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Vibronic spectra of the allyl radical at 6—8 eV with resonance-enhanced multiphoton ionization technique

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Abstract The allyl radical was produced in molecular beam by pyrolysis of allyl iodide. The vibronic spectra from ground state to six new electronic states of the allyl radical at 6—8 eV, $\pi\rightarrow 3d_{xz}$, $\pi\rightarrow 3d_{xy}$, and $\pi\rightarrow n$s (n=4, 6, 7, 8) were observed firstly with the aid of time-of-flight mass spectroscopy and resonance-enhanced multiphoton ionization technique. Vibrational progression of ν_7 (C_3 bend) with gross spacing of about 430 cm^{-1} was observed in ns Rydberg states. The adiabatic ionization potential of the allyl radical was obtained to be (65641 ± 20) cm^{-1} ((8.138 ± 0.002) eV) by fitting the term values of ns (n=4,6,7,8) Rydberg states with Rydberg formula.

Keywords: time-of-flight mass spectroscopy, resonance-enhanced multiphoton ionization, allyl radical, Rydberg state, ionization potential.

Neutral free radicals are very common and important intermediate species in atmospheric chemistry, combustion processes, and organic reactions. Spectroscopic studies on them can lay bare their energy levels, molecular structures and other physical and chemical properties, which are very important for understanding their reaction mechanisms and pathways in chemical reactions. However, in comparison with neutral molecules, relatively less information on the spectra of neutral free radicals is available owing to the difficulties of producing purified radicals with high density in laboratory. In this paper, the allyl radical was produced in molecular beam by pyrolysis of allyl iodide and the spectra of high-lying excited electronic states of the allyl radical were studied with resonance-enhanced multiphoton ionization (REMPI) combinding with time-of-flight mass spectroscopy technique.

The allyl radical, CH_2CHCH_2, is the simplest conjugated π-electron hydrocarbon radical and is the prototype for an extended conjugated system with odd number of electrons. It plays important roles in many combustion, photochemical and thermal reactions. Because of these, it is one of hydrocarbon radicals that have been studied most extensively and in detail.

Electronic spin resonance[1] and electronic diffraction[2] investigations have indicated that the allyl radical has a C_{2v} planar structure in ground state. The vibration frequencies of some of vibrational modes were measured by IR spectroscopy at low temperature[3] and ultraviolet resonance

Raman spectroscopy[4], and the vertical and adiabatic ionization potentials were measured with photoelectron spectroscopy[5].

The spectra from ground state to four excited electronic states, A, B, C, and D have also been studied with ultraviolet absorption and REMPI[6—12]. These four excited electronic states are all at the energy levels below 6.0 eV. This work reports experimentally observed six new electronic states of the ally radical at 6—8 eV and the adiabatic ionization potential determined from the *n*s Rydberg states.

1 Experimental

In experiment, a Q-swich Nd:YAG laser (Spectra Physics, Quanta Ray GCR-190) pumping a tunable dye laser (Lambda Physik, Scanmate 2E) was used as light source. The repeat rate of the laser pulse is 30 Hz, and half pulse width at half maximum is ~7 ns. The wavelength of the dye laser was calibrated with the optogalvanic spectroscopy of Ar/Ne within 2 cm^{-1} accuracy. The vacuum chamber includes two parts, ionization chamber and flight chamber, which were vacuumized by a mechanic pump and two turbo pumps. In experiments, the vacuum of ionization chamber was 2.67×10^{-3} Pa, and the vacuum of the flight chamber was 6.67×10^{-5} Pa. The dye laser was frequency-doubled with BBO crystal and focused to the ionization chamber by a 25 cm focal length quartz lens perpendicular to molecular beams. The cations produced via REMPI were repelled in electric field perpendicular to both molecular and laser beams. The cations flew across a field-free TOF tube (80 cm) and were detected by a microsphere plate (MSP) (EI-MUI technologies). The output signals of MSP were amplified by a preamplifier (EG&G, VT120) and then sent to a 500 MHz digital oscilloscope (LECroy 9344) and a gated integrator (SRS, SR250) simultaneously. The average output of the gated integrator was recorded by a PC computer after A/D conversion. The time sequence of laser and molecular beams was controlled by a data pulse/delay generator (SRS, DG535).

The allyl radical was produced by pyrolysis of allyl iodide under about 1500℃. Allyl iodide was seeded in 2.02×10^{5} Pa He with 0.1% concentration and sprayed out to the ionization chamber through a pulsed valve (General Valve with 0.5 mm orifice). The sample passed through a ceramic tube (8 mm length, 1 mm inner-diameter) electrically heated with molybdenum, and the allyl iodide was pyrolized to iodine atom and allyl radical within this tube and then spayed out with ultrasonic speed, then after free expansion, the temperature of the sample can reach 70 K.

