PE chamber was separately evacuated by a turbomolecular pump with a pumping speed of 400 l/s, and maintained at a pressure of less than $8 \times 10^{-7}$ Torr.

Since different kinds of electrons are formed at different times with different energies, the voltage setting of the electron spectrometer can be tuned to optimize either PFI–ZEKE PEs or prompt electrons. In the present experiment, it is critical to tune the electron spectrometer properly to optimize PFI–PEs and suppress prompt electrons produced from direct photoionization and/or autoionization. The procedures for optimizing PFI–ZEKE PEs are best described using the Ar TPE and PFI–ZEKE PE spectra shown in Fig. 1a–c. Fig. 1a is a typical TPE spectrum for Ar observed near the Ar $^{2}P_{3/2}$ ionization threshold. This spectrum with a high-energy electron tail was obtained when the electron spectrometer was optimized as a TPE spectrometer and the application of the pulsed field was not in perfect overlap with the 48 ns dark gap. Under these voltage settings for the electron spectrometer, the TPE peak marked as $^{2}P_{3/2}$ corresponds to true zero kinetic energy electrons formed in the ionization of Ar. The PFI–ZEKE PE peak for Ar $^{+}(^{2}P_{3/2})$ is expected to be lower than this TPE peak by 0.3 meV, which corresponds to the Stark shift for the 0.67 V/cm pulsed electric field used in the present study. Thus, the condition for PFI–ZEKE PE detection can be obtained by changing the voltage settings such that the maximum electron transmission appears at an energy 0.3 meV lower than the TPE peak (see Fig. 1b). We note that
Fig. 2. (a) PFI–ZEKE PE band of Kr $^2P_{3/2}$ in the energy range of 13.997–14.003 eV obtained at a pulsed field of 0.67 V/cm. The PFI–ZEKE PE energy resolution achieved is 0.4 meV (FWHM). (b) PFI–PE band of Ar $^3P_{3/2}$ in the energy range of 15.757–15.763 eV obtained at a pulsed field of 0.67 V/cm. (c) PFI–ZEKE PE band of Ar $^3P_{3/2}$ in the energy range of 15.757–15.763 eV obtained at a pulsed field of 0.33 V/cm. The monochromator slits used in (a), (b), and (c) are 25 μm.

A small peak due to prompt electrons originating from the autoionizing Ar(1s') Rydberg level is still discernible in Fig. 1b. This small prompt electron background can be completely eliminated by a proper adjustment of the timing of the pulsed electric field so that it coincides properly with the 48 ns dark gap. Upon completion of the tuning process, the resulting Ar PFI–ZEKE PE spectrum shown in Fig. 1c is free of the prompt electron background. Furthermore, the width for the Ar $^3P_{3/2}$ PFI–ZEKE PE band is noticeably narrower than that of Fig. 1b.

The energy resolution achieved in a PFI–ZEKE PE experiment is determined by the resolution of the excitation light source and the magnitude of the pulsed electric field. An energy resolution of 0.4 meV (FWHM) is observed in the Kr $^2P_{3/2}$ PFI–ZEKE PE spectrum (Fig. 2a). The latter spectrum was measured using monochromator slits of 25 μm and a pulsed field of 0.67 V/cm. As mentioned earlier, the highest obtainable resolution of the monochromatized undulator synchrotron radiation is 0.3 meV (FWHM) at 21.6 eV and should be better than 0.3 meV (FWHM) at lower photon energies. We find that the energy resolution remains essentially unchanged when the monochromator slits are set in the range of 30–50 μm in the Ne and Ar PFI–PE experiment. The best resolution observed in the PFI–ZEKE PE spectrum for Ar $^3P_{3/2}$ is 0.45 meV (FWHM) using monochromator slits of 30 μm and a pulsed field of 0.5 V/cm. The energy resolution of the Ar PFI–ZEKE PE spectrum was also examined by varying the height of the pulsed electric field, while keeping the monochromator slits unchanged at 25 μm. The decrease of the pulsed electric field from 0.67 to 0.33 V/cm was found to result in a moderate improvement in the PFI–ZEKE PE energy resolution as shown in Fig. 2b,c. As expected, the PFI–ZEKE PE intensity is lower for a lower pulsed electric field.

As shown by the data simulation, the rotational temperature of O$_2$ achieved in the continuous neat O$_2$ supersonic beam was $\approx$100 K. Recently, a rotational temperature of $\approx$50 K was observed for the O$_2$ beam after the skimmer was changed to an electroformed skimmer with a sharper conical edge. The upper spectrum in Fig. 3a (open circles) is the rotationally resolved PFI–ZEKE PE band for O$_2$ ($^b\Sigma^+_g, v^+ = 0$) using an effusive beam which has a temperature of 298 K. This spectrum (Fig. 3b, solid circles) is shown together with its simulation (Fig. 3b, open circles) using a rotational temperature of 298 K. The good fit obtained can be taken as support of the rotational temperatures obtained in the simulation presented here. All O$_2$ spectra (except that of Fig. 3a,b) presented below were obtained using the old skimmer and can be characterized with rotational temperatures in the range of 100–120 K.

The absolute photon energy scale for the O$_2$ spectra were calibrated using the Ne $^2P_{3/2}$ and Ar $^3P_{3/2}$ PFI–ZEKE PE bands measured under
the same experimental conditions [28]. The Ne and Ar PFI–ZEKE PE spectra were obtained before and after each PFI–ZEKE PE measurement. If the $^2P_{3/2}$ resonance positions for these separate scans of Ar and Ne agreed within the PFI–ZEKE PE energy resolution, then the average of the $^2P_{3/2}$ resonance positions for Ar and Ne were used to calibrate the $O_2$ PFI–ZEKE PE spectra. This calibration procedure is believed to have an accuracy better than ±1 meV. As described below, this calibration procedure yields a value of 18.1720 ± 0.0010 eV for $IE[O_2^+(b^4\Sigma_g^+, \nu^+ = 0, N^+ = 1)]$ [27]. On the basis of the known (0, 0) band origin for the $O_2^+(a^4\Pi_u) \rightarrow O_2^+(b^4\Sigma_g^+)$ transition [47] and the $IE[O_2^+(a^4\Pi_u)] = 16.1046 \pm 0.00025$ eV reported in a recent VUV laser PFI–ZEKE PE study [14], we calculate a value of 18.1713 ± 0.00025 eV for $IE[O_2^+(b^4\Sigma_g^+, \nu^+ = 0, N^+ = 1)]$. Since this latter value is more accurate than the $IE$ value determined in the present study, we have further calibrated the energy scale of our experiment by normalizing the $IE[O_2^+(b^4\Sigma_g^+, \nu^+ = 0, N^+ = 1)]$ to 18.1713 eV.

In the present experiment, the photon energy step size used is in the range of 0.2 meV. The dwell time at individual steps is in the range of 2–8 s.

