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Wales, N.P.L.; Buma, W.J.; de Lange, C.A.

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$(3 + 1)$ resonance enhanced multiphoton ionization–photoelectron spectroscopy on the E, F, and G Rydberg states of ClO

N.P.L. Wales, W.J. Buma, C.A. de Lange

Laboratory for Physical Chemistry, University of Amsterdam, Nieuwe Achtergracht 127, 1018 WS Amsterdam, The Netherlands

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Abstract

$(3 + 1)$ resonance enhanced multiphoton ionization–photoelectron spectroscopy is employed to investigate the spectroscopy and ionization dynamics of the E, F, and G Rydberg states of ClO. The results establish that the E and F Rydberg states converge upon the $X^3\Sigma^-$ ground ionic state, while the G state belongs to a Rydberg series with an excited $^1\Delta$ ionic core. Improved ionization thresholds of these two ionic states are determined as 10.887 ± 0.005 and 11.750 ± 0.005 eV.

1. Introduction

Resonance enhanced multiphoton ionization in combination with photoelectron spectroscopy (REMPI–PES) has proven to be a powerful tool for characterizing excited states and for understanding their ionization dynamics [1]. One of the particularly attractive features of REMPI–PES is its ability to identify unambiguously the vibrational levels of Rydberg states by examination of the final ionic states reached in the photoionization process [2–5]. Moreover, spectroscopic data on the ionic manifold, such as vibrational constants and ionization energies of the various ionic states, can be derived accurately from the photoelectron (PE) spectra.

In this Letter, the REMPI–PES technique is employed to investigate the E, F, and G Rydberg states of the ClO radical. These Rydberg states have been observed before [6,7], but their precise electronic origins have remained uncertain. This uncertainty stems from the fact that the Rydberg states of ClO

converging upon the lowest ionic states are more bonding than the $X^2\Pi$ ground electronic state due to the promotion of an anti-bonding electron. As a result the vibrational overlap between the $v'' = 0$ level of the ground state with the $v' = 0$ level of the excited state is unfavourable, and the 0–0 transition has a considerably reduced intensity. In this study we will confirm the E, F, and G Rydberg state origins tentatively proposed in Refs. [6,7], with some reassignment of resonances previously thought to be associated with transitions to the D state of ClO [7], but shown in our study to belong to hot bands of the E state. Another aspect of these states, which has not been elucidated as yet, concerns the ionic core upon which they are built. Photoelectron spectroscopy is the method of choice to answer such questions and will indeed be shown to provide the ionic states upon which these Rydberg states converge. Finally, from the PE spectra improved ionization energies are derived for the ground, $X^3\Sigma^-$, and first excited, a $^1\Delta$, ionic states.

2. Experimental

A description of the experimental setup has been reported previously [8]. Ground-state ClO radicals were generated by photolysis of ClO₂ via its dissociative \tilde{A}^2A_2 excited state situated between 480 and 260 nm [9,10]. A single excimer-pumped dye laser provided photons for both the ClO₂ photolysis and for the subsequent three-photon resonant MPI spectroscopy of the ClO radicals. Both wavelength scans, using either mass-resolved ion or electron detection, and photoelectron spectra were taken. Dyes used in these experiments were Coumarin 440, Exalite 428, and 416. No attempt was made to correct the excitation spectra for the various dye gain curves. The energy scale of the photoelectrons was calibrated using known (3 + 1) REMPI signals of Xe [11], which was introduced into the spectrometer simultaneously with ClO₂. An energy resolution of ≈ 15 meV with an absolute accuracy of ± 5 meV was achieved for all photoelectrons. ClO₂ was produced by passing pure chlorine gas (Matheson, 99.5%) through a glass tube packed with NaClO₂ (Aldrich, 80% technical grade) [12]. The resulting ClO₂ gas was used without any further purification.

