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► **To cite this version:**

Xiaofeng Tang, Xiaoxiao Lin, Gustavo A. Garcia, Jean-Christophe J.-C. Loison, Christa Fittschen, et al.. Threshold photoelectron spectroscopy of the HO₂ radical. *Journal of Chemical Physics*, 2020, *The Journal of Chemical Physics*, 153 (12), 10.1063/5.0022410 . hal-02960864

HAL Id: hal-02960864

<https://hal.univ-lille.fr/hal-02960864>

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Cite as: J. Chem. Phys. **153**, 124306 (2020); <https://doi.org/10.1063/5.0022410>

Submitted: 20 July 2020 . Accepted: 10 September 2020 . Published Online: 30 September 2020

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ABSTRACT

We report a synchrotron radiation vacuum ultraviolet photoionization study of the hydroperoxyl radical (HO₂), a key reaction intermediate in combustion and atmospheric chemistry as well as astrochemistry, using double imaging photoelectron photoion coincidence spectroscopy. The HO₂ radical is formed in a microwave discharge flow tube reactor through a set of reactions initiated by F atoms in a CH₄/O₂/He gas mixture. The high-resolution threshold photoelectron spectrum of HO₂ in the 11 eV–12 eV energy range is acquired without interferences from other species and assigned with the aid of theoretically calculated adiabatic ionization energies (AIEs) and Franck–Condon factors. The three vibrational modes of the radical cation HO₂⁺, the H–O stretch, the H–O–O bend, and the O–O stretch, have been identified, and their individual frequencies are measured. In addition, the AIEs of the X³A'' ground state and the a¹A' first excited electronic state of HO₂⁺ are experimentally determined at 11.359 ± 0.003 eV and 11.639 ± 0.005 eV, respectively, in agreement with high-level theoretically computed results. Furthermore, the former AIE value provides validation of thermochemical networks used to extract the enthalpy of formation of the HO₂ radical.

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I. INTRODUCTION

The hydroperoxyl radical (HO₂) is a key reaction intermediate and plays essential roles in combustion and atmospheric chemistry as well as astrochemistry.^{1–3} In the atmosphere, it is formed from low-temperature oxidation of hydrocarbons and involved in many reactions,^{1,4} i.e., as an important reservoir of the OH radical through the reaction HO₂ + NO → OH + NO₂ to control the concentration of OH in the lower troposphere,⁵ that affect global climate change and regional air quality. Consequently, the kinetics, spectroscopy, and thermodynamics of the HO₂ radical have

attracted a great deal of attention in the past decades, and many advances have been made by the constant development of theoretical and experimental methods such as optical spectroscopy and mass spectrometry.^{4,5}

As shown by the measured geometries of the HO₂ radical compiled in Table I, the HO₂ radical has a bent structure with a Cs symmetry and an open-shell valence electronic configuration of (6a')²(1a'')²(7a')²(2a'')¹ in the X²A'' ground electronic state. Its three vibrational frequencies were measured at ν₁ = 3410 cm⁻¹ (H–O stretch), ν₂ = 1095 cm⁻¹ (H–O–O bend), and ν₃ = 1390 cm⁻¹ (O–O stretch) by molecular-modulation absorption spectroscopy.⁶

TABLE I. Equilibrium geometry for the ground state of HO₂ and HO₂⁺.

	r(H–O) (Å)	r(O–O) (Å)	α(H–O–O) (deg)	Method	Reference
HO ₂ (Expt.)	0.96	1.3	108	Absorption	6
	0.971	1.331	104.3	Absorption	13
HO ₂ ⁺ (Calc.)	1.0102	1.2272	112.743	RCCSD(T)/CBS ^a	3
	1.0065	1.2304	113.884	CHIPR ^b	14

^aCalculated with RCCSD(T) at the valence complete basis set limit with core-valence corrections.^bCHIPR: the combined hyperbolic inverse power representation method.