### 2.2. Measurements of effective lifetimes for high-$n$ Rydberg states

The effective lifetimes ($\tau$) of high-$n$ Rydberg states converging to the $O_2^+(b^4\Sigma_g^+, \nu^+)$ ionization states can be examined by measuring the PFI–ZEKE PE intensity as a function of the delay for the pulsed electric field. Unlike experiments using pulsed VUV lasers [36,37], where the delay time for each extraction of PFI–ZEKE PEs formed from high-$n$ Rydberg states is well defined within the laser pulse width of less than 10 ns, the multibunch ALS light generates high-$n$ Rydberg states at 2 ns intervals except during the 48 ns dark gap. As mentioned above, the pulsed electric field can only be applied after an 8 ns delay with respect to the beginning of the 48 ns dark gap. In the present experiment, the intensity of individual PFI–ZEKE PE vibrational bands was measured by employing a pulsed electric field every two (three) periods, i.e. the delay time between the formation of high-$n$ Rydberg states and the application of a pulsed electric field is varied between 8 ns and 1.27 μs (1.93 μs). Bearing in mind that a set of high-$n$ Rydberg levels converging to a given ionization threshold is excited, the measured lifetimes are effective lifetimes characteristic of the set of Rydberg
states involved. Considering that the PFI–ZEKE PE peak is lower than the TPE peak (or true ionization limit) by 0.3 meV, we estimate that the most probable n value is ≈ 150. When applying a pulsed electric field every two periods, the observed PFI–ZEKE PE intensity $I_{ob}(2)$ can be calculated by the equations,

$$I_{ob}(2) = \left[ \sum_{n=0}^{N-1} I(t_0 + n\Delta t) + \sum_{n=0}^{N-1} I(t_0 + t_p + n\Delta t) \right] \times \frac{N_s}{2},$$

(1)

where $I(t_0 + n\Delta t) = I_0 \exp[(t_0 + n\Delta t)/\tau]$ and $I(t_0 + t_p + n\Delta t) = I_0 \exp[(t_0 + t_p + n\Delta t)/\tau]$ are the intensities of PFI–ZEKE PEs produced by the nth light pulse before the first and second 48 ns dark gap, respectively. Here, $\Delta t = 2$ ns (time separation between two successive light pulses), $t_p = 656$ ns (one period of the ALS light pulses), $N = 304$ (number of the light pulses in one period), $N_s$ is number of the periods in a second, and $I_0$ is the initial intensity of high-\(n\) Rydberg states produced by a single light pulse.

Eq. (1) can be simplified as

$$I_{ob}(2) = I_0 e^{-t_p/\tau} \times \left( 1 + e^{-\tau/\tau} \right) \frac{1 - e^{-N\Delta t/\tau}}{1 - e^{-\Delta t/\tau}} \times \frac{N_s}{2},$$

(2)

Similarly, when applying a pulsed electric field every three periods, the observed PFI–ZEKE PE intensity $I_{ob}(3)$ can be expressed as:

$$I_{ob}(3) = I_0 e^{-t_p/\tau} \times \left( 1 + e^{-\tau/\tau} + e^{-2\tau/\tau} \right) \frac{1 - e^{-N\Delta t/\tau}}{1 - e^{-\Delta t/\tau}} \times \frac{N_s}{3}.$$

(3)

The $\tau$ value can be solved exactly using Eqs. (2) and (3), and is expressed as:

$$\tau = -\frac{t_p}{\ln(x)},$$

(4)

where $x = (-2r + 3 + 3(-2r + 3)(2r + 1))/4r$ and $r = I_{ob}(2)/I_{ob}(3)$. Thus, the $\tau$ value for high-\(n\) Rydberg states converging to an ionization threshold can be calculated using Eq. (4) by measuring the ratio $r = I_{ob}(2)/I_{ob}(3)$. Here, we use the PFI–ZEKE PE peak area as a measure of the $I_{ob}(2)$ and $I_{ob}(3)$.

In the present experiment, we measured $I_{ob}(2)$ and $I_{ob}(3)$ by applying a pulsed electric field to the photoionization region every two and three periods, respectively. The intensity contribution from the last two periods before the application of a pulsed electric field in an $I_{ob}(3)$ measurement is identical to that contributed from the same two periods in an $I_{ob}(2)$ measurement. The intensity difference of these two measurements comes from the intensity contribution of the first period in an $I_{ob}(3)$ measurement. As indicated in Eqs. (2) and (3), $I_{ob}(2)$ should be smaller than 1.5$I_{ob}(3)$.

Since $\tau$ depends on the ratio of PFI–PE intensities of two measurements, greater sensitivity requires that the intensity difference of the measurements is large. Instead of deriving $\tau$ from the ratio $I_{ob}(2)/I_{ob}(3)$, it would be more accurate to calculate $\tau$ using $I_{ob}(1)/I_{ob}(3)$ because the difference between $I_{ob}(1)$ and $I_{ob}(3)$ is larger than that between $I_{ob}(2)$ and $I_{ob}(3)$. However, due to the limitation of our pulser, we cannot apply a pulsed electric field every synchrotron ring period, i.e. $I_{ob}(1)$ cannot be measured.

Another uncertainty in high-\(n\) Rydberg lifetime measurements, which is inherent in the present measurement as well as in laser-based experiments, could come from the possibility that the detection efficiencies for PFI–PEs formed at different locations in the ionization region are different. Those high-\(n\) Rydberg states generated immediately after the last pulsed electric field, will travel as far as 1 mm along the molecular beam axis before the pulsed electric field is applied in an $I_{ob}(3)$ measurement. Here, we assume that the collection efficiencies are the same for all PFI–PEs regardless of the location where they are field ionized.

3. Results and discussion

The spectra in the lower panels of Fig. 4a–c show the PFI–ZEKE PE bands for $O_2^+(b^3\Sigma_g^-, v^+)$ in the energy range 18.1–20.2 eV. The TPE spectra showing the $O_2^+(b^3\Sigma_g^-, v^+)$ bands in the same energy range are displayed in the upper panels of Fig. 4a–c. We note that these PFI–ZEKE PE (TPE) spectra are
Fig. 5. Comparison of the TPE (upper curve) and PFI–ZEKE PE (lower curve) spectra for (a) $\text{O}_2^+$ ($b^2 \Sigma_g^+, v^* = 4$), (b) $\text{O}_2^+$ ($b^2 \Sigma_g^+, v^* = 5$), and (c) $\text{O}_2^+$ vibronic band at 19.633 eV. The PFI–ZEKE PE and TPE resolutions are 0.5 meV and 0.8 meV at FWHM, respectively.

Fig. 4. (a) PFI–ZEKE PE (lower panel) and TPE (upper panel) spectra for $\text{O}_2^+$ ($b^4 \Sigma_g^+, v^* = 0–4$) in the energy range of 18.12–18.74 eV. (b) PFI–ZEKE PE (lower panel) and TPE (upper panel) spectra for $\text{O}_2^+$ ($b^4 \Sigma_g^+, v^* = 5–9$) in the energy range of 18.74–19.36 eV. (c) PFI–ZEKE PE (lower panel) and TPE (upper panel) spectra for $\text{O}_2^+$ ($b^4 \Sigma_g^+, v^* > 9$) in the energy range of 19.36–20.00 eV. The PFI–ZEKE PE and TPE energy resolution are 0.5 and 0.8 meV at FWHM, respectively. The vibrational progression for the $\text{O}_2^+$ ($b^4 \Sigma_g^+$) state is marked up to $v^* = 18$ in the TPE spectrum to correlate with the observed features. The positions of two other vibrational progressions suggested in Ref. [10] are also marked. Note that the same $I(e^-)/I(h\nu)$ units are used for the spectra of (a), (b), and (c). The upper curve of each spectrum is magnified by 40 times from the lower trace which is scaled as the ordinate.
plotted with the same normalized intensity scale, i.e., $I(e^-)/I(h\nu)$, where $I(e^-)$ and $I(h\nu)$ are the PFI–ZEKE PE (or TPE) and VUV intensities, respectively.