3. Results and discussion

In Fig. 1 the three-photon excitation spectrum in the one-photon energy region between 21650 and 23050 cm⁻¹ is depicted. This spectrum was obtained using mass-resolved ion detection and monitoring the $m/e = 51$ [³⁵ClO⁺] channel. On the basis of the photoelectron spectra obtained for ionization via each of the resonances observed in Fig. 1, all the vibronic transitions can be assigned consistently as three-photon transitions from vibrational levels of the X²Π_{3/2,1/2} ground state to vibrational levels of the E Rydberg state of ClO [6,7] as indicated in the figure. The origin of the E state at ≈ 67467 cm⁻¹, as previously proposed by Basco and Morse [6], is confirmed, as can be concluded from the PE spectrum obtained via the E ($v' = 0$) ← X²Π_{3/2} ($v'' = 0$) transition, which is depicted in Fig. 4a. Clearly, ionization takes place to the X³Σ⁻ ground ionic state with conservation of vibrational quantum number, i.e. only the $\Delta v = v^+ - v' = 0$ transition is ob-

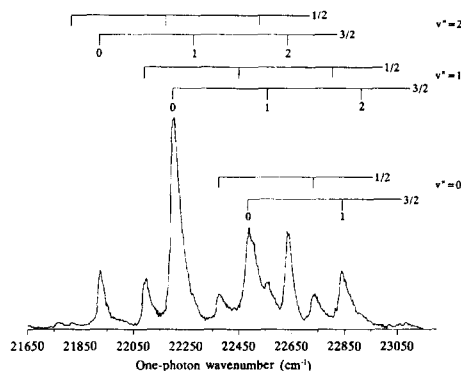
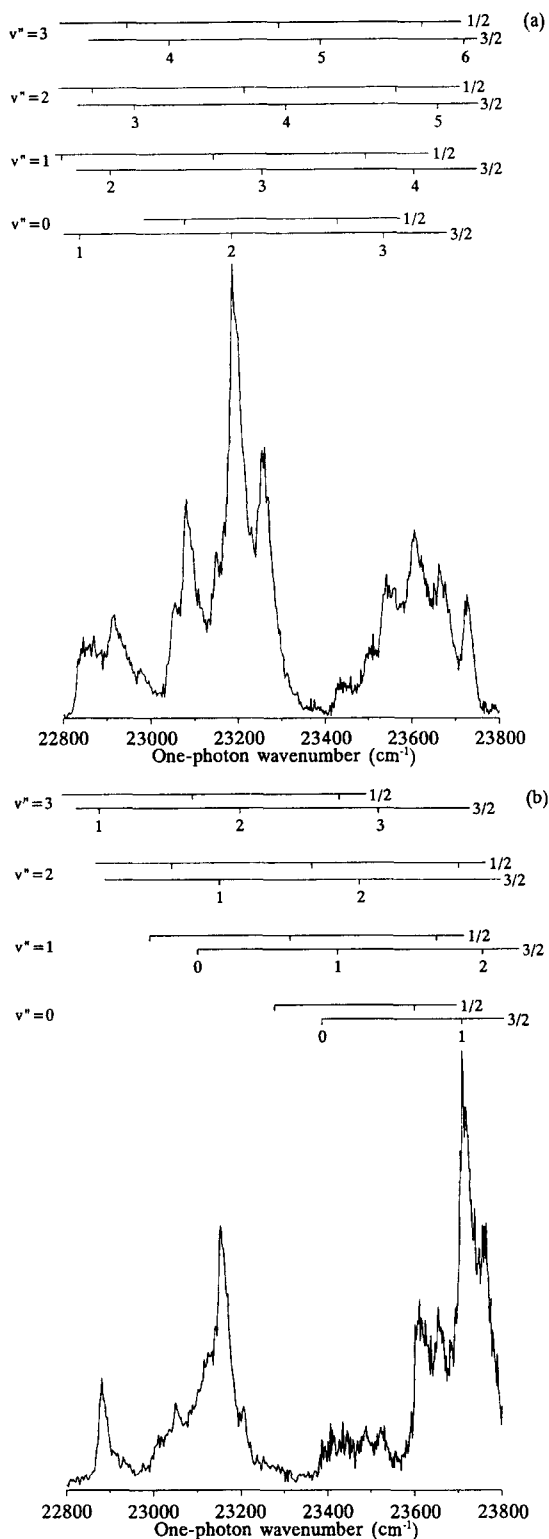