The enthalpy of formation for the HO₂ radical was reported by a number of groups, e.g., $\Delta_f H_{0K}^0(\text{HO}_2) = 15.12 \pm 0.15 \text{ kJ mol}^{-1}$ recommended by the Active Thermochemical Tables (ATcT) database,⁷ $15.21 \pm 0.35 \text{ kJ mol}^{-1}$ by NIST,⁸ and $14.85 \pm 0.22 \text{ kJ mol}^{-1}$ by Ganyecz *et al.* using a composite theoretical/thermochemical network approach.⁹

Upon ionization, removing an electron from the outer-valence orbitals can produce the radical cation HO₂⁺ in different electronic states. For example, the ground electronic state of the cation HO₂⁺ is X³A'' formed via the (7a')⁻¹ ionization, while the cationic first excited electronic state a¹A' arises from the (2a'')⁻¹ ionization.¹⁰ As seen in Table I, the calculations show that the cation HO₂⁺ in the X³A'' ground state has a similar geometry as the neutral HO₂ radical. The HO₂ radical and its cation HO₂⁺ were first experimentally identified by Foner and Hudson using electron impact mass spectrometry (EIMS) in their study of the reaction of hydrogen atoms with oxygen.^{11,12}

The experimental determination of the adiabatic ionization energy (AIE) of the HO₂ radical is of major significance for thermochemical networks needed to accurately model processes leading to the formation and destruction of the HO₂ radical.^{5,15} Thus, the AIE of the HO₂ radical has been the subject of several studies. The AIE of the HO₂ radical was measured to be $11.53 \pm 0.1 \text{ eV}$ ¹¹ and $11.53 \pm 0.02 \text{ eV}$ ¹² by EIMS, $11.35 \pm 0.01 \text{ eV}$ by HeI photoelectron spectroscopy (PES),¹⁶ and $11.352 \pm 0.007 \text{ eV}$ by synchrotron radiation photoionization mass spectrometry (PIMS)^{15,17} with improved accuracy with the advanced techniques used. Table II compiles

TABLE II. Adiabatic ionization energies of the HO₂ radical. The uncertainties are in parentheses.

	AIE (eV)	Method	References
Expt.	11.53(10), 11.53(2)	EIMS	11 and 12
	11.35(1)	HeI PES	16
	11.352(7)	PIMS	15 and 17
	11.359(3), 11.639(5) ^a	TPES	This work
Calc.	11.370	G2	15
	11.356(5) ^b	Thermochemical	9
	11.357, 11.616 ^a	RCCSD(T)/CBS ^c	This work

^aAdiabatic ionization energy of the a¹A' first excited state.^bCalculated with the literature enthalpies of formation $\Delta_f H_{0K}^0(\text{HO}_2) = 14.85 \pm 0.22 \text{ kJ mol}^{-1}$ and $\Delta_f H_{0K}^0(\text{HO}_2^+) = 1110.56 \pm 0.40 \text{ kJ mol}^{-1}$.⁹^cCalculated at the RCCSD(T)/CBS//M062X/aug-cc-pVTZ level of theory.

the experimental and theoretically calculated AIEs available in the literature.

On the other hand, the direct measurement of the vibrational frequencies of the cation HO₂⁺ is challenging due to the difficulty in generating the reactive HO₂⁺ in the experiment, and at present, the knowledge is mainly based on the data of *ab initio* calculations.^{3,14,18,19} As far as we know, only a few reports on the experimental measurements of the cationic vibrational frequencies can be found in the literature. The ν₁ (H–O stretch) frequency was measured at $3016.726 \pm 5 \text{ cm}^{-1}$ by Kohguchi *et al.* using rovibrational spectroscopy with a cryogenic ion trap,¹⁸ and Nizkorodov *et al.* predicted a value of $3020 \pm 40 \text{ cm}^{-1}$ extrapolated from infrared predissociation spectra of He–HO₂⁺ and Ne–HO₂⁺ complexes.²⁰ The ν₂ (H–O–O bend) frequency of HO₂⁺ in the Ne matrix was measured at $1026.5 \pm 0.1 \text{ cm}^{-1}$ by Jacox and Thompson using Fourier-transform infrared (FTIR) spectroscopy,²¹ and the ν₃ (O–O stretch) vibrational frequency was estimated at $1560 \pm 50 \text{ cm}^{-1}$ by Dyke *et al.* via HeI PES.¹⁶