In Fig. 5, comparison of the TPE band (upper curve, open circles) and PFI–ZEKE PE band (lower curve, solid circles) for $O_2^+(b^4\Sigma_g^-, v^+ = 4)$ (Fig. 5a) and $O_2^+(b^4\Sigma_g^+, v^+ = 5)$ (Fig. 5b) are shown in a magnified scale. Although rotational structures are discernible in the TPE bands, the resolution achieved in the PFI–ZEKE PE spectra is clearly higher. The hot electron tail associated with the transmission function in TPE measurements conceals much of the weaker rotational structures.

![Fig. 6. Comparison of the simulated (●) and experimental (○) PFI–ZEKE PE bands for $O_2^+(b^4\Sigma_g^+)$ (a) $v^+ = 0$, ($C_0$, $C_s$) = (0.60, 0.40), $T_{rot} = 100$ K; (b) $v^+ = 1$, ($C_0$, $C_s$) = (0.50, 0.50), $T_{rot} = 100$ K; (c) $v^+ = 2$, ($C_0$, $C_s$) = (0.58, 0.42), $T_{rot} = 100$ K; (d) $v^+ = 3$, ($C_0$, $C_s$) = (0.70, 0.30), $T_{rot} = 100$ K; (e) $v^+ = 4$, ($C_0$, $C_s$) = (0.28, 0.72), $T_{rot} = 100$ K; (f) $v^+ = 5$, ($C_0$, $C_s$) = (0.15, 0.85), $T_{rot} = 100$ K; (g) $v^+ = 6$, ($C_0$, $C_s$) = (0.71, 0.29), $T_{rot} = 100$ K; (h) $v^+ = 7$, ($C_0$, $C_s$) = (0.62, 0.38) $T_{rot} = 100$ K; (i) $v^+ = 8$, ($C_0$, $C_s$) = (0.40, 0.60), $T_{rot} = 100$ K; and (j) $v^+ = 9$, ($C_0$, $C_s$) = (0.52, 0.48), $T_{rot} = 100$ K. The PFI–ZEKE PE energy resolution = 0.5 meV (FWHM).
Individual PFI–ZEKE PE vibronic bands for 
\( \mathrm{O}_2^+ (b^+ \Sigma_g^+, \nu^+ = 0\rightarrow 9) \) showing the rotational assignments and their comparisons with corresponding simulated spectra are depicted in Fig. 6a–j. The rotational assignments and simulations are discussed in Sections 3.2 and 3.3 below.

3.1. Relative intensities of \( \mathrm{O}_2^+ (b^+ \Sigma_g^+, \nu^+ = 0\rightarrow 9) \) vibronic bands

The relative vibronic band intensities for the 
\( \mathrm{O}_2^+ (b^+ \Sigma_g^+, \nu^+ = 0\rightarrow 9) \leftarrow \mathrm{O}_2 (X^3 \Sigma_g^+, \nu^+ = 0) \) transitions obtained from HeI–PE [3], HeII–PE [3], TPE [6], and PFI–ZEKE PE spectroscopic studies are compared in Table 1. The vibrational band intensity for \( \nu^+ = 0 \) has been arbitrarily normalized to 100. Here, the relative intensities for the PFI–ZEKE PE or TPE vibronic bands are approximated by the height of the most intense peak in each band, which mostly corresponds to the band head of the Q branch \((N^\prime = 1) \) (see Section 3.2 below). The relative PFI–ZEKE PE and TPE vibrational band intensities of 
\( \mathrm{O}_2^+ (b^+ \Sigma_g^+, \nu^+ = 0\rightarrow 9) \) are based on the average of at

![Fig. 6 continued.](image-url)
least two independent measurements. The TPE vibrational band intensities obtained in the present experiment are consistent with those reported in Ref. [6] except that the order for the relative intensities of \(v^+ = 4\) and 5 are reversed.

Taking into account the estimated uncertainties of \(\pm 10-20\%\) for both the PFI–ZEKE PE and TPE measurements of this study, we find relatively good agreement between the PFI–ZEKE PE and TPE results. Due to the continuity of oscillating strength across the ionization threshold, the TPE and PFI–PE intensities are expected to be identical provided that the effective lifetime for high-\(n\) Rydberg states involved are sufficiently long. Furthermore, the relative intensities for PFI–ZEKE PE vibrational bands should be the same as those for TPE vibrational bands when the effective lifetimes for high-\(n\) Rydberg states converging to the corresponding \(\Omega_g^+(b^\prime \Sigma_g^+, v^+)\) vibronic states are identical. As indicated below in Section 3.4 regarding the effective

![Fig. 6 continued.](image)
lifetime measurements, this is the case for \( v^+ = 0 \rightarrow 5 \). Thus, the similar relative intensities for the \( \Omega_2^+ (b^+ \Sigma_g^+, v^+ = 0 \rightarrow 5) \) vibronic bands observed in the PFI–ZEKE PE and TPE spectra are to be expected. It seems that the relative PFI–ZEKE PE intensities for \( v^+ = 5 \rightarrow 9 \) are consistently lower than the corresponding TPE values. Due to the decreasing PFI–ZEKE PE and TPE peak intensities observed for the \( v^+ = 5 \rightarrow 9 \) vibrational bands with respect to the electron background level, this discrepancy may reflect the lack of accuracy in these measurements.

We have included in Table 1 the normalized Franck–Condon factors (nFCF) for the \( \Omega_2^+ (b^+ \Sigma_g^+, v^+ = 0 \rightarrow 7) \leftrightarrow \Omega_2 (X^3 \Sigma_g^-, \ v^+ = 0) \) transitions calculated in this study and in Ref. [3]. The values obtained here are calculated by assuming that both the \( \Omega_2 (X^3 \Sigma_g^-) \) and \( \Omega_2^+ (b^+ \Sigma_g^+) \) states have the form of a Morse potential. The present results show a more rapid decrease in FCFs as \( v^+ \) increases in comparison to those of Ref. [3].

The vibrational band intensities measured by the HeII–PE study [3] are in good agreement with the
nFCFs of Ref. [3]. However, the relative vibrational intensities for \( v^+ = 0–6 \) obtained by the HeI–PE study [3] fall off more slowly than the nFCFs, while the relative vibrational intensities for \( v^+ = 0–4 \) obtained by TPE and PFI–ZEKE PE measurements fall off more quickly. The deviation from the FCF behavior indicates that the vibrational intensities determined in the HeI–PE, TPE, and PFI–ZEKE PE experiments are perturbed. The intensity perturbation observed in these experiments could originate from near-resonance autoionization [13,15], shape resonance, [16–18] and/or interactions with dissociative states.

The possible influence of near-resonance autoionization on the TPE \( \text{O}_2^+ \left( b^+ \Sigma_g^+, v^+ \right) \) vibronic band intensities has been discussed in the recent TPE study [6]. As pointed out by Merkt et al. [6], the PIE spectrum [2] for \( \text{O}_2 \) in this region is dominated by several series of autoionizing Rydberg states converging to the first four vibrational levels of

Fig. 6 continued.
O$_2$(B$^2\Sigma^+_g$). These Rydberg states autoionize predominantly to form O$_2$(b$^4\Sigma^+_g$, $v^+$) [50]. The comparable geometry of the O$_2$(b$^4\Sigma^+_g$, $v^+$) and O$_2$(B$^2\Sigma^+_g$, $v^+$) states suggests that autoionization is favored by the propensity rule $\Delta v = 0$. Thus, the intensities of the lower vibrational levels of O$_2$(b$^4\Sigma^+_g$) are expected to be enhanced. Both the TPE [9] and Hel–PE [3] spectra of the O$_2$(B) state show significant intensities only for $v^+ = 0$–6. Assuming that autoionization is governed by the $\Delta v = 0$ propensity rule, an autoionization process should lend little intensity to the formation of O$_2$(b$^4\Sigma^+_g$, $v^+$ $>6$), i.e. the TPE band intensities for $v^+>6$ should have negligible contribution from autoionization.

