PFI-ZEKE spectroscopy using coherent vacuum UV: \( \text{O}_2^+ (a^4 \Pi_u) \leftarrow \text{O}_2 (X^3 \Sigma_g^-) \)

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Abstract

The PFI-ZEKE spectra of the first four vibrational levels of \( \text{O}_2(a^4 \Pi_u) \) are reported. The rotationally resolved photoelectron spectra were assigned by diagonalizing the appropriate Hamiltonian in a Hund’s case \( a \) basis set. An extension of a previous model for rotational line strengths (the BOS model) to the intermediate coupling case was applied to the three vibrational bands with \( v^+ = 1-3 \). As has been observed with several \( \text{O}_2 \) states in previous ZEKE studies, the intensities of the spin–orbit sub-levels were not in accord with calculated line strengths. The \( a^4 \Pi_u \) vibrational levels \( v^+ = 0 \) and \( 1 \) were overlapped by the Franck–Condon forbidden \( v^+ = 21 \) and \( 22 \) levels of the \( X^3 \Pi_g \) state, allowing for a direct comparison between the intensities of the Franck–Condon allowed and forbidden bands in the ZEKE spectra. These data allowed us to determine an accurate ionization energy for the \( a^4 \Pi_u \) state: 129892 ± 2 cm\(^{-1}\) (16.1046 eV).

Keywords: PFI-ZEKE spectra; Ionization energy

1. Introduction

The combination of pulsed field ionization zero kinetic energy photoelectron spectroscopy (PFI-ZEKE) [1] and coherent vacuum ultraviolet (VUV) radiation allows for the universal study of photoelectron spectroscopy with rotational resolution [2–7]. For the most part, research in PFI-ZEKE spectroscopy, whether with single photon or multiple photon excitation of the ionization threshold, has focused on the energy region at or just above the lowest ionization threshold in molecules, clusters, and radicals. Little of the published work has discussed the PFI-ZEKE spectra of ionization thresholds far above the lowest ionization threshold, generally corresponding to formation of ions in electronically excited states. It has now been clearly established that the PFI-ZEKE process is quite general, and can be applied to the spectroscopy of excited states of ions, as well as ground states, even in cases where those excited states decay, either radiatively or non-radiatively.

In previous papers, we reported a series of studies on excited states of ions using PFI-ZEKE and coherent VUV [8–12]. The scope of our investigation covered both electronically and highly vibrationally excited states of the ion. Our results on \( \text{NO}^+(a^3 \Sigma^+) \) [9] and \( \text{CO}^+(A^2 \Pi) \) [11] showed that PFI-ZEKE could be applied to stable excited states, and revealed the different dynamical effects that could be observed at high photon...
energies. The work on $\text{N}_2\text{O}^+(\text{A}^2\Sigma^+)$ [10] and $\text{HBr}^+(\text{A}^2\Sigma^+)$ [12] proved the applicability of PFI-ZEKE for studying excited ionic states which decayed before field ionization. Further, in previous work directly related to the data discussed in this paper Franck–Condon forbidden highly vibrationally excited $\text{O}_2^+(X^2\Pi_g)$ thresholds, with $v' \geq 6$, were studied by PFI-ZEKE [13,14]. For these states, the rotational line intensity distributions were simulated using the one-electron model developed by Buckingham et al. [15] (the BOS model), where only two coupling cases (cases b and a) were considered for the initial and final states. While pure case a or case b coupling was a reasonable approximation for the above studies, it is not always adequate for other systems, such as $\text{O}_2^+(\text{a}^4\Pi_u)$. This paper presents a more general approach to this problem, suitable for intermediate coupling cases.