2 Results and discussion

2.1 Experimental results

Fig. 1 is the time-of-flight mass spectrum excited at 369.447 nm (equivalent two-photon energy is 54135 cm^{-1}). Under the condition of heating on, the signals of $\mathrm{C_3H_5^+}$ and $\mathrm{C_3H_3^+}$ can be observed, however, under the condition of heating off, no ions signals can be observed. It was demonstrated that the ions signals observed in experiment definitely come from the ionization of the allyl radical pyrolyzed from allyl iodide. It was also demonstrated that the allyl radical produced by photolysis can be ignored. We optimized other experimental conditions at this wavelength to get strong $C_3H_5^+$ signal with best ratio of signal to noise. Fig. 2 is the 2+1 REMPI spectra of allyl radical at 6—8 eV obtained under these best experimental conditions. It can be seen that there is a strong band at 52000—56000 cm^{-1}, and another weak band at 61000—64000 cm^{-1}.

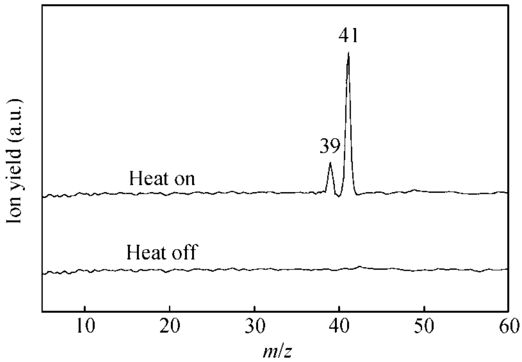

Fig. 1. Time-of-flight mass spectrum excited at 369.447 nm.

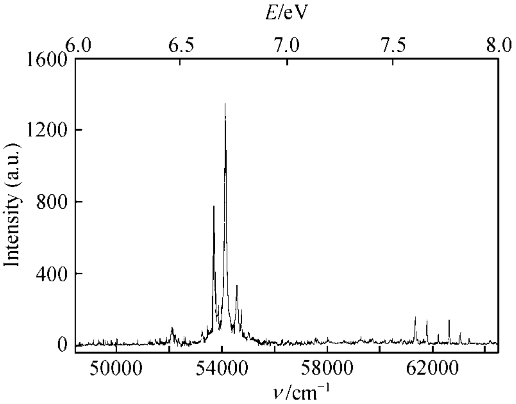

Fig. 2. Composite 2+1 REMPI spectra of allyl radical at 6—8 eV.

2.2 Assignment of the spectra

Fig. 3 is the 2+1 REMPI spectra of allyl radical between 52000 and 56000 cm^{-1}. Ha et al.[13] predicted that two excited electronic states of the allyl radical lie at 6.41 eV (51703 cm^{-1}) and 6.61 eV (53316 cm^{-1}) respectively according to their *ab initio* calculations, thereafter, we assigned the two weak peaks at 52123 and 53264 cm^{-1} to be the transitions from ground state to these two states, that is to say, $\pi\rightarrow 3d_{xz}$ and $\pi\rightarrow 3d_{xy}$. The peak lying at 53708 cm^{-1} is the band origin of $\pi\rightarrow 4s$. Vibronic transitions of ν_7, ν_6, and $\nu_5$1) vibrations were also observed. Especially, a ν_7 vibrational progression is shown in this vibronic spectrum. The peak at 55012 cm^{-1} has two possibilities, $\pi\rightarrow 4s+\nu_7(0—3)$ and/or $\pi\rightarrow 4s+\nu_5(0—1)$, because their frequencies are very close and cannot be distinguished in our experiment. The small peaks at 53446 and 53876 cm^{-1} are definitely observed in our experiment, however, they cannot be assigned exactly. Here we only propose a possible assignment, the vibronic transition of $\pi\rightarrow 4s$ and $\pi\rightarrow 3d_{xy}$ combined with $\nu_5-\nu_6$, because $\nu_5-\nu_6$ is about 180 cm^{-1} at electronic excitation states[14] and the frequencies of these two peaks are coincident with the frequencies of $\pi\rightarrow 4s+(\nu_5-\nu_6)$ and $\pi\rightarrow 3d_{xy}+(\nu_5-\nu_6)$.

In order to assist assignment of the vibronic spectra observed in experiment, we did calculations on the Franck-Condon factors of the vibronic transitions of $\pi\rightarrow 4s$. The theoretical method

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1) ν_5, CH_2 rock; ν_6, C_3 stretch; ν_7, C_3 bend.

has already been described in detail in ref. [15]. The calculated results show that the progression of ν_7 is the most easily detected vibronic transition, and the second one is vibronic transition including ν_6 or ν_5. The detailed calculation processes and results are to be reported in another paper.