The effect of autoionization on a PFI–ZEKE PE spectrum is also manifested as local intensity enhancements. In a recent Stark field ionization study of high-$n$ Rydberg states converging to Ne$^+$(2P$^3/2$) by detecting the Ne$^+$(2P$^3/2$) ions, the Ne(13s) state was found to manifest as a strong peak in the field ionized Ne$^+$(2P$^3/2$) band at a Stark field of <1 V/cm [28]. The Ne(13s) state lies 3 meV lower than the Ne$^+$(2P$^3/2$) threshold, and is a member of a Rydberg series that converges to the spin–orbit excited Ne$^+$(2P$^3/2$) state.

In order for the near-resonance autoionization mechanism to significantly influence the TPE (or PFI–ZEKE PE) intensities for O$_2$(b$^4\Sigma^+_g$, $v^+$, $N''$), the threshold of these rovibronic states have to lie close to one or more autoionizing Rydberg states [15]. However, from the comparison of the PIE [2] and the TPE (or PFI–ZEKE PE) spectra, we find that the majority of the vibrational bands are far from prominent autoionizing Rydberg states. Since the rotational state distribution within individual vibrational bands is not severely distorted, as can be seen from the relatively good fit of the Buckingham–Orr–Sichel (BOS) model [51] (see Section 3.3 below), we conclude that the near-resonance autoionization mechanism plays an insignificant role in the formation of O$_2$(b$^4\Sigma^+_g$, $v^+ = 0$–9).

The observation that the TPE (or PFI–ZEKE PE) intensities of lower vibrational bands fall off more quickly than the calculated FCFs could be attributed to the $\sigma_\alpha$ shape resonance in the photoionization of

<table>
<thead>
<tr>
<th>$v^+$</th>
<th>IE (eV)</th>
<th>Relative intensity</th>
<th>$\Delta\nu$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PFI–ZEKE$^a$</td>
<td>TPE$^b$</td>
<td>Hel$^c$</td>
</tr>
<tr>
<td>0</td>
<td>18.1713</td>
<td>18.171</td>
<td>18.171</td>
</tr>
<tr>
<td>1</td>
<td>18.3153</td>
<td>18.314</td>
<td>18.315</td>
</tr>
<tr>
<td>2</td>
<td>18.4553</td>
<td>18.452</td>
<td>18.454</td>
</tr>
<tr>
<td>3</td>
<td>18.5910</td>
<td>18.586</td>
<td>18.590</td>
</tr>
<tr>
<td>4</td>
<td>18.7224</td>
<td>18.716</td>
<td>18.721</td>
</tr>
<tr>
<td>5</td>
<td>18.8496</td>
<td>18.847</td>
<td>18.848</td>
</tr>
<tr>
<td>6</td>
<td>18.9725</td>
<td>18.970</td>
<td>18.968</td>
</tr>
<tr>
<td>7</td>
<td>19.0912</td>
<td>19.085</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>19.2059</td>
<td>19.200</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>19.3161</td>
<td>19.308</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ This work. The IE values determined here correspond to transitions O$_2$(b$^4\Sigma^+_g$, $v^+ = 0$–9) $\rightarrow$ O$_2$(X$^2\Sigma^+_g$, $v'' = 0$, $N'' = 1$). Estimated uncertainties are $\pm 0.00025$ eV for $\Delta E$($O_2$(b$^4\Sigma^+_g$, $v^+ = 0$, $N'' = 1$), $\pm 0.0006$ eV for $\Delta E$($O_2$(b$^4\Sigma^+_g$, $v^+ = 1$–9, $N'' = 1$), $\pm 0.0006$ eV for $\Delta E$ values, and $\pm 10\%$ for the relative PFI–ZEKE PE intensities of $v^+ = 0$–4 and $\pm 25\%$ for those of $v^+ = 5$–9.

$^b$ Ref. [6].

$^c$ Ref. [3].

$^d$ Values based on a Morse potential with $\omega_a^2 = 1196.77$ cm$^{-1}$, $\omega_b^2 \chi_b^2 = 17.09$ cm$^{-1}$, and the adiabatic IE of 18.1713 eV for $v^+ = 0$. Refs. [6,47–49].

$^e$ The values in parentheses are obtained in the present study. Estimated uncertainties are $\pm 10\%$ for $v^+ = 0$–5 and $\pm 20\%$ for $v^+ = 6$–9.

$^f$ Normalized FCF. Ref. [3].

$^g$ The values in parentheses are normalized FCFs calculated in the present study by assuming that both O$_2$(X$^2\Sigma^+_g$) and O$_2$(b$^4\Sigma^+_g$) have the form of a Morse potential.
O₂ [16–18]. Because of the internuclear distance dependence of the electronic transition moment, the intensity of a vibrational band would deviate from the FCF behavior in the near resonance. The electronic excited state O₂⁺(b^4Σ−) is formed through the ionization of a 3σg electron from O₂(X^1Σ−). The shape resonance of this electron is around 21.5 eV which is near the ionization threshold of the O₂⁺(b^4Σ−) state. The effect of shape resonance in the partial photoionization cross-sections for the O₂⁺(b^4Σ−) state has been investigated by Raseev et al. [16]. The branching ratios for the formation of ν⁺ = 0–3 of the O₂⁺(b^4Σ−) state were calculated at different excitation energies. At low excitation energies near the ionization onset, the calculated results showed that the branching ratios (ν⁺ = 1 and 2)/(ν⁺ = 0) are smaller than those predicted from FCFs. However, the branching ratios will approach Franck–Condon ratios as the photon energy increases (> 40 eV) far above the ionization threshold. The results of this calculation appear to be in qualitative agreement with the observed relative vibrational intensities measured by TPE [6] and PFI–ZEKE PE spectroscopy, which involve threshold ionization, and by HeII–PE [3] spectroscopy, which uses a photoionization energy of 40.8 eV. Unfortunately, no theoretical results are available for the formation of vibrational bands ν⁺ > 3.

3.2. Ionization energies for O₂⁺(b^4Σ−, ν⁺ = 0–9, N⁺ = 1) ↔ O₂(X^1Σ−, ν⁺ = 0, N⁺ = 1)

The spectroscopic constants for the O₂(X^1Σ−) and O₂⁺(b^4Σ−) states are known [47–49]. Both of these neutral and ionic states have a value of zero for A' and A" (the projected orbital angular momentum along the molecular axis), respectively. The angular momentum coupling of these states can be well described by Hund case (b) [50]. The spin–rotation splittings for O₂(X^1Σ−) are in the range of 0.1–0.2 meV for each rotational state. Although the present PFI–ZEKE PE energy resolution of 0.5 meV (FWHM) is insufficient to resolve these splittings, we have taken into account rotational transitions originating from the three fine structure sublevels F₁, F₂ and F₃ of O₂(X^1Σ−, ν⁺ = 0) over the rotational states N⁺ = 0–25. This results in broadening the rotational lines by ≈ 0.1 meV in the simulated spectra.

It is convenient to designate the rotational branches in terms of ΔN (= N⁺ − N⁻), which is the change in the core angular momentum apart from the spin of the ion and neutral molecule. Due to nuclear spin statistics, the even levels of N⁻ in O₂(X^1Σ−) and N⁺ in O₂⁺(b^4Σ−) do not exist. Thus, only the rotational branches originating from the odd values of N⁻ to odd values of N⁺ are possible, i.e. ΔN = 0, ±2, ±4, etc.