Fig. 1. Three-photon excitation spectrum of the E Rydberg state of ClO, employing mass-resolved ion detection monitoring the $m/e = 51$ [³⁵ClO⁺] channel. The various combs indicate the vibrational numbering of the excited states accessed via various vibrational levels of the X²Π_{3/2,1/2} ground state (indicated on the right-hand side of the figure).

served. The latter observation is made for all the PE spectra via higher vibrational levels of the E state up to $v' = 8$. This is indicative of an essentially unperturbed Rydberg state with a potential energy curve very similar in shape and with a minimum at an internuclear distance very comparable to that of the ionic state upon which it converges. We can thus conclude that the E state is built upon the X³Σ⁻ ionic core. From the PE spectra an improved value of the ionization energy of ClO [X³Σ⁻ ($v^+ = 0$) ← X²Π_{3/2} ($v'' = 0$)] is found to be 10.887 ± 0.005 eV. This value compares well with the ionization energy of 10.87 ± 0.01 eV obtained in a previous He(I) PES study [13].

A recent ab initio study of Rydberg states of ClO [14] has shown that the E state has an outer Rydberg electron with strong p-character at the equilibrium internuclear distance of the X³Σ⁻ ground ionic state. However, due to the rather mixed composition of the Rydberg orbital a discussion in terms of a quantum defect for the E state is not very meaningful. Nevertheless, if the E state has ²Σ⁻ symmetry, as suggested in previous studies [6,7], then the electronic configuration of the E state would correspond to [³Σ⁻]4pσ.

The presently obtained three-photon excitation spectrum of the E state has a different appearance from that reported previously by Duignan and Hudgens [7]. The reason for this dissimilarity can be



found in the production mechanism of the ClO radicals. In the previous study ClO has been produced by the reaction of Cl atoms with O₃, leading to vibrationally cold ClO radicals. In contrast, in the present study vibrationally hot ClO radicals result from the photodissociation of ClO₂. Transitions starting from as high as the $v'' = 4$ ground-state vibrational level were identified in our excitation spectra. In fact, the distribution over the spin-orbit components of the X ²Π ground state and their vibrational levels as observed in this work is in nice agreement with previous conclusions regarding the final state distribution after one-photon photodissociation of ClO₂ in this energy region [15]. Though vibrationally hot, the ClO radical is predominantly produced in its ²Π_{3/2} neutral ground state. The production of ClO by photolysis of ClO₂ is known to vary with wavelength [9]. Moreover, the dye gain curves have intensity dips in some of the excitation spectra, resulting in a low ClO yield. As a consequence no attempt was made to extract vibrational and spin-orbit temperatures of the ground state from the present spectra. Although the present assignments given in Fig. 1 are in good agreement with those of Ref. [7], they differ with respect to the assignment of the 66275 and 66601 cm⁻¹ resonances. Previously these resonances have been assigned to the D ²Σ ($v' = 2$) ← X ²Π_{3/2,1/2} ($v'' = 0$) transitions, but our PE spectra show that they derive from the E ²Σ ($v' = 0$) ← X ²Π_{3/2,1/2} ($v'' = 1$) hot band transitions instead.

Fig. 2 depicts three-photon excitation spectra in the one-photon energy region of 22800 to 23800 cm⁻¹ employing electron detection of low ($E_k < 0.5$ eV; Fig. 2a) and of high ($E_k > 0.5$ eV; Fig. 2b) kinetic energy electrons. From the PE spectra obtained for the resonances in Fig. 2a it can be concluded that they are associated with higher vibronic bands of the E state. In contrast, the higher kinetic energy electrons in Fig. 2b are attributed to ionization of the F Rydberg state of ClO. Again, the

Fig. 2. Three-photon excitation spectrum of the (a) E and (b) F Rydberg states of ClO, employing electron detection in (a) of low ($E_k < 0.5$ eV) and in (b) of high ($E_k > 0.5$ eV) kinetic energy electrons. The various combs indicate the vibrational numbering of the excited states accessed via various vibrational levels of the ²Π_{3/2,1/2} ground state (indicated on the left-hand side of the figure).