The inherent complexity in the spectroscopy of the quartet state and the intermediate coupling scheme of the $\text{O}_2^+(\text{a}^4\Pi_u)$ state provides a test of using PFI-ZEKE for spectroscopic studies. High resolution spectroscopic data for $\text{O}_2^+(\text{a}^4\Pi_u)$ is available from the photofragment spectroscopy of $\text{b}^4\Sigma_g^- \rightarrow \text{a}^4\Pi_u$, [16],[17] but no absolute term values have been determined yet. In addition, as stated in a previous paper, the thresholds of $\text{O}_2^+(X^2\Pi_g, v' = 21-24)$ are nearly degenerate with the thresholds of $\text{O}_2^+(\text{a}^4\Pi_u, v' = 0-3)$ [14,18]. Although the high-resolution photofragment spectroscopy did not find any perturbations for the near-degenerate states [17], there is a possibility for interactions among the Rydberg states involved in PFI-ZEKE. Observation of the $\text{O}_2^+(X^2\Pi_g, v' \geq 8)$ bands was due to a modified “resonant autoionization” mechanism which resulted in formation of Franck–Condon forbidden vibrational levels of the $\text{O}_2^+$ ion in both TPES [18] and PFI-ZEKE, [14] but the effect of this mechanism on the nearby states needs to be clarified. This can be compared with another investigation on $\text{CO}^+(\text{A}^2\Pi_{1/2}, \nu^+ = 0)$ and $\text{CO}^+(X^2\Sigma^+, \nu^+ = 10)$, [11] where the interaction between the two ionic states resulted in a depletion of the Rydberg states converging to the relatively unstable CO$^+(\text{A}^2\Pi_{1/2}, \nu^+ = 0)$ rotational levels.

To form the $\text{O}_2^+(\text{a}^4\Pi_u)$ state, a $\pi_u$ bonding electron is removed from the neutral $\text{O}_2$, an allowed one-electron photoionization. In conventional photoelectron spectra, the bands corresponding to the $\text{O}_2^+(\text{a}^4\Pi_u)$ state are of comparable intensity to those for the $X^2\Pi_g$ state (ionization of a $\pi_g$ electron), as one would expect. In the current study, it is possible to make a direct comparison between the intensities of Franck–Condon forbidden bands corresponding to high $\nu^+$ levels of $\text{O}_2^+(X^2\Pi_g)$ with Franck–Condon allowed low $\nu^+$ bands of the $\text{O}_2^+(\text{a}^4\Pi_u)$ state. These ZEKE results can be compared with previous TPES work in the same photon energy range [18].

In the following, the experimental setup will be briefly explained, and the experimental results will be analyzed based on previous spectroscopic work. To interpret the rotational line intensities, the BOS model [15] will be briefly summarized and the application of this model in the intermediate coupling case will be discussed.

2. Experimental

The experimental setup has been explained in detail elsewhere [8,9]. The optical system is similar to the one used in the experiments on $\text{CO}^+(\text{A}^2\Pi)$ [11]. Coherent VUV radiation in the energy region 16.22–16.49 eV was generated by resonant four wave sum mixing in a pulsed jet of Kr. The 5p[1/2,0] two photon resonant level of Kr at 94,093.7 cm$^{-1}$ ($2\omega_1$) was used for resonant enhancement, and $\omega_2$ was generated using another BBO doubled dye laser, tunable between 36,700 cm$^{-1}$ and 38,910 cm$^{-1}$. The generated photon frequency was $\omega_{\text{VUV}} = 2\omega_1 + \omega_2$. The similarity between $\omega_1$ and $\omega_2$ made it impossible to overlap the two fundamentals using a dichroic mirror, thus the optical path was arranged as the following: The fundamental of $\omega_1$ ($\omega_1/2$) was
transmitted by the dichroic mirror, and overlapped with the $\omega_2$ beam, which was reflected by the dichroic mirror. The doubling crystal used to generate $\omega_1$ was set after the mirror. Calibration of the VUV photon energy was performed through calibrating the wavelengths of the fundamental output of the dye lasers, and the uncertainty was 2 cm$^{-1}$.

Field ionized photoelectrons were detected by a time of flight spectrometer. The delayed electric pulse (1 V, corresponding to a field strength of 0.8 V cm$^{-1}$) was triggered 1 $\mu$s after the VUV pulse, and the field ionized electron signal were recorded by a gated integrator. The target beam was a collimated pulsed molecular beam of pure O$_2$, and the rotational temperature was 10 K, based on the spectral simulations described below.