The energy expression used for O₂(X^1Σ−, ν⁺, N⁺) and O₂⁺(b^4Σ−, ν⁺, N⁺) are

\[
E(ν⁺, N⁺) = E^+_c + α^+_c (ν⁺ + \frac{1}{2}) - α^+_c \chi^+_c (ν⁺ + \frac{1}{2})^2 + B^+_c N^+ (N^+ + 1),
\]

and

\[
E^-(ν⁺, N⁺) = E^-_c + α^-_c (ν⁺ + \frac{1}{2}) - α^-_c \chi^-_c (ν⁺ + \frac{1}{2})^2 + B^-_c N^- (N^- + 1),
\]

respectively, where \(B^+_c = B^-_c = α^+_c (ν⁺ + \frac{1}{2})\) and \(B^-_c = B^-_c - α^-_c (ν⁺ + \frac{1}{2})\). The values \(B^+_c = 1.44563 \text{ cm}^{-1}\), \(B^-_c = 1.28729 \text{ cm}^{-1}\), \(α^+_c = 0.01593\), \(α^-_c = 0.0206\), \(α^+_c = 1196.77 \text{ cm}^{-1}\), and \(α^-_c = 17.09 \text{ cm}^{-1}\) are taken from Ref. [47]. We calculate the ionizing transition energies as:

\[
\Delta E(ν⁺, N⁺, N⁻) = E(ν⁺, N⁺) - E(ν⁺ = 0, N⁻)
\]

\[
= ΔE_0 + \omega^-_c (ν⁺ + \frac{1}{2}) - \omega^-_c \chi^-_c (ν⁺ + \frac{1}{2})^2 + B^-_c N^- (N^- + 1) - [B^-_c N^- (N^- + 1)].
\]

where \(ΔE_0 = [E^-_c - E^-_c + α^-_c (\frac{1}{2})^2 + α^-_c \chi^-_c (\frac{1}{2})^2]\). As indicated above, only odd \(N^-\) and \(N^+\) are allowed. We find that only the rotational branches \(ΔN = -2, 0, +2\) (O, Q, and S branches, respectively) are observed in the spectra shown in Fig. 6a–j.

The \(IEs\) for different \(ν⁺\) states correspond to energies for the ionization transitions \(O₂⁺(b^4Σ−, ν⁺, N⁺ = 1) ↔ O₂(X^1Σ−, ν⁺ = 0, N⁻ = 1)\). Thus,

\[
IE(ν⁺, ν⁻ = 0, N⁺ = 1, N⁻ = 1) = \Delta E(ν⁺, N⁺ = 1, N⁻ = 1)
\]

\[
= [ΔE_0 + 2B^-_c + 2B^+_c] + α^-_c \chi^-_c (ν⁺ + \frac{1}{2})
\]

\[
- α^-_c \chi^-_c (ν⁺ + \frac{1}{2})^2.
\]

Although \(2B^-_c\) depends on \(ν⁺\), its variation between \(ν⁺ = 0\) and \(ν⁺ = 10\) is only \(≈ 0.45 \text{ cm}^{-1}\), and is less
than the resolution of the present study. Hence, \( [\Delta E_x + 2 B_{x_z} - 2 B_{y_z}] \) can be considered constant for \( \nu^+ = 0-10 \), and Eq. (8) is essentially a Morse function with the known vibrational constants (\( \omega_x^\prime = 1196.77 \text{ cm}^{-1} \) and \( \omega_y^\prime = 17.09 \text{ cm}^{-1} \)). Table 1 lists the IE values for the \( \text{O}_2^+(b^4 \Sigma_g^-, \nu^+ = 0-9, N^+ = 1) \leftrightarrow \text{O}_2 (\text{X}^3 \Sigma_g^-, \nu^+ = 0, N^+ = 1) \) ionization transitions determined by the peak positions of the Q branch \([Q(N^+ = 1)]\) for \( \nu^+ = 0-9 \). The peak positions are identified based on the BOS simulation (see Section 3.3 below). As expected, the experimental IE values agree with the corresponding fitted values obtained using a Morse potential to within \( \pm 0.3 \text{ meV} \) for \( \nu^+ = 0-9 \).

### 3.3. Simulation of the rotational intensities

The relative intensities for rotational structures resolved in individual vibrational bands were simulated using the BOS model, which is described by the formula [51],

\[
\sigma (N^+ \leftrightarrow N^+) \propto \sum_i Q(\lambda; N^+, N^+) C_\lambda \tag{9}
\]

This model was derived to predict rotational line strengths \( \sigma (N^+ \leftrightarrow N^+) \) observed in one-photon ionization of diatomic molecules. Basically, the rotational line strength was separated into two factors. The factor \( C_\lambda \) is associated with the electronic transition moments, which is the linear combination of electron transition amplitudes for the possible angular momenta \( l \) of the ejected electron. The other factor \( Q \) is determined by the angular momentum coupling scheme. The parameter \( \lambda \) can be interpreted as the orbital angular momentum quantum number of the electron in the ground state of the neutral molecule before photoexcitation. The more general interpretation of \( \lambda \) is that of the angular momentum transfer in the photoionization process. The angular momentum coupling factor \( Q \), for a Hund’s case (b) to (b) transition, can be expressed by [51]

\[
Q(\lambda; N^+, N^+) = (2N^+ + 1) \left( \frac{N^+}{-\Delta A} \frac{\lambda}{\Delta \lambda} \frac{N^+}{A^+} \right)^2. \tag{10}
\]

The contributions of \( C_\lambda \) were determined from the fit to the experimental data. The simulated spectra were obtained using a Gaussian lineshape with a FWHM of 5 cm\(^{-1}\). We assume that the rotational population for \( \text{O}_2 \) is characterized by a rotational temperature according to the Boltzmann distribution. Generally, we find that a satisfactory fit can be obtained when the rotational temperature used is in the range of 100–120 K. The properties of the 3-j symbol are such that \( \left( J^+ \lambda \lambda' A'' \right)^2 \) vanishes for odd values of \( \lambda \), \( \lambda' = 0 \), and \( \lambda'' = 0 \). Thus, the rotational line intensities have only contributions from \( \lambda = \text{even} \). The observation that only the \( \Delta N = -2, 0, +2 \) rotational branches have significant contributions indicates that only the BOS coefficients \( C_0 \) and \( C_2 \) are needed in the simulation. The contributions of \( C_\lambda \) with \( \lambda \geq 4 \) would have resulted in the observation of rotational branches \( |\Delta N| \geq 4 \), which are found to be negligible in the experimental spectra. The values for \( C_0 \) and \( C_2 \) obtained from the simulations of the \( \text{O}_2^+(b^4 \Sigma_g^-, \nu^+ = 0-9) \) PFI–ZEKE PE bands are plotted in Fig. 7. The error bars given for the \( C_0 \) and \( C_2 \) values account for the variation of independent measurements and PFI–ZEKE PE counting statistics. Generally, \( C_0 \) is larger than \( C_2 \) for most of the vibrational states except \( \nu^+ = 4, 5, \) and 8.