In our recently published work, we have demonstrated that double imaging photoelectron photoion coincidence (i²PEPICO) spectroscopy is a powerful method to get the spectral fingerprint for very dilute and elusive species in complex reaction mixtures.^{22,23} At present, the synchrotron radiation vacuum ultraviolet (VUV) photoionization of the HO₂ radical is investigated in detail by using the i²PEPICO method combined with a microwave discharge flow tube reactor to generate the radical. The high-resolution mass-selected threshold photoelectron spectrum (TPES) corresponding to the HO₂ radical is acquired in the region close to its ionization threshold and exhibits a series of fine vibrational structures. The three vibrational modes of the radical cation HO₂⁺, together with their combination modes, are populated in the photoionization process and assigned with the aid of theoretically calculated Franck–Condon factors. The AIEs of the X³A'' ground state and the a¹A' first excited electronic state are determined at $11.359 \pm 0.003 \text{ eV}$ and $11.639 \pm 0.005 \text{ eV}$, respectively.

II. METHODS

Experiments were performed with the i²PEPICO spectrometer, DELICIOUS III, on the undulator-based DESIRS beamline of synchrotron SOLEIL, France.^{24–26} A 6.65 m normal incidence monochromator with a 200 l mm⁻¹ grating was adopted to disperse synchrotron radiation photons and provide high photon flux and an energy resolution of ~3 meV with the chosen slits. A gas filter located at the upstream of the beamline and filled with Ar (0.3 mbar)

was utilized to remove high harmonics emitted from the undulator. The monochromatic VUV light was softly focused onto a 200/70 μm (H/V, FWHM) spot at the ionization region. The i^2 PEPICO spectrometer was installed vertically inside the ionization chamber of SAPHIRS, a permanent molecular beam endstation on the beamline, and mainly composed of a modified Wiley–McLaren time-of-flight (TOF) 3D-momentum ion imaging device and an electron velocity map imaging analyzer equipped with two position sensitive detectors (PSDs). The coincidence scheme can yield a mass-selected electron image corresponding to a definite mass with ion position-selection to separate from background gas.^{22,27} An Abel inversion algorithm, pBasex, was used to analyze the electron image and obtain the PES.²⁸

A continuous fast flow tube mainly consisting of a Pyrex main tube and a sliding coaxial injector was employed as a chemical reactor to produce radicals.^{22,27} Fluorine atoms were generated from diluted F_2 gas in helium (5%, 10 sccm) in a commercial microwave discharge generator (2.45 GHz, Sairem GMP03 KSM) and utilized to initiate reactions in the flow tube, in which methane (30 sccm) and oxygen (600 sccm) were added as reactant gases, together with helium carrier gas (1100 sccm). The pressure inside the flow tube was fixed at 2 Torr, and the microwave discharge power was set at 100 W. A series of reactants and products together with their mutual reactions inside the flow tube have already been identified and can be found in the literature.²³ At present, the HO_2 radical was primarily formed from the reaction of the methoxy radical (CH_3O) with oxygen,



whereby the CH_3O radical was mostly formed in the fast reaction between the methyl radical (CH_3) and the methyl peroxy radical (CH_3O_2). The gas mixture inside the flow tube was sampled and passed through two skimmers, and then crossed the monochromatic VUV light in the ionization chamber of SAPHIRS.²⁶ The photoelectrons and photoions formed by photoionization were collected with DELICIOUS III and analyzed in coincidence.

Theoretical computations were also carried out to predict the AIEs and the Franck–Condon factors. Concretely, the AIEs of the X^3A'' ground electronic state and the a^1A' first excited electronic state of the cation HO_2^+ are calculated at the RCCSD(T)/CBS//M062X/aug-cc-pVTZ level of theory as implemented in the *MOLPRO* software.²⁹ The Franck–Condon factors in the photoionization process, as well as for the geometry optimizations and the vibrational frequency computations with a harmonic approximation required as input parameters, were calculated using the time-independent adiabatic Hessien Franck–Condon model. These calculations were done at the B3LYP/6-311+G(3df,2p) level of theory, as implemented in the *Gaussian 16* program.³⁰

III. RESULTS AND DISCUSSION

Synchrotron radiation photoionization TOF mass spectra have been measured in the 11 eV–12 eV energy range and are presented as a matrix in Fig. 1, together with their integrated mass spectrum shown below. Numerous mass peaks can be observed, some of which can readily be attributed. For example, the mass peaks at

