

RESONANCE AND ANTIRESONANCE IN THE AUTOIONIZATION SPECTRA INDUCED BY RYDBERG VIBRATIONAL STATES OF BENZENE MOLECULE

—ULTRA SENSITIVE LASER MULTIPHOTON IONIZATION SPECTROSCOPY

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I. INTRODUCTION

In recent years laser multiphoton ionization spectroscopy is developed rapidly^[1-3]. The main reason is that it has many substantial advantages, such as high sensitivity, low background noise and easy detection. In fact, it is a very effective method for investigating the higher excited states of atoms and molecules as well as for studying Rydberg autoionization process^[4,5]. Antiresonance was studied by Floride et al. First of all, they observed it from Rydberg absorption spectroscopy in Naphthalene molecule^[6]. This phenomenon, however, for a variety of reasons, was not clearly observed, especially that of the resonance and antiresonance above the threshold value in large molecules was even rare. With the development of investigation of multiphoton ionization process the resonance enhanced MIP attracts much attention due to its capability of increasing the ionization cross section dramatically. However, on the other hand, the antiresonance appeared in the ionizing spectrum implies the decrease in the ionization cross section and must be noticed. To study the resonance in the continuum is also of interest in obtaining further knowledge of the mechanism of the breakdown of Born-Oppenheimer Approximation in the high excited state of molecule.

We first report the experimental results of the resonance and antiresonance structure in the two-color laser one photon resonance enhanced ionizing spectra of C_6H_6 . This interference effect was explained quantitatively on the basis of the mixing of continuum states with Rydberg vibrational states above the threshold value.

II. EXPERIMENT

The experimental arrangement is shown in Fig. 1. Two UV photons were provided by two frequency doubling dye lasers (LAMBDA PHYSIK FL 2002) pumped simultaneously by an excimer laser (LAMBDA PHYSIK EMG 102) at wavelength 308 nm.

UV output energy is up to $2 \times 250 \mu\text{J}$ with pulse width (FWHM) of 10 ns and the wavelength tuning range is 260–285 nm with a line width of 0.1 cm^{-1} . The laser intensity of the expanded beam in the interaction region was about $1.7 \times 10^5 \text{ W/cm}^2$. In order to overlap the two counter-propagating laser beams well in the 40-cm long interaction area two pinholes were used. We monitored the pulse energies by reflecting a fraction of 10% of the total energy to the energy meter EM (Laser Precision Corp. Rj 7100). The gas pressure is measured with a capacitive pressure gauge to be about 50–80 μbar . Two electrically driven shutters can block any of the two UV-beams by computer control.

Two computers were used in the experiment. TRS-80 controlled the frequency scanning of the dye laser. Another PDP/11 read the data from EM and PM and ion signal, and stored the data after the data were temporarily stored by S/H (Sample & Hold Devices) and processed by ADC (Camac-module Le Croy 2232). The PDP/11 also was used for data reduction and plotting.

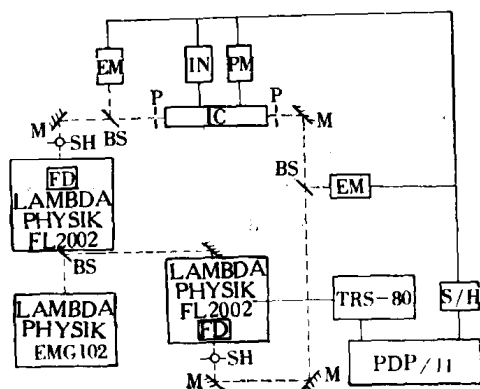


Fig. 1. Experimental Arrangement.
S/H, Sample and hold; M, mirror;
EM, energy meter Rj 7100;
BS, beamsplitter;
IN, integrator;
FD, frequency doubling;
PM, Pressure meter;
SH, shutter;
IC, ionization chamber;
P, pinhole.

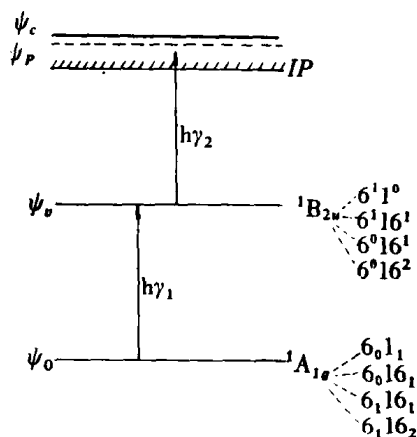


Fig. 2. The excitation scheme of two-color one photon resonance enhancing two photon ionization process.
 ψ_0 is the ground state of the molecule;
 ψ_v the excited state in the intermediate;
I. P. the first ionization potential;
 ψ_R the Rydberg vibrational state above I. P.;
 ψ_C the vibrational state of the ion.