3. Experimental results and spectroscopic analysis

The O$_2^+(a \, ^4\Pi_u)$ state has four spin–orbit components, separated by $\approx 50$ cm$^{-1}$: $^{2}\Pi_{5/2}$ (F$_1$), $^{2}\Pi_{3/2}$ (F$_2$), $^{2}\Pi_{1/2}$ (F$_3$), and $^{2}\Pi_{1/2}$ (F$_4$). At a rotational temperature of $\approx 10$ K, only two of the ground rotational levels with $N''=1$ and 3 are populated (even $N''$ levels are prohibited because of nuclear statistics). Although the angular momentum coupling case is complicated, it is still easy to separate the different components in the rotationally cold spectrum. The PFI-ZEKE spectra of the first four vibrational bands of O$_2^+(a \, ^4\Pi_u, \nu^+=0-3)$ were recorded. Two of the four spin–orbit components of the $\nu^+=0$ band, $^{2}\Pi_{1/2}$ (F$_4$) and $^{2}\Pi_{5/2}$ (F$_1$), are overlapped almost exactly with the two spin–orbit components of O$_2^+(X \, ^3\Pi_g, \nu^+=21)$, making a detailed analysis difficult. Because of this, detailed assignments were made for the $\nu^+=1-3$ bands, and only a tentative assignment was made for $\nu^+=0$. The rotationally resolved PFI-ZEKE spectra for the $\nu^+=1-3$ bands is shown as the solid lines in Fig. 1. The spectra are plotted on the same scale, with the relative intensities normalized by the photon flux.

Based on previous spectroscopic analysis, [19] by expanding the wavefunction in terms of the Hund's case a basis set, a Hamiltonian containing the various interactions can be constructed. Using the constants from Cosby et al., [17] the relative positions of each spin–orbit component and each rotational transition can be obtained. Assignment of the observed spectra using this information can therefore provide the absolute term values of the corresponding vibrational energy levels. Fig. 2 shows the result of the assignment for the $\nu^+=2$ level with the four components labelled as F$_n$. The fractional numbers indicate the change in the nuclear rotational quantum number $J''-N''$, where the initial rotational quantum numbers $N''$ are labelled as subscripts to avoid space congestion in the diagram. There is no overlapping between the
rotational transition of adjacent components and the assignment is unique without noticeable uncertainties for \( v^+ = 1 \). Taking the Stark shift of the thresholds into account, the term values are 130 904 ± 2 cm\(^{-1}\) for \( v^+ = 1 \), 131 903 ± 2 cm\(^{-1}\) for \( v^+ = 2 \), and 132 875 ± 2 cm\(^{-1}\) for \( v^+ = 3 \). These term values are relative to \( \text{O}_2 \, X \, ^3\Sigma_u^+ \, v = 0 \), \( N = 1(\text{F}_2) \). The separations between different vibrational levels obtained from these values are in good agreement with previous high resolution data [17]. Using the known spectroscopic constants for the \( a \) state, the term value for the \( v^+ = 0 \) level is calculated as 129 892 cm\(^{-1}\). This ionization energy (16.1046 eV) is in good agreement with the previous TPES measurement [18], and the electronic term value for the \( a \, ^4\Pi_u \) state with respect to the \( X \, ^2\Pi_g \) state, \( T_e = 32.977 \) cm\(^{-1}\), is in reasonable agreement with previous estimates [20].

For both the \( v^+ = 0 \) and \( v^+ = 1 \) bands, there is a problem with overlap with \( X \) state high \( v^+ \) thresholds: a \( v^+ = 0 \) with \( X \, v^+ = 21 \), and a \( v^+ = 1 \) with \( X \, v^+ = 22 \). For the \( v^+ = 0 \) and \( v^+ = 21 \) bands, the ZEKE spectrum is shown in Fig. 3. The very low intensity of the \( v^+ = 0 \) band makes it difficult to assign peaks with confidence, but an appropriately shifted \( v^+ = 1 \) simulation allows for a reasonable assignment of the \( F_2 \) and \( F_3 \) spin components, and confirms the term value calculated from the other bands. For the \( v^+ = 1 \) and \( v^+ = 22 \) bands, there is an overlap of the \( a \) state \( F_4 \) component with the \( X \) state \( F_1 \) component. In Fig. 4, part of the \( a \) state \( v^+ = 1 \) band is plotted, along with the shifted \( X \, ^2\Pi_{3/2} \, v^+ = 22 \) sub-band. The \( X \) state sub-band has been shifted to match the spin–orbit splitting of the \( v^+ = 21 \) band, which is also plotted in Fig. 4. As can be seen from the data shown in Fig. 4, it is somewhat difficult to assign the lines around 130 980 cm\(^{-1}\) as clearly
belonging to the $a$ state or the $X$ state, but based on the simulation, and the intensity of the $a$ state F$_3$ sub-band, it seems reasonable to assign most of the intensity in this part of the ZEKE spectrum to $a$ state thresholds.