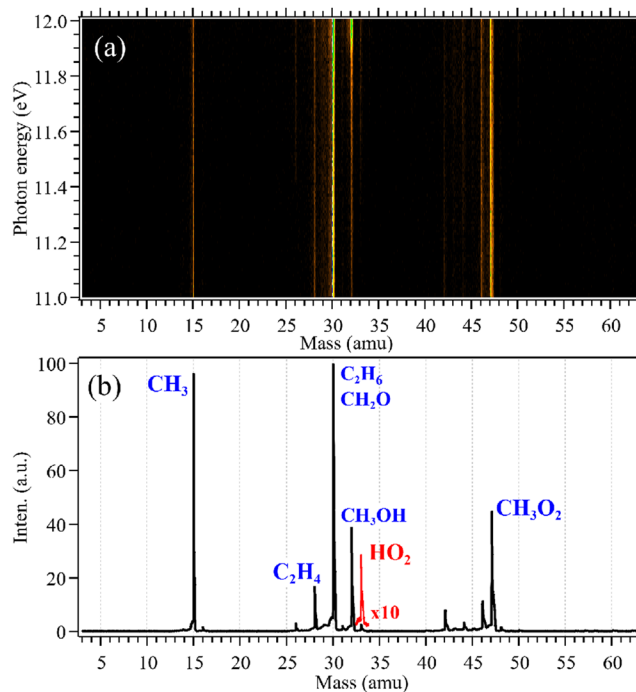


FIG. 1. (a) Synchrotron photoionization TOF mass spectra matrix and (b) the integrated mass spectrum in the 11 eV–12 eV energy range.

$m/z = 15, 28, 30, 32,$ and 47 are assigned as CH_3 , ethene (C_2H_4), ethane and formaldehyde (C_2H_6 and CH_2O with the same isobaric mass $m/z = 30$), methanol (CH_3OH), and CH_3O_2 , respectively.^{22,23,31} In particular, the mass peak at $m/z = 33$ exhibits a very weak signal, as shown by the 10-time magnified data in red, and is assigned to the HO_2 radical.

The HO_2 coincident signal as a function of electron kinetic energy (eKE) and photon energy was measured by scanning the synchrotron photon energy with a step size of 10 meV and is presented in Fig. 2, providing rich and multiplex information of the photoionization process. In the image, energy conservation dictates that direct photoionization transitions appear as diagonal lines of unity slope,

$$e\text{KE} = h\nu - \text{IE}_{\text{th}}, \quad (2)$$

where IE_{th} is the ionization energy of the i th cationic state. The photoionization efficiency (PIE) curve of the cation HO_2^+ is obtained directly by the integration of the matrix over all electron kinetic energies and has been added as a white line in Fig. 2. The signal of HO_2^+ increases progressively with photon energy, and several steps can be observed in the PIE curve, whose overall shape is in good agreement with previous results.^{15,17}

The threshold photoelectron signal can be acquired when the photon energy is resonant with the energy levels of the cation and provides more spectrally and structural sensitive information than PIE.^{32,33} Through the coincident scheme, the mass-selected TPES of the HO_2 radical is obtained, without interferences from the other

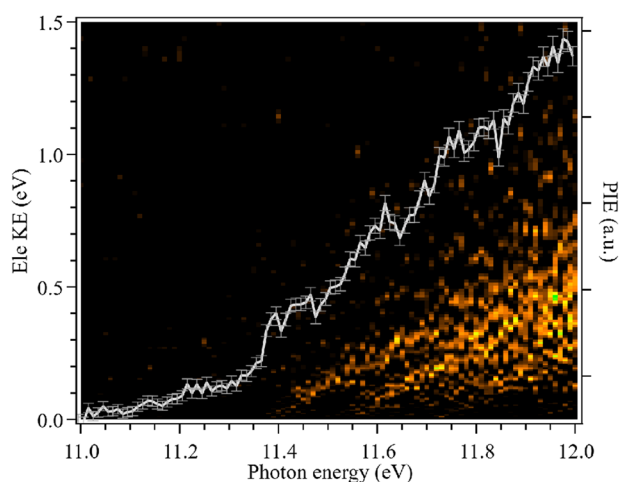


FIG. 2. Mass-selected photoelectron kinetic energy matrix corresponding to the HO_2 radical and its photoionization efficiency (PIE) curve shown as a white line.