According to the dipole selection rule, \( \lambda \) can only have integer values from \( |l - 1| \) to \( l + 1 \). Also, for a one-photon ionization process, \( l \) must be odd for a \( g \leftrightarrow g \) transition [52]. Therefore, the partial waves of

![Fig. 7](image-url)
the ejected electron are restricted to \( l = 1 \) and 3 for \( \lambda = 2 \), and \( l = 1 \) for \( \lambda = 0 \). The Q branch gains the majority of its intensity through the excitation of an \( s \)-wave electron. However, the O and S branches can only acquire their intensities through the photoexcitation of a \( d \)-wave electron. Since both the O and S branches involve the excitation of the same partial wave electron, they are expected to have the same transition dipole moment. As a consequence, the O and S branches should have equal intensities. The simulated spectra for \( v^* = 0 \sim 9 \) are displayed as the lower curves (solid circles) in Fig. 6a–j. The experimental spectra were reasonably reproduced by the simulated spectra. However, for all spectra, the intensities of the O branch are generally higher than the predicted intensities, when the simulation is normalized to the S branch intensity. The phenomena that the intensity for \( \Delta N < 0 \) is larger than that for \( \Delta N > 0 \) has been observed previously and is attributed to electric-field-induced rotational autoionization [53,54]. In addition, the experimental intensities for the Q branch generally are found to be significantly higher than those predicted in the simulated spectra. Unlike all the other \( v^* \) states where the Q branch is the most intense, the intensity of the S branch is higher or comparable to that of the Q branch for \( v^* = 4, 5, \) and 8. This suggests that the rotational branch intensities for \( v^* = 4, 5, \) and 8 have a greater contribution from the photoexcitation of a \( d \)-wave electron.

The BOS model predicts that \( C_\lambda \) coefficients should be identical for an ionization transition to different vibrational levels of an ionic electronic state. The variation of \( C_\lambda \) values over different vibrational states has been observed previously and was attributed to different causes, including shape resonance, and near-resonance autoionization. Braunstein et al. [11] have observed a systematic change in the rotational branch intensities for the vibrational levels \( O^+_2 (X^2 \Pi_g, v^* = 0, 1, \) and 2), and have attributed this observation to the effect of shape resonance associated with the \( 1 \pi_g \) electron [11]. However, in a similar PFI–ZEKE PE study covering the \( O^+_2 (X^2 \Pi_g, v^* \geq 6) \) states, Kong and Hepburn [13] pointed out that the rotationally resolved PE spectra are not sensitive to shape resonance. A variance of the near-resonance autoionization mechanism was proposed to rationalize the experimental observation in the latter study.

As shown in Fig. 7, the \( C_0/C_2 \) ratio for \( v^* = 0 \sim 3, 6, \) and 9 are in the range of 1.04 2.4, i.e. \( C_0 \geq C_2 \). A dramatic change in the \( C_0/C_2 \) ratio from the latter values is observed at \( v^* = 4 \) and 5, where \( C_0 \) is significantly smaller than \( C_2 \). This observation suggests that shape resonance may not have a significant effect on the rotational branch intensities of the \( O^+_2 (b^4 \Sigma_g^-, v^+) \) PFI–PE bands. We pointed out earlier that the smaller ratio for the vibrational band intensity of \( v^* = 1 \) and 2 to that of \( v^* = 0 \) observed in the TPE and PFI–PE spectra as compared to the predicted FCF ratios may be the result of shape resonance. A theoretical study on the change of both rotational and vibrational distributions should help to clarify these seemingly contradictory experimental implications concerning the role of shape resonance on the formation of \( O^+_2 (b^4 \Sigma_g^-, v^+, N^+) \) by photoionization.

Since the BOS coefficient \( C_\lambda \) is associated with the electronic transition moment in a photoionization process, the large deviation of the ratio \( C_0/C_2 \) at \( v^* = 4 \) and 5 compared to those observed for other vibrational states indicates that the mechanism for the production of PFI–ZEKE PEs and TPEs at \( v^* = 4 \) and 5 are perturbed. As pointed out above, since no significant local intensity enhancements are observed in the spectra of Fig. 6a–j, together with the fact that no distinct Rydberg states are found to be in the vicinity of the ionization energies of \( v^* = 0 \sim 9 \), near-resonance autoionization is unlikely to be a cause for the reversed ratio \( C_0/C_2 \) observed at \( v^* = 4 \) and 5. It is possible, however, that there are broader autoionization features resulting from dissociative valence states which would appear nearly continuous over the rotational spectrum of a given \( v^* \) band.

The first dissociation limit \( O^+(4S) + O(3P) \) from \( O^+ \) is at 18.733 eV [51] which lies near the threshold of \( O^+_2 (b^4 \Sigma_g^-, v^* = 4, N^* = 9) \). Previous experiments show that \( O^+_2 (b^4 \Sigma_g^-, v^+, N^+) \) states prepared at energies above this dissociation limit are dissociative with a lifetime in the range of \( \approx 0.01 \sim 4 \) ns [55–58]. These ion predissociation lifetimes depend on the ion fine structure levels, \( F_i^* \) (\( i = 1 \sim 4 \)), but are relatively insensitive to the \( N^+ \) value. We note
that the intensities for the $Q(\geq 9)$ peaks of $v^+ = 4$ with respect to $Q(1)$ (see Fig. 6e) are significantly enhanced compared to those of $v^+ < 4$, suggesting that the perturbation resulting in abrupt change in the $C_0/C_2$ ratio for the $O_2^+(b^4\Sigma_g^-, v^+ = 4$ and $5$) bands is predissociative in nature. Theoretical calculations indicate that the $d^4\Sigma_g^+$, $f^4\Pi_g$, $E^2\Sigma_g^+$, and $a^4\Pi_g$ states correlating to the $O^+(4S) + O(3P)$ limit cross the $O_2^+(b^4\Sigma_g^-)$ surface at $v^+ > 4$. Previous high-resolution laser ion beam dissociation studies of $O_2^+(b^4\Sigma_g^-, v^+ = 3–8$, $N^\pi$, $F^\pi$) lead to the conclusion that predissociation of $O_2^+(b^4\Sigma_g^-, v^+ = 4–8)$ is mostly through the $d^4\Sigma_g^+$ and/or $f^4\Pi_g$ states via spin–orbit couplings. For $O_2^+(b^4\Sigma_g^-, v^+ = 4$ and $5$), the $d^4\Sigma_g^+$ state plays a dominant role, whereas the $f^4\Pi_g$ state is mainly responsible for the predissociation of $O_2^+(b^4\Sigma_g^-, v^+ = 8)$. We note that $C_0$ is also observed to be less than $C_2$ for the $O_2^+(b^4\Sigma_g^-, v^+ = 8)$ band. The calculations of Carre et al. [59] show that the $d^4\Sigma_g^+$ and $O_2^+(b^4\Sigma_g^-$) potential curves intersect slightly above the $O_2^+(b^4\Sigma_g^-, v^+ = 4$) state. The results of the high-resolution laser ion beam dissociation study of Hansen et al. [57] suggests that the crossing occurs slightly above the $O_2^+(b^4\Sigma_g^-, v^+ = 5$) state. The finite interaction between the $d^4\Sigma_g^+$ dissociative state and the $O_2^+(b^4\Sigma_g^-, v^+ = 4$ and $5$) vibrational levels (or high-$n$ Rydberg states converging to these levels) may be responsible for the abrupt change in the $C_0/C_2$ ratio observed in the PFI–PE spectra of Fig. 6e,f. As an extension of the above interpretation, we are tempted to suggest that the $C_0/C_2$ ratio of 0.40/0.60 observed for $v^+ = 8$ is caused by crossing of the $f^4\Pi_g$ state. Although the exact location of this curve crossing has not been determined, the theoretical and laser ion beam studies suggest that the $f^4\Pi_g$ state crosses the $O_2^+(b^4\Sigma_g^-$) between $v^+ = 6$ and $7$, which is not consistent with the latter interpretation. Rigorous theoretical calculations are required to confirm the above speculation.