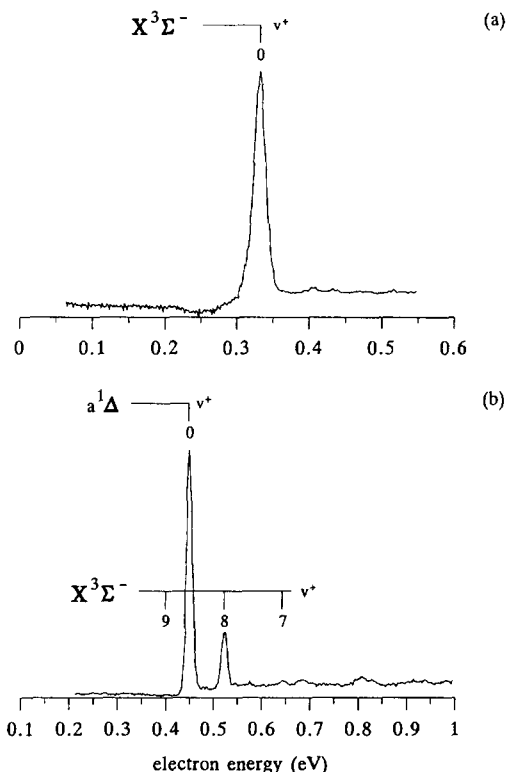
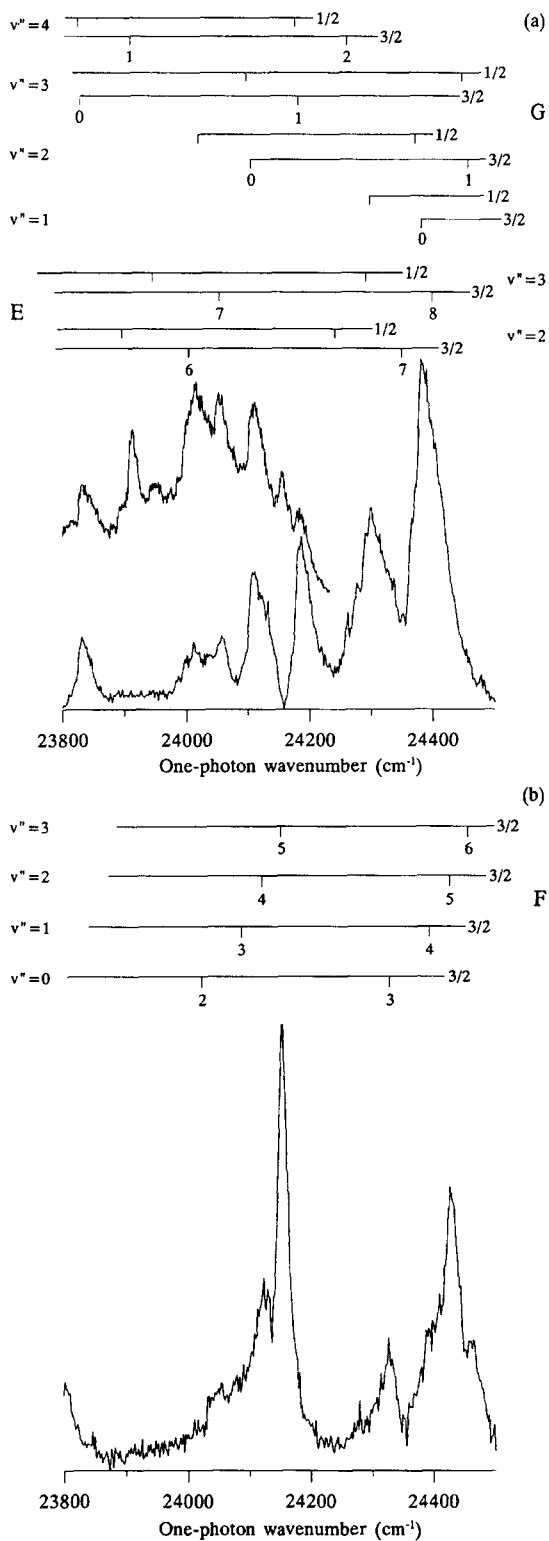