dominant species inside the flow tube, by integrating the photoelectron signal $A(h\nu, \text{KE})$ of the matrix in Fig. 2 along constant cationic states (diagonal lines) and up to a maximum value of $\text{KE}_{\text{max}} = 100$ meV, according to the equation below, and presented in Fig. 3(a).^{34,35} The 100-meV integration limit yields an electron energy resolution of 20 meV,

$$\text{TPES}(h\nu) = \int_0^{\text{KE}_{\text{max}}} A(h\nu + \text{KE}, \text{KE}) d\text{KE}. \quad (3)$$

Unlike the smooth change in the unstructured PIE curve in Fig. 2, the TPES shows a rich structure within the photon energy range of 11 eV–12 eV, which is assigned as the vibrational progression of the X^3A'' ground electronic state and/or the a^1A' first excited electronic state. The AIEs of the X^3A'' ground electronic state and the a^1A' first excited electronic state of the cation HO_2^+ are calculated in the present work at the RCCSD(T)/CBS//M062X/aug-cc-pVTZ level of theory using the *MOLPRO* software,²⁹ with values of 11.357 eV and 11.616 eV, respectively.

In order to assign the TPES, the Franck–Condon factors for the ionization transitions from the X^2A'' neutral ground electronic state to the X^3A'' cationic ground electronic state have been calculated at the B3LYP/6-311+G(3df,2p) level of theory, as implemented in the *Gaussian 16* program,³⁰ and the computed results are listed in Table III. The Franck–Condon factors are also presented in Fig. 3(c) together with the transition labels.

The cation HO_2^+ in the X^3A'' ground state possesses a similar structure as the neutral HO_2 radical in the X^2A'' ground state^{6,36} (see Table I), and thus, the vibrational origin (0–0) band should be the most intense of the PES, agreeing very well with our experimental and calculated results. Our calculated data also show that the ν_2 and ν_3 vibrational modes, together with their combination modes, are populated upon photoionization, whereas the intensity of the ν_1 vibrational transition is weaker, in coherence with the corresponding geometric changes of the cation HO_2^+ , as compared to the neutral.

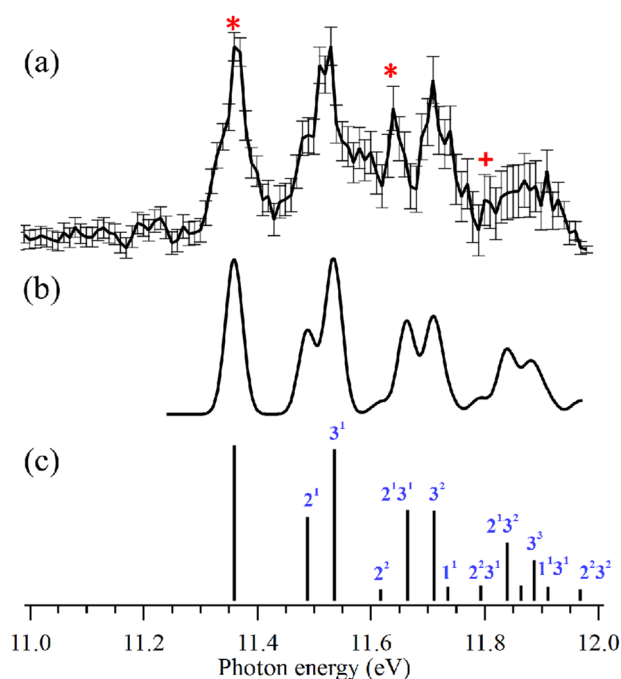


FIG. 3. (a) Mass-selected threshold photoelectron spectrum (TPES) of the HO_2 radical. (b) Simulated PES and (c) calculated Franck–Condon factors as a stick-PES, corresponding to the $X^2A''(v_m = 0) \rightarrow X^3A''(v_m = n), m^n$, ionization transition. The AIEs of the X^3A'' ground state and the a^1A' first excited electronic state are marked with red stars together with the vibrational excitation of the a^1A' state as a red cross.