4. BOS simulation

The original BOS model only considered the two ideal coupling cases a and b for the initial and final states [15]. Although intermediate coupling cases can be dealt with by representing the wavefunction in the case a basis set, there has been no such work reported on the BOS model. When dealing with the different spin–orbit components in a pure case a coupling scheme, the least squares fitting program only needs to consider one component at a time [11,14], but in the intermediate coupling case, the different spin–orbit components cannot be separated, and a universal fit to all the components has to be considered.

The BOS model uses dipole transitions from an initial one-electron wavefunction to atomic-like continua to describe the photoionization process. The final state rotational distribution is determined by two factors: one which includes the transition dipole moment and radial wavefunction overlap, and the other is determined by the angular momentum coupling algebra. By re-organizing the formulae for the rotational line strength [21], this model can be used to interpret the rotational line intensity distributions in terms of contributions from the different atomic orbitals in the initial wavefunction of the ionized electron. This interpretation should be viewed with some caution, as it ignores important effects such as autoionization and shape resonances, which often play an important role in the determination of the rotational line strengths in photoelectron spectra. Thus, the results of the BOS modelling, which are empirical fitting coefficients, provide only an indication of the character of the initial orbital. However, the coefficients do provide an indication of the angular momentum distribution of the outgoing photoelectrons, no matter what the ionization dynamics are.

We have been using a least squares fitting program to simulate the radial coefficients $C_n$ in the
BOS model, [9] where \( \lambda \) represents the orbital angular momentum quantum number of the ionized electron in the initial ground neutral state. In extending this procedure to intermediate coupling cases, the angular momentum coupling factors to all the possible spin–orbit components are pre-calculated, and the wavefunction of a certain state is determined from diagonalization of an appropriate Hamiltonian. The final angular momentum coupling factor is the weighted sum of all the corresponding factors from all the components with the expansion factors in the wavefunction as the weighing factors. Using the same least squares procedure, the contributions of each atomic orbital can be determined.

Specifically for the \( \text{a}^4\Pi_u \) state of \( \text{O}_3 \), spin–orbit splitting and \( \Lambda \) doubling result in 8 spin components, but nuclear statistics determines that only the negative states are accessible [19]. Diagonalizing the \( 4 \times 4 \) Hamiltonian gives the energy of each component, and the squares of each element in each eigenvector provide the weighing factors. The angular momentum coupling factors from \( \text{O}_3 \text{X}^2\Sigma_g^+ \) to \( ^2\Pi_{1/2}, ^2\Pi_{3/2}, ^2\Pi_{5/2} \) and \( ^2\Pi_{7/2} \) are then calculated and summed with proper weighting.

This procedure deals with the four components at the same time, allowing a universal fit for a complete vibrational band. With the present data, there was difficulty including the \( \text{F}_4 \) components of all the bands in the fit. For \( \nu^* = 1 \), there was an overlap with the \( \text{X} \nu^* = 22 \text{ F}_1 \) sub-band, as has been described. In addition, the \( \text{F}_4 \) components in the \( \nu^* = 2 \) and 3 bands are weaker than any other components, and some other mechanism might be playing a role for these components. During the fitting process, only the \( \text{F}_1, \text{F}_2, \text{and} \text{F}_3 \) sub-bands were used, and the spectra for the \( \text{F}_4 \) component were calculated using the fitted coefficients. The broken lines in Fig. 1 are the calculated results for the three vibrational bands. The fitted spectra are reasonable for the \( \text{F}_1-\text{F}_3 \) components, but the calculated line strengths are much stronger than the experimental data for the \( \text{F}_4 \) components. Since the relative intensities of the four components are determined by angular momentum coupling, this discrepancy either means that the \( \text{F}_4 \) sub-band has lost intensity, or the \( \Gamma_1 \) to \( \Gamma_3 \) sub-bands have gained intensity. There also appears to be a consistent discrepancy between simulation and experiment for the \( \text{F}_1 \) sub-bands, with the simulated line strengths for the lower energy lines being weaker than the data.

The results of the BOS simulation were that the observed line strengths could be well described by expanding the initial \( \pi_u \) molecular orbital as a roughly equal mixture of \( l = 1 \) and 3 atomic orbitals (even \( l \) values are forbidden by symmetry). A significant \( l = 3 \) component was necessary to get any intensity in the \( \text{F}_1 \) sub-band, while higher \( l \) components would have been inconsistent with the limited range of transferred angular momentum observed. The same \( C_\lambda \) coefficients could be used for all 3 bands, and the simulations shown in Fig. 1 were calculated in this way. As pointed out earlier, the \( l \) values found by the BOS analysis can also arise from interactions in the continuum, such as a shape resonance, which would also promote higher \( l \) partial waves.