3.4. Effective lifetimes for high-$n$ Rydberg states

The success of the PFI–ZEKE PE technique relies on the prolonged lifetimes of high-$n$ Rydberg states [33,34]. The investigation of the factors, such as electric field, magnetic field, and ions, which affect the lifetimes of high-$n$ Rydberg states is still of great interest to the field of PFI–ZEKE PE spectroscopy [35–45]. In the absence of external perturbations, the lifetime of a Rydberg state [38] is scaled as $n^3$. The existence of an homogeneous electric field may induced $l$-mixings. The complete $l$-mixings enhance the lifetime by a factor of $n$ [35,38]. The lifetime can be further prolonged by another factor of $n$ if complete $m_l$-mixing occurs [35,37–39]. In a usual PFI–ZEKE PE study, stray fields always exist and would cause partial $l$-mixing. Finite $m_l$-mixing can be induced by inhomogeneous fields due to the presence of ions produced together with high-$n$ Rydberg species in the photoexcitation process. In a pulsed laser PFI–ZEKE PE experiment, [36,37,39–45] the ion densities produced are generally in the range of $10^4$–$10^7$ ions/cm$^3$. Thus, the measured lifetime could be strongly influenced by $m_l$-mixing. The effects of these factors on Rydberg state lifetime measurements are quite complex, and depend on the magnitude of the stray field and the concentration of ions involved.

Since the ALS light is a pseudo-continuous light source, the ion density produced simultaneously with high-$n$ Rydberg state species in the photoionization region is negligibly small. For example, the ion counting rate of this experiment is $\approx 10000$ counts/s, which corresponds to an ion density of $\approx 22$ ions/cm$^3$. Thus, the high-$n$ Rydberg lifetimes measured using synchrotron radiation, such as the ALS, are not expected to be strongly influenced by ions, i.e. the lifetime lengthening effect due to $m_l$-mixing, which result from the presence of ions, is minimized.

The $\tau$ values for high-$n$ Rydberg states converging to $O_2^+(b^4\Sigma_g^-, v^+ = 0$, $2$, $3$, $4$, and $5$) states measured in the present experiment are given in Table 2. These $\tau$ values were determined to be in the range of 1.8–2.0 $\mu$s. The uncertainties for the measured intensity ratio $I_{ob}(2)/I_{ob}(3)$ are estimated to be about $\pm 3\%$. The $\tau$ values calculated by increasing and decreasing 3% of the $I_{ob}(2)/I_{ob}(3)$

---

The height of the VUV beam is 0.03 cm. Assuming that the width of the $O_2$ beam is 0.3 cm and the $O_2$ molecular beam velocity is $\approx 5 \times 10^4$ cm/s, the volume traced out by the beam in 1 s is $0.03 \times 0.3 \times 5 \times 10^4$ cm$^3$. Thus, the number density is $(10^4$ ions/s)/(0.045$\times 10^3$ cm$^3$/s) $\approx 22$ ions/cm$^3$. 

---
Table 2

<table>
<thead>
<tr>
<th>( v^+ )</th>
<th>( \tau ) (( \mu s ))</th>
<th>( \tau + \Delta \tau ) (( \mu s ))</th>
<th>( \tau - \Delta \tau ) (( \mu s ))</th>
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<tbody>
<tr>
<td>0</td>
<td>1.9</td>
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</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>2.6</td>
<td>1.6</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>2.7</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>1.8</td>
<td>2.3</td>
<td>1.4</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
<td>2.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*Effective lifetimes are calculated using Eq. (4), which depends on the ratio \( \tau = I_{eb}(2)/I_{eb}(3) \). Here \( I_{eb}(2) \) and \( I_{eb}(3) \) are measured using the area of individual PFI–ZEKE PE vibronic bands. Thus, the \( \tau \) values are assumed to be independent of \( N^+ \). See the text.*

*Effective lifetimes calculated assuming that \( I_{eb}(2)/I_{eb}(3) \) increases by 3%.*

*Effective lifetimes calculated assuming that \( I_{eb}(2)/I_{eb}(3) \) decreases by 3%.*

The ratio is also shown in Table 2. This amounts to uncertainties of about ±0.8 \( \mu s \) for the \( \tau \)s. Since these \( \tau \) values are nearly identical, similar vibrational intensity ratios and signal intensities are expected for PFI–ZEKE PE and TPE measurements. These expectations are consistent with the experimental observations of this study. We note that \( I_{eb}(2) \) and \( I_{eb}(3) \) are measured by the areas of the observed PFI–ZEKE PE bands. This procedure in essence assumes that the \( \tau \) value is independent of the rotational level within a vibronic state.

As mentioned above, since the detection of the PFI–ZEKE PEs is very sensitive to the position where they are formed, a finite decay of the PFI–ZEKE PE signal can be attributed to the finite speed of the \( \text{O}_2 \) molecular beam. Assuming the speed of the molecular beam to be \( \approx 6 \times 10^4 \) cm/s, the \( \text{O}_2 \) molecules formed in high-\( n \) Rydberg states should travel < 1.2 mm before the application of the Stark electric field pulse in a three-period operation, i.e. a Stark pulsed electric field is applied every 1.97 \( \mu s \). The maximum displacement of 1.2 mm should still be within the detection zone of the electron spectrometer, which has an entrance aperture of 3 mm in diameter. We believe that the decay of the PFI–ZEKE PE signal contributed by the displacement of the \( \text{O}_2 \) beam is not important. The \( \tau \) values for high-\( n \) Rydberg states converging to \( \text{O}_2^+(b^4\Sigma_g^+, v^+ = 0–6) \) have also been measured using the same experimental conditions [60]. These lifetimes are found to be \( \approx 0.5 \) \( \mu s \). The detailed examination of the displacement factor on the lifetime measurements for high-\( n \) Rydberg states will be addressed in a forthcoming paper [60].

It is interesting that the \( \tau \) values for the \( v^+ = 4 \) and 5 states are essentially the same as those of the lower vibrational states. As pointed out above, \( IE[O_2^+(v^+ = 5)] \) and \( IE[O_2^+(v^+ = 4, N^+ > 9)] \) are above the \( O^+(4S) + O(3P) \) dissociation limit of 18.733 eV. For an electron in a sufficiently high-\( n \), high-\( l \), and high-\( m \) Rydberg state with a near circular orbit, the coupling between the electron and the core is small. Such a Rydberg electron may not respond rapidly even when the core is dissociating, i.e. the lifetime of the Rydberg electron with respect to autoionization may be longer than the dissociative lifetime of the ion core. The latter conclusion should be valid if the kinetic energy for \( O^+(4S) + O(3P) \) resulting from the dissociation of the \( O_2^+ \) ion core is sufficiently small, such that \( O^+(4S) \) and \( O(3P) \) depart from each other at a speed significantly slower than the electron orbiting speed. On the basis of this consideration, we believe that the (autoionization) lifetime of a high-\( n \) Rydberg state is effectively decoupled from the dissociative lifetime of the ion core. In view of the fact that the pulsed electric field was applied once for every 1.31 \( \mu s \) (or 1.97 \( \mu s \)), and that the PFI–ZEKE PE intensity was as strong as the TPE intensity, the high-\( n \) Rydberg electrons involved must have survived autoionization for at least 1.3 \( \mu s \). Thus, this observation can be taken as strong evidence that the coupling between the high-\( n \) Rydberg electron and the \( O_2^+(b^4\Sigma_g^+, v^+) \) ion core involved is negligibly small.