Fig. 4. Photoelectron spectra observed following three-photon excitation of (a) the E ($v' = 0$) state and (b) the G ($v' = 0$) state. The $X^3\Sigma^-$ ionization channel in (b) derives from ionization via an overlapping resonance to the E ($v' = 8$) level (see Fig. 3a).

assignments given in Fig. 2b were derived from the associated PE spectra. This state, believed to be of $^2\Sigma$ symmetry, has also been observed before [6,7]. In the previous (3 + 1) REMPI study on the F state no unambiguous conclusion on the electronic origin of the F state could be reached. Here, our PE spectra allow for the confirmation of the 0–0 transition which is at an excitation energy of $\approx 70179 \text{ cm}^{-1}$ as previously suggested [7]. The photoelectron spec-

Fig. 3. Three-photon excitation spectrum of the E, F, and G Rydberg states of ClO, employing electron detection in (a) of low ($E_k < 0.6 \text{ eV}$) and in (b) of high ($E_k > 0.6 \text{ eV}$) kinetic energy electrons. The insert in Fig. 3a is a wavelength scan employing mass-resolved ion detection [$^{35}\text{ClO}^+$, $m/e = 51$] (see text for explanation). The various combs indicate the vibrational numbering of the excited states accessed via various vibrational levels of the $^2\Pi_{3/2,1/2}$ ground state (indicated on the left- and right-hand side of the figure).

tra associated with ionization via various vibrational levels of the F state are shown in Fig. 5. Apart from photoelectrons deriving from ionization of the F state, these spectra also show photoelectrons deriving from ionization of the higher vibronic bands of the E state mentioned above. In addition, ionization is observed to occur to the excited $a^1\Delta$ ionic state. This latter ionization channel is associated with the

G state (vide infra). Ionization of the F state is observed to occur to the $X^3\Sigma^-$ ionic state with $\Delta v = 0$ transitions being dominant. However, this $\Delta v = 0$ propensity is not as strictly obeyed as seen previously for the E state, and deviations become more apparent for ionization via higher vibrational levels. This behaviour implies that the F Rydberg state has a slightly different potential energy curve