In Fig. 3(a), the first peak of the TPES is measured at 11.359 ± 0.003 eV, after taking into account the correction of the DC Stark shift³⁷ and agreeing well with the theoretically calculated result of 11.357 eV, and is assigned as the vibrational origin (0–0) band of the X^3A'' cationic ground state. The absolute photon energy of the TPES has been calibrated with the literature AIEs of CH_3 (9.83891 ± 0.00019 eV)³⁸ and H_2CO (10.8887 ± 0.0005 eV),³⁹ for which TPES are presented in Fig. S1, and its uncertainty is less than 1 meV. The combined influences of the uncertainty in the photon energy calibration, the step size during the synchrotron photon energy scan, and the signal-to-noise ratio of the TPES have been taken into account in the determination of the error bar, and its magnitude is within 0.003 eV.⁴⁰ As shown in Table II, the AIE value of 11.359 ± 0.003 eV is in accordance with the previous values of 11.35 ± 0.01 eV measured with HeI PES¹⁶ and 11.352 ± 0.007 eV with PIE,^{15,17} their differences being within the range of the error bars, but at present, the uncertainty has been reduced by a factor of 2–3.

The simulated PES is obtained by convolving the stick-PES with a Gaussian function (FWHM = 35 meV), whose width is larger than the electron energy resolution (20 meV) due to the rotational population of the radical, and presented in Fig. 3(b). The stick-PES and the simulated PES are energetically shifted to match the experimental results. The overall shape of the simulated PES agrees well with that of the experimental TPES. Note that the anharmonicity and

TABLE III. Calculated Franck–Condon (F–C) factors in the ionization transitions of HO₂.

v^a	0	2 ¹	3 ¹	2 ²	2 ¹ 3 ¹	3 ²	1 ¹	2 ² 3 ¹	2 ¹ 3 ²	1 ¹ 2 ¹	3 ³	1 ¹ 3 ¹	2 ² 3 ²
Energy ^b	0	1038	1417	2076	2455	2834	3031	3493	3872	4069	4251	4448	4910
F–C	0.171	0.092	0.167	0.013	0.100	0.099	0.016	0.017	0.064	0.017	0.045	0.016	0.013

^a m^n corresponds to the $X^2A''(v_m = 0) \rightarrow X^3A''(v_m = n)$ ionization transition.

^bCalculated energies relative to the AIE of HO₂, with vibrational frequencies scaled by 0.96. The unit is cm⁻¹.

TABLE IV. Fundamental vibrational frequencies of ground-state HO₂⁺ (unit: cm⁻¹).

	v_1 (HO stretch)	v_2 (HOO bend)	v_3 (OO stretch)	Method	Reference
Expt.	3020 ± 40			IR predissociation	20
	3016.726 ± 5			IR + ion trap	18
		1026.5 ± 0.1		FTIR + Ne matrix	21
			1560 ± 50	HeI PES	16
Calc.	3060 ± 50	1040 ± 50	1370 ± 50	TPES	This work
	3066.6	1071.5	1361.6	MRCI ^a	19
	3028	1068	1440	RCCSD(T)/CBS	3
	3054	1089	1399	CHIPR ^b	14
	3032.9	1037.0	1405.9	UB3LYP/cc-pVTZ ^c	21
	3031	1038	1417	B3LYP/6-311+G(3df,2p) ^c	This work

^aAnharmonic frequencies calculated with the multi-reference configuration interaction method.

^bCHIPR: the combined hyperbolic inverse power representation method.

^cScaled by 0.96.

Duschinsky rotation are not included in the Franck–Condon calculations, which could account for the slight differences between simulated and experimental data. Based on the calculated results, the peaks of the TPES can be unambiguously assigned as the v_1 , v_2 , and v_3 vibrational populations of the X^3A'' ground state, together with their combination modes, as shown in Fig. 3 and listed in Table III. The three vibrational frequencies of the cation HO₂⁺ at the X^3A'' ground state are measured at $v_1 = 3060$ cm⁻¹, $v_2 = 1040$ cm⁻¹, and $v_3 = 1370$ cm⁻¹, respectively. The precise determination of the vibrational frequencies is difficult, however, due to rotational broadening, insufficient signal-to-noise ratio, and overlapping structures in the TPES, which yields an estimated error bar of ~50 cm⁻¹. The experimental vibrational frequencies are in good agreement with the high-level theoretically calculated results from the literature, as shown in Table IV. In addition, in comparison to existing experimental data, the present v_1 frequency agrees with the results of Kohhbuchi *et al.*¹⁸ and Nizkorodov *et al.*,²⁰ and the v_2 frequency concurs with that of Jacox and Thompson,²¹ whereas our v_3 frequency value is smaller than the estimated data of Dyke *et al.*,¹⁶ which could be due to the different experimental energy resolutions.