The \( \tau \) values for high-\( n \) Rydberg states converging to \( O_2^+(b^4\Sigma_g^+, v^+ = 6–9) \) have not been measured. The observation that the relative vibronic band intensities for \( O_2^+(b^4\Sigma_g^+, v^+ = 0–9) \) observed in the PFI–ZEKE PE measurement are similar to those found in the TPE study suggests that the \( \tau \) values for \( O_2^+(b^4\Sigma_g^+, v^+ = 6–9) \) are likely similar to those for \( O_2^+(b^4\Sigma_g^-, v^+ \leq 5) \).

3.5. TPE and PFI–ZEKE PE spectra in the 19.4–20.0 eV range

In the recent TPE study of Merkt et al. [6], the \( O_2^+(b^4\Sigma_g^-, v^+ = 10–18) \) states are identified in the
energy region of 19.4–20.0 eV. Two weak vibrational progressions in this energy region were also suggested. The PFI–ZEKE PE and TPE spectra in this energy range (Fig. 4c) were obtained with higher resolution (0.8 meV (FWHM)) than that (5 meV (FWHM)) of Ref. [10]. Due to the lower signal intensity observed in the PFI–ZEKE PE experiment, only two strong PFI–ZEKE PE bands at 19.634 and 19.949 eV are recorded. We have marked the expected position of the $O_2^+(b^4\Sigma_g^-, \nu = 10–18)$ in the TPE spectrum (upper panel of Fig. 4c) to correlate with the observed structures. A weak, broad TPE peak is found to correlate with the $O_2^+(b^4\Sigma_g^-, \nu = 10)$ vibronic state. The predicted positions for the $\nu = 12, 13, 14$, and 16 states are in the vicinity of TPE peaks belonging to other progressions. Within the signal-to-noise ratios achieved in this experiment, the existence of TPE peaks for $O_2^+(b^4\Sigma_g^-, \nu = 11–18)$ is not confirmed.

Four peaks are observed in this energy range, which may be members of the two weak progressions suggested in the previous TPE study [6,56]. Other features are either very weak or diffuse. The possible origin of these peaks as gained by autoionization has been discussed [6]. The positions of these TPE and PFI–ZEKE PE peaks observed here are compared to those reported previously in Table 3. We note that the peak positions observed in the present study are quite different from those reported in previous studies. The vibrational spacing for the first two vibrational levels of the progression starting at 19.6339 eV was measured to be 0.1104 eV as compared to 0.100 eV reported in Ref. [6]. A second-order polynomial fit of these yields $\omega_v = 918.7$ cm$^{-1}$ and $\omega_v \chi_v = 17.74$ cm$^{-1}$ for this progression.

## Table 3

<table>
<thead>
<tr>
<th>Progression $\nu^+$</th>
<th>PFI–ZEKE PE (eV)$^a$</th>
<th>TPE (eV)$^b$</th>
<th>TPE (eV)$^c$</th>
<th>HeI (eV)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.6326</td>
<td>19.6339</td>
<td>19.643</td>
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</tr>
<tr>
<td>1</td>
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<td>19.7434</td>
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<tr>
<td>2</td>
<td>–</td>
<td>–</td>
<td>19.836</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>19.9473</td>
<td>19.9492</td>
<td>19.924</td>
<td>–</td>
</tr>
<tr>
<td>0</td>
<td>–</td>
<td>19.8112</td>
<td>19.78</td>
<td>19.79</td>
</tr>
<tr>
<td>1</td>
<td>–</td>
<td>–</td>
<td>19.89</td>
<td>19.9</td>
</tr>
</tbody>
</table>

$^a$This work. $^b$Ref. [6]. $^c$Ref. [61]. $^d$Ref. [62].

Merkt et al. proposed that the peaks for these transitions may belong to the $^4\Delta_g$ state with a calculated $IE$ of 20.07 eV and $\omega_v = 665$ cm$^{-1}$. However, the large difference in the vibrational constant $\omega_v$ between the theoretical value calculated by Beebe et al. [54] and our measurement leads us to suggest that this state may not belong to the $^4\Delta_g$ state. The $2^1\Pi_u$ state [5] with a calculated $IE$ of 19.55 eV and $\omega_v = 968$ cm$^{-1}$ may be a more attractive candidate for the assignment of these peaks. A definite assignment requires further investigations.

The TPE and PFI–ZEKE PE bands observed at 19.6339 eV are compared in Fig. 5c. Rotational structures are discernible in the spectra. Due to the limited resolution and the lack of spectroscopic information, a satisfactory simulation using the BOS model has not been made.

The peak observed at 19.8112 eV in the TPE spectrum of Fig. 4c seems to correspond to that observed at 19.78 eV in Ref. [10] and that at 19.79 eV in Ref. [61]. It was assigned to the $^2\Delta_g$ state. In order to compare with the spectra measured previously, the position of the $\nu = 1$ level of the $^2\Delta_g$ state is also marked in the TPE spectrum of Fig. 4c. However, no noticeable peak is observed at this position.

## 4. Conclusion

The rotationally resolved PFI–ZEKE PE bands for $O_2^+(b^4\Sigma_g^-, \nu = 0–9)$ have been measured using high-resolution monochromatized VUV multibunch undulator synchrotron radiation. Within the accuracy of the present experiment, the $IE$ values for the ionization transitions $O_2^+(b^4\Sigma_g^-, \nu^+ = 0–9, N^+ = 1) \rightarrow O_2(X^3\Sigma_g^-, \nu^v = 0, N^v = 1)$ are well predicted using a Morse potential. Vibrational structures correlating to $O_2^+(b^4\Sigma_g^-, \nu^+ = 11–18)$ are not found in the present TPE measurement.

Simulated spectra based on the BOS model are in fair agreement with the experimental spectra except that the BOS model generally underestimates the rotational transitions of the Q branch. Only the rotational branches $\Delta N = -2, 0, +2$ (O, Q, and S branches, respectively) are observed for the $O_2^+(b^4\Sigma_g^-, \nu^+ = 0–9)$ PFI–ZEKE PE bands, indicat-
ing that the outgoing electron \( l = 1 \) and 3 continuum channels dominate in the threshold ionization process. The Q branch is found to dominate over the O and S branches except for \( \nu^+ = 4 \), 5, and 8, where the intensities for the S and O branches are higher or comparable to the Q branch intensities. Since the dissociation limit for \( O^+ (4S) + O(3P) \) lies between the \( \nu^+ = 4 \) and \( \nu^+ = 5 \) states, we suggest that the perturbation interactions due to predissociative \( d^4 \Sigma_g^\pm \) states in the vicinity of the \( O_2^+ (b^4 \Sigma_g^-, \nu^+ = 4 \) and 5) states are responsible for the abrupt change in rotational distributions observed for these vibronic states.

The \( \tau \) values for high-\( n \) Rydberg states converging to the \( O_2^+ (b^4 \Sigma_g^-, \nu^+ = 0\rightarrow 5) \) vibrational levels are estimated to be \( 1.9 \pm 0.8 \) \( \mu \)s. An interesting observation is that the \( \tau \) values for high-\( n \) Rydberg states converging to \( \nu^+ = 4 \) and 5 are significantly longer than that for the corresponding predissociative lifetimes of \( O_2^+ (b^4 \Sigma_g^-, \nu^+ = 4 \) and 5). This observation confirms the expectation that the couplings between the high-\( n \) Rydberg electron and the dissociating ion core are negligibly small.

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References


[60] C.-W. Hsu, M. Evans, S. Stimson, C.Y. Ng, P. Heimann, manuscript to be published.