5. ZEKE intensities

The observed ZEKE spectral intensities can be compared with the BOS simulations for rotational line strengths, or with Franck–Condon factors (FCF) for vibrational band intensities. The FCFs for transitions from \( \text{O}_2 \text{X}^2\Sigma_g^+ \nu = 0 \) to \( \text{O}_3 \text{a}^4\Pi_u \nu^* \) were calculated using the LEVEL program [22], and are given in Table 1. Also given in Table 1 are the measured ionization energies and integrated band intensities for the \( \nu^* = 0–3 \) ZEKE bands. The band intensity for \( \nu^* = 0 \) was estimated from the \( \text{F}_3 \) and \( \text{F}_1 \) components, while the \( \nu^* = 1 \) band contains an unknown contribution from the \( \text{X}^2\Pi_{1/2} \nu^* = 22 \) sub-band, as discussed earlier. For all of the bands discussed in this paper, the low signal levels (about one
Table 1
Ionization energies, relative band intensities for TPES [17] and ZEKE (current work), and Franck-Condon factors (FCF) for the \( a \) state \( v' = 0 \)–3 ZEKE bands

<table>
<thead>
<tr>
<th>( v' )</th>
<th>Ionization energy (eV)</th>
<th>TPES band</th>
<th>ZEKE band</th>
<th>FCF</th>
<th>Relative FCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>16.1046</td>
<td>0.10</td>
<td>0.10</td>
<td>0.010</td>
<td>0.09</td>
</tr>
<tr>
<td>1</td>
<td>16.2301</td>
<td>0.43</td>
<td>0.00</td>
<td>0.037</td>
<td>0.34</td>
</tr>
<tr>
<td>2</td>
<td>16.3540</td>
<td>0.71</td>
<td>0.81</td>
<td>0.074</td>
<td>0.68</td>
</tr>
<tr>
<td>3</td>
<td>16.4745</td>
<td>1.00</td>
<td>1.00</td>
<td>0.108</td>
<td>1.00</td>
</tr>
</tbody>
</table>

electron per laser shot) meant that extensive signal averaging was used to collect the spectra. Thus the different bands were recorded on different days, making the relative intensities somewhat uncertain. This, coupled with the spectral overlap for the \( v^* = 0 \) and 1 bands, means that only a qualitative comparison can be made between our measured band intensities and the calculated FCFs. Qualitatively, the measured band intensities are in agreement with the FCFs. This, in turn, is in agreement with earlier TPES work done on the \( a \) state [18], which showed a good agreement between the TPES band intensities and the FCFs, for low \( v' \) levels.

This Franck-Condon behaviour is in stark contrast with the non-Franck-Condon intensities observed for the \( X \) state vibrational bands, both in TPES [18] and in ZEKE [13,14], where significant intensity is observed for very high vibrational levels, which have zero FCFs. In Figs. 3 and 4, it can be seen that the intensities of the \( X \) state bands are comparable with the Franck-Condon allowed \( a \) state bands. For the \( a \ v^* = 0 \) band, the integrated intensity is about 15% of the \( X \ v^* = 21 \) band, the \( a \ v^* = 1 \) is about 3 times larger than the \( X \ v^* = 22 \), and the \( a \ v^* = 2 \) is about 4 times the \( X \ v^* = 23 \). These comparisons are similar to results from TPES [18], results that must be viewed with caution since they come from deconvoluting unresolved bands. Since the \( X \) state \( v^* = 21 \) and 22 bands are much weaker than the other high \( v' \) levels that have been observed in TPES and ZEKE, for some of the stronger Franck-Condon forbidden bands, such as \( v^* = 16 \), the band intensity is stronger than the \( a \) state \( v^* = 3 \) band, which has an FCF of 0.11.