The excitation scheme of the two-color laser ionizing used in the experiment is shown in Fig. 2. The molecule was selectively excited from a certain vibrational state ψ_0 in $^1A_{1g}$ to an intermediate state ψ_v in $^1B_{2u}$, and then ionized by the second photon $h\nu_2$. As it is shown in Fig. 2., we have chosen four pairs of states excited in our experiment, $6_0 1_1(^1A_{1g}) \rightarrow 6^1 1^0(^1B_{2u})$, $6_1 16_1(^1A_{1g}) \rightarrow 6^0 16^1(^1B_{2u})$, $6_0 16_1(^1A_{1g}) \rightarrow 6^1 16^1(^1B_{2u})$, $6_1 16_2(^1A_{1g}) \rightarrow 6^0 16^2(^1B_{2u})$. Here we used the nomenclature of [9] for the excitation transition, in the example $6^0 1_1$ the quantum number of ν_6 is 0 in $^1A_{1g}$, and is 1 in $^1B_{2u}$. The quantum number of ν_1 is 1 in $^1A_{1g}$ and is 0 in $^1B_{2u}$.

III RESULTS AND DISCUSSION

The spectra of $6_0^1 1_1^0$, $6_0^1 16_1^1$, $6_1^0 16_1^1$ and $6_1^0 16_2^2$ are shown in Figs. 3, 4 and 5, respectively. As we can see they are very typical spectra.

(1) Fig. 3 shows two typical asymmetric resonance and antiresonance in the ionization spectrum of $6_0^1 1_1^0$ transition. They are indicated by arrows ①, ② and ③, ④ respectively.

(2) Two spectra $6_1^0 16_1^1$ and $6_0^1 16_1^1$ are shown in Fig. 4. By comparing them, it can be seen that the appearance of resonance peaks is very sensitive to which transition excited we have chosen.

(3) The ionization spectrum of $6_1^0 16_2^2$ excitation (note the exciting wavelength of 269.10nm^{10}) gives an approximate Lorentzian symmetric line shape as shown in Fig. 5.

Fano's theory^[7] indicates that the optical transition from a bound state below the

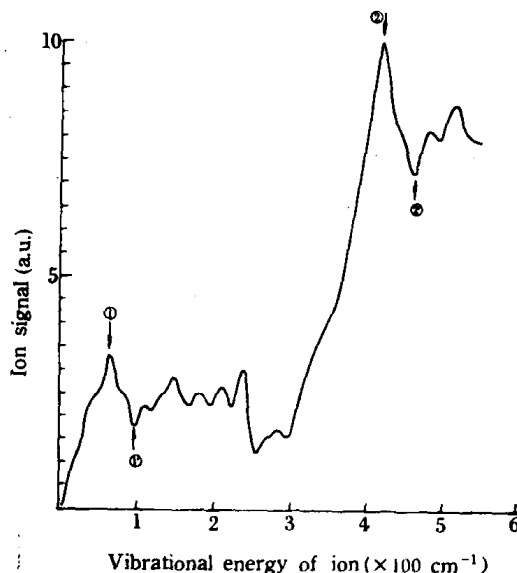


Fig. 3. The ionization spectrum for $6_0^1 1_1^0$ excited state, its resonance and antiresonance are shown by arrows ①, ② and ③, ④.

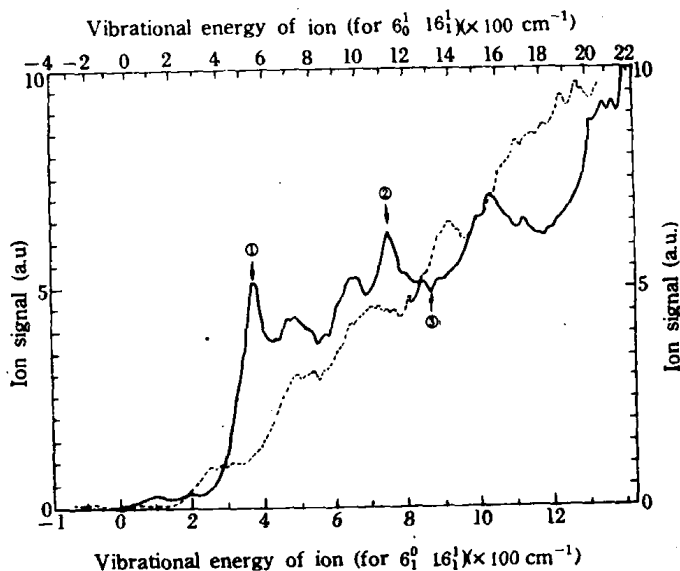


Fig. 4. The ionization spectra of $6_1^0 16_1^1$ and $6_0^1 16_1^1$ excited transitions, its resonances are shown by arrows ①, ②, ③. ---, $6_1^0 16_1^1$ excited transition; —, $6_0^1 16_1^1$ excited transition.