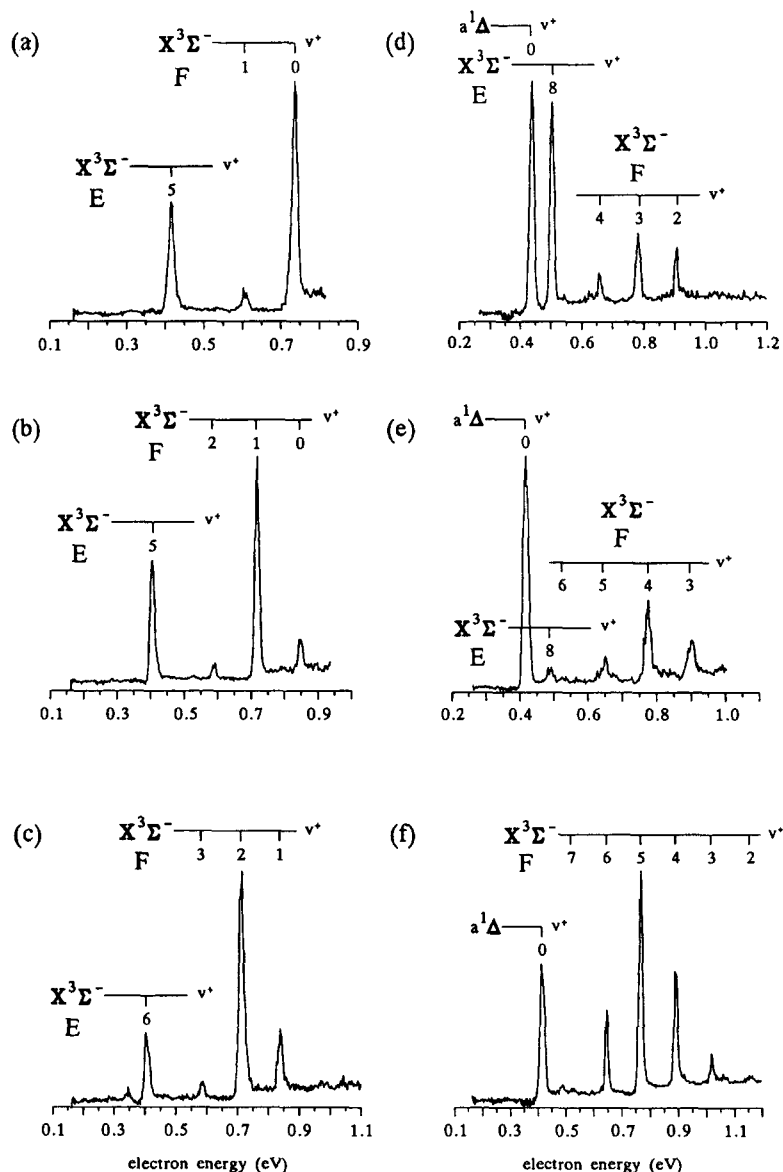


Fig. 5. Photoelectron spectra observed following three-photon excitation of the F Rydberg state via the (a) $v' = 0$, (b) $v' = 1$, (c) $v' = 2$, (d) $v' = 3$, (e) $v' = 4$, and (f) $v' = 5$ vibrational level.

and/or equilibrium distance from that of the $X^3\Sigma^-$ ionic state. Again, it is not meaningful to calculate a quantum defect for this state, since ab initio calculations [14] show that s and d characters contribute equally to the angular momentum composition of the Rydberg electron.

Fig. 3 shows excitation spectra in the energy region of 23800 to 24500 cm^{-1} , employing electron detection of low ($E_k < 0.6$ eV; Fig. 3a) and of high ($E_k > 0.6$ eV; Fig. 3b) kinetic energy electrons. Due to a dip in the dye gain curve of the Exalite 428 dye around 23900 cm^{-1} , a second scan was performed using Exalite 416 employing mass-resolved ion detection, shown as an insert in Fig. 3a. The high kinetic energy electrons (Fig. 3b) are associated with ionization from the higher vibrational levels of the F state. The low-energy electrons, on the other hand, not only derive from ionization of ClO from high vibrational levels of the E state, but also from the G Rydberg state. The symmetry of this latter state, also observed in a one-photon VUV study [6], is unknown. The suggested symmetry of $^2\Pi$ or $^2\Delta$ cannot be determined in our experiments, but its previously proposed origin [6] at ≈ 73997 cm^{-1} is confirmed. Fig. 4b shows a PE spectrum via the $v' = 0$ level of the G state. Ionization takes place only to the $v^+ = 0$ level of the first excited $a^1\Delta$ ionic state, thereby indicating that the G state has an excited $a^1\Delta$ ionic core. In all the PE spectra measured via higher vibrational levels of the G state $\Delta v = 0$ transitions prevail, suggesting a potential energy curve of the G state similar in shape and with a minimum at an internuclear distance very comparable to that of the $a^1\Delta$ ionic state. The PE spectra allow for an improved value of the ionization energy of the $a^1\Delta$ ($v^+ = 0$) ionic state [$a^1\Delta$ ($v^+ = 0$) $\leftarrow X^2\Pi_{3/2}$ ($v'' = 0$)] which is found to be 11.750 ± 0.005 eV. This agrees well with a previously derived value of 11.74 ± 0.01 eV [16].

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