For the \( a \ v^* = 1, X \ v^* = 22 \) bands, the overlap of the \( a \ F_4 \) and \( X \ F_1 \) components presents a situation reminiscent of the CO \( ^2 \Pi_{1/2} \ v^* = 0 \) band, which is perturbed by the \( X \ ^2 \Sigma^+ \ v^* = 10 \) state [11]. For CO, a depletion of \( A \) state core Rydberg levels was observed, resulting in the observation of \( X \) state rotational thresholds in the ZEKE spectrum. In the present case, there is no evidence for an interaction between the \( a \) and \( X \) state vibrational levels in the high resolution spectra [17]. However, the ZEKE spectrum shows little evidence for a significant \( X \) state contribution to the sub-band at 130 980 cm\(^{-1}\). Relative to the \( v^* = 2 \) and 3 bands, the \( F_4 \) component of the \( v^* = 1 \) band is stronger by about a factor of two relative to the \( F_4 \) component. Based on this, it might be possible to assign half the observed intensity to the \( a \) state \( v^* = 22 \) level.

A detailed comparison between the BOS simulations and the ZEKE spectra shown in Fig. 1 allows us to make some general observations. In all bands, the \( F_1( (+3/2) \) line is much stronger than the simulation. Since this line excites to the lowest possible rotational level of a given vibrational state \( ^4 \Pi_{5/2}, J = 5/2 \), and since the simulation indicates that the \( (+5/2) \) and \( (+7/2) \) lines should be equally strong, the extra intensity of
the (+3/2) \textsubscript{1} line is almost certainly coming from forced rotational autoionization [23]. The BOS simulation gives the following for relative intensities: \( F_4 > F_3 > F_2 > F_1 \) (integrated relative intensities 42:25:18:15), while from the ZEKE spectra we obtain \( F_4 < F_3 < F_2 \approx F_1 \), with the discrepancy between simulation and experiment being most dramatic for the \( F_4 \) component.

The disagreement for the \( F_4 \) component is reminiscent of what has been observed in previous work on PFI-ZEKE of hydrogen halides, where the ground state of the ion is \( ^2\Pi \). For HF, which also has intermediate case coupling in the ion, the lower energy \( F_1 \) component lines are significantly enhanced compared with the \( F_2 \) lines [24]. This enhancement of the \( F_1 \) lines in HF is probably a result of a forced spin–orbit/rotational autoionization. This effect has been discussed in some detail in a recent paper on HCl by Zhu et al. [25], where the experimental and theoretical PFI-ZEKE spectra for the two spin–orbit components of HCl' (\( X^2\Sigma_u^+ \)) were compared. A theoretical study of ZEKE for \( ^2\Pi \) thresholds has been carried out by Lefebvre-Brion [26], who looked specifically at CO\textsubscript{2} and HCl. In these cases, intensity anomalies similar to what has been observed for the \( \text{O}_2^+ \) \( a \) state were explained by the excited spin–orbit–level decaying by rotational and spin–orbit autoionization before pulsed field ionization. This mechanism would explain our observations, in that one would expect transitions to the higher energy spin–orbit components to lose intensity due to autoionization. In this case, the strongest loss is for the highest energy \( F_4 \) component, although there would appear to be loss for the \( F_2 \) and \( F_3 \) components as well, based on comparison with the BOS simulation.

6. Conclusion

We have reported the PFI-ZEKE spectra of \( \text{O}_2^+ \) (\( a \) \( ^4\Pi_u \), \( \nu' = 1–3 \)) using coherent VUV radiation. This electronically excited ionic state belongs to an intermediate Hund’s coupling case, and based on previous spectroscopic analysis, the spectra can be successfully assigned with no ambiguity. Furthermore, the wavefunction of each state can be expanded in the case a basis set, and the BOS model can be thus generalized for any kind of angular momentum coupling cases. The least square fitting result based on this model successfully reproduced the main feature of the observed PFI-ZEKE spectra.

For the low vibrational levels of the \( a \) state investigated in this work, the band intensities are Franck–Condon, and have intensities comparable to those of the Franck–Condon forbidden high \( \nu' \) bands of the \( X \) state. For both \( a \) state and \( X \) state bands, ZEKE and TPES give qualitatively the same results. The rotational line strengths observed are influenced by both forced rotational autoionization, which enhanced the lowest energy lines in the \( \nu' = 1–3 \) ZEKE spectra, and by rotational and spin–orbit autoionization, which decreased the intensity of the high energy lines in the same three bands.

This work demonstrated the application of PFI-ZEKE and coherent VUV in both high resolution spectroscopy and dynamics studies of photoionization processes. To summarize the results of our previous and present studies on excited ionic states, PFI-ZEKE can be used to study ground or metastable or unstable excited ionic states, and the basic hypotheses of PFI-ZEKE appear to be generally valid, and the method of spectroscopy appears to be universally applicable.

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