- 1) The band $6_1^0 16_2^2$ is expected to consist of three (first order Herzberg-Teller) peaks, being separated due to their angular momentum terms, which are $L=2$, $L=-2$, and $L=0$. In LIF (Laser Induced Fluorescence) spectra only two peaks appear at exciting wavelength, 269.10 and 269.13 nm respectively.

threshold value to the bound state above has Fano line shape as shown in Fig. 2. If the zero-order Born Oppenheimer states are expressed as the continuum states ϕ_c , and the isoenergy Rydberg bound states ϕ_R , above the ionization threshold, then the line shape is

$$L(\varepsilon) = \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}, \quad (1)$$

where

$$\varepsilon = \frac{h\nu - E_R}{\pi\rho U_{RC}}, \quad (2)$$

$$U_{RC} = \langle \phi_R | H | \phi_C \rangle, \quad (3)$$

$$q = \frac{A |\langle \phi_V | \mu | \phi_R \rangle|}{|A| |\langle \phi_V | \mu | \phi_C \rangle| \pi\rho U_{RC}}, \quad (4)$$

ε is a reduced energy, E_R the energy of the zero-order Rydberg state, ρ the density of the state ϕ_C , U_{RC} the matrix element coupling the zero state ϕ_R and ϕ_C , $h\nu$ the photon energy. q is called the index of the line profile. A is the cosine of the angle between the transition moments $|\langle \phi_V | \mu | \phi_R \rangle|$ and $|\langle \phi_V | \mu | \phi_C \rangle|$. The line width is

$$\Gamma_P = 2\pi\rho U_{RC}. \quad (5)$$

From Eq. (4) it can be seen that when the transition to the zero-order Rydberg state carries none of oscillator strength, i. e. $|\langle \phi_V | \mu | \phi_R \rangle| = 0$, then $q = 0$ and line shape becomes a symmetric one:

$$L(\varepsilon) = \frac{\varepsilon^2}{1 + \varepsilon^2}, \quad (6)$$

when $\langle \phi_V | \mu | \phi_C \rangle = 0$ and the transition to the ϕ_R state does carry oscillator strength, then $q \rightarrow \infty$. An approximate symmetric line shape will be obtained as follows:

$$L(\varepsilon) = \frac{1}{1 + \varepsilon^2}. \quad (7)$$

A more interesting case is when the transition strength of $\phi_V \rightarrow \phi_C$ and $\phi_V \rightarrow \phi_R$ are comparable. For example, $q = 0.5-5.0$, within this range of q the resonance and antiresonance structure will be observed as indicated by Eq. (1).

The spectrum for $6_0^1 1_1^0$ has the line shape of Eq. (1). The resonance indicated by arrows ① and ② are situated at 60 cm^{-1} and 415 cm^{-1} above I. P. respectively. The antiresonances indicated by ④ and ⑤ are 100 cm^{-1} and 450 cm^{-1} above I. P. respectively. We can obtain the line width of 20 cm^{-1} and the lifetime of the autoionization state $\tau_P = \frac{\hbar}{\Gamma_P}$, being about $3 \times 10^{-13} \text{ s}$.

From Eq. (1), it can be found that there is an autoionizing zero at $q = -\varepsilon$, while an autoionizing maximum is at $q = \frac{1}{\varepsilon}$. Therefore, the energy value of the

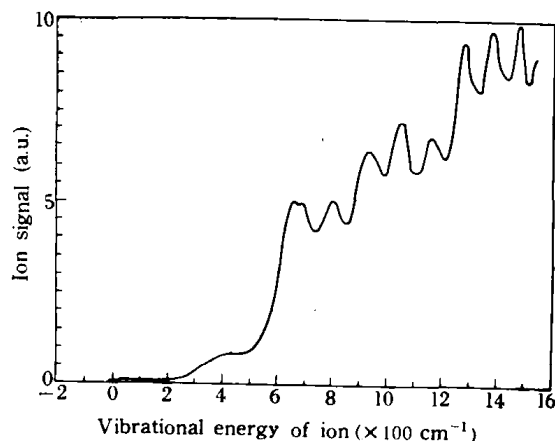


Fig. 5. The ionization spectrum of $6_0^1 1_6^2$ excited transition.

zero-order Rydberg states, E_R , can be obtained. In example $6_0^1 1_1^0$, we obtained three values of E_R as 437.5 cm^{-1} , 502.0 cm^{-1} and 1026 cm^{-1} above I. P. It is known from Ref. [10] that there are four Rydberg series with quantum defect, 0.46, 0.16, 0.11 and 0.04, converging to the first I. P. and at 9.16 eV there is the state E_{1u} , $n = 3$ converging to 11.49 eV (the second ionization potential). The transition from ϕ_V , $6^1(^1B_{2u})$, to the vibronic states above I. P. belonging to E_{1u} , $n = 3$ Rydberg state can be induced optically by E_{2g} symmetric vibration. The selection rule is determined by the overlap integral, $\int \phi_V'^* \phi_V'' d\tau_V$. Therefore, direct product $\Gamma(\phi_V') \otimes \Gamma(\phi_V'')$ must contain the totally symmetric group representation. This necessitates that $\Gamma(\phi_V')$ and $\Gamma(\phi_V'')$ belong to the same symmetry species. Adding 653 cm^{-1} to the E_R values mentioned above, we found that the values of $(653 \text{ cm}^{-1} + E_R)$ lie just near to