In the TPES of Fig. 3(a), the peak at $h\nu = 11.639 \pm 0.005$ eV does not fully coincide with any of the simulated $X^3A'' \leftarrow X^2A''$ transitions shown in Fig. 3(b) and is therefore assigned to the AIE of the a^1A' first excited electronic state based on the presently calculated AIE of 11.616 eV at the RCCSD(T)/CBS//M062X/aug-cc-pVTZ level of theory. The vibrational frequencies of the a^1A' electronic state were reported at $v_1 = 3194.93$ cm⁻¹, $v_2 = 1404.68$ cm⁻¹,

and $v_3 = 1496.42$ cm⁻¹ by Robbe *et al.* using the multi-reference configuration interaction (MRCI) approach.¹⁹ Within the present photon energy range, the fundamental transitions of the v_2 and v_3 vibrational modes of the a^1A' state can be excited and contribute somewhat to the minor peak at $h\nu = 11.809$ eV in the TPES, which is marked as a red cross in Fig. 3(a).

The recommended value in the ATcT database for the enthalpy of formation of the HO₂ radical is $\Delta_f H_{0K}^0(\text{HO}_2) = 15.12 \pm 0.15$ kJ mol⁻¹,⁷ and NIST suggests a value of 15.21 ± 0.35 kJ mol⁻¹.⁸ Ganyecz *et al.* used the composite theoretical/thermochemical network approach to find the enthalpies of formation of 14.85 ± 0.22 kJ mol⁻¹ for the neutral HO₂ radical and of 1110.56 ± 0.40 kJ mol⁻¹ for the cation HO₂⁺, which yields an AIE of the HO₂ radical at 11.356 ± 0.005 eV.⁹ Our directly measured AIE value, 11.359 ± 0.003 eV, corroborates the network data of Ganyecz *et al.*⁹ within the error bars and could be used to further refine it.

IV. CONCLUSIONS

We have studied the VUV photoionization of the HO₂ radical close to its ionization threshold by using the state-of-the-art method of i²PEPICO at the DESIRS beamline of synchrotron SOLEIL. A fast flow tube reactor combined with a microwave discharge generator was utilized to generate the HO₂ radical through the reaction of the methoxy radical with oxygen. The mass-selected high resolution TPES of the HO₂ radical without interferences from other species is measured in coincidence and then assigned with the aid of calculated AIEs and Franck–Condon factors. The X^3A'' cationic

ground electronic state and the $1^1A'$ first excited electronic state have been observed in the TPES, exhibiting fine vibrational structures in the 11 eV–12 eV energy range. The three vibrational modes of the X^3A'' ground state, the H–O stretch, the HOO bend, and the O–O stretch, have been excited in the photoionization process, and their vibrational frequencies are measured with the assignments. In addition, the AIEs of the X^3A'' ground state and the $1^1A'$ excited state are determined at 11.359 ± 0.003 eV and 11.639 ± 0.005 eV, respectively, agreeing well with our high-level theoretically calculated results. In particular, the first AIE value provides experimental evidence to extract the enthalpy of formation for the HO_2 radical.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the mass-selected TPES corresponding to $m/z = 15$ (CH_3) and 30 (H_2CO , C_2H_6) utilized to calibrate the photon energy.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 21773249, 91961123, and U1832184), the International Partnership Program of Chinese Academy of Sciences (Grant No. 116134KYSB20170048), and the French Agence Nationale de la Recherche (ANR) under Grant No. ANR-12-BS08-0020-02 (Project No. SYNCHROKIN). C.F. would like to thank the CAS President's International Fellowship Initiative (Grant No. 2018VMA0055). A.R. and D.S. would like to acknowledge support by the Deutsche Forschungsgemeinschaft, Research Training School GRK 2112 (Molecular Biradicals). The authors are grateful to the SOLEIL staff for smoothly running the facility and providing synchrotron beamtime under Proposal No. 20150802.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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