Fig. 4 is the 2+1 REMPI spectra of allyl radical from 61000 to 64000 cm^{-1}, and the assignments of all spectroscopic lines are indicated in the figure. Only the vibronic spectra of ν_7 vibration can be observed. The positions and assignments of all the spectral lines of the allyl radical between 6—8 eV observed in our experiment are listed in table 1.

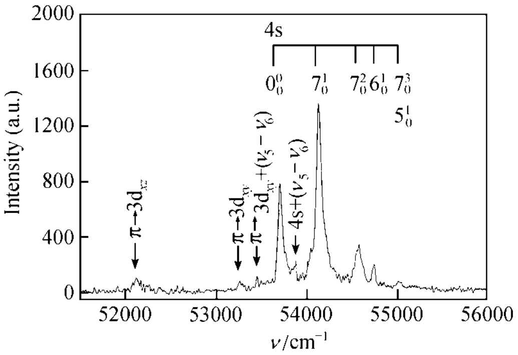

Fig. 3. 2+1 REMPI spectra of the allyl radical between 52000—56000 cm^{-1} and assignments.

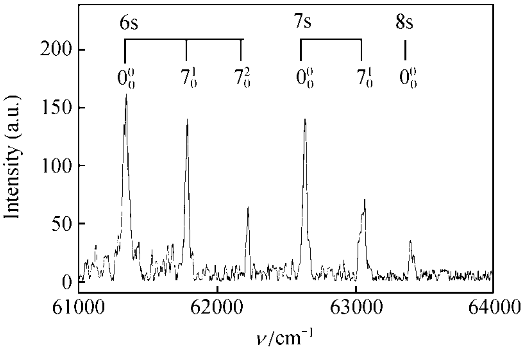

Fig. 4. 2+1 REMPI spectra of the allyl radical between 61000—64000 cm^{-1} and assignments.

Table 1 2+1 REMPI spectra of the allyl radical at 6—8 eV and assignments

Position/ cm^{-1}	Assignments	Vibration frequency/cm^{-1}	Ref.
52123	$\pi\rightarrow 3d_{xz}$		[13]
53264	$\pi\rightarrow 3d_{xy}$		[13]
53446	$\pi\rightarrow 3d_{xy}+(\nu_5-\nu_6)$	182	[14]
53708	$\pi\rightarrow 4s$		
53876	$\pi\rightarrow 4s+(\nu_5-\nu_6)$	168	[14]
54135	$\pi\rightarrow 4s+\nu_7(0—1)$	427	
54581	$\pi\rightarrow 4s+\nu_7(0—2)$	873	
54784	$\pi\rightarrow 4s+\nu_6(0—1)$	1076	
55012	$\pi\rightarrow 4s+\nu_7(0—3)/\nu_5(0—1)$	1304	[4], [14]
61338	$\pi\rightarrow 6s$		
61777	$\pi\rightarrow 6s+\nu_7(0—1)$	439	
62216	$\pi\rightarrow 6s+\nu_7(0—2)$	878	
62630	$\pi\rightarrow 7s$		
63067	$\pi\rightarrow 7s+\nu_7(0—1)$	437	
63394	$\pi\rightarrow 8s$		

According to the 2+1 REMPI spectra of the allyl radical between 6—8 eV, a conclusion can be made as that the ν_7 vibration is the most active mode in electronic excitation states of the allyl radical, and the second is the ν_6 and ν_5 vibrations. The transition of π→5s was not observed in our experiment, possibly due to low laser energy at this wavelength or that 5s state is easier to dissociate than other s Rydberg states.

2.3 The adiabatic ionization potential of the allyl radical

The adiabatic ionization potential of atoms and molecules can be obtained by fitting the observed Rydberg states to the Rydberg formula of

$$v = IP - \frac{R}{(n-\delta)^2},$$

where IP is the ionization potential, R is Rydberg constant, for allyl radical R=109735.86 cm^{-1}, n is principal quantum number and δ is the corresponding quantum defect. Fitting the experimental results of 4s, 6s, 7s and 8s Rydberg states of the allyl radical to the Rydberg formula, the adiabatic ionization potential of the allyl radical can be obtained to be (65641 ± 20) cm^{-1}, and the quantum defect δ = (0.967 ± 0.005).

3 Conclusions

The allyl radical was produced by pyrolysis of allyl iodide and the 2+1 REMPI spectra of the allyl radical at 6—8 eV were observed in experiment. Six new electronic states, d_{xz}, d_{xy}, and ns (n=4, 6, 7, 8), were observed firstly and the vibronic spectra of ν_7, ν_6 and ν_5 vibrations were also observed. It is shown that ν_7 vibration is the most active mode in electronic excitation states of the allyl radical, and the second is the ν_6 and ν_5 vibration modes. The adiabatic ionization potential of the allyl radical was obtained to be (65641 ± 20) cm^{-1} ((8.138 ± 0.002) eV) by fitting the term values of ns (n = 4, 6, 7, 8) Rydberg states to the Rydberg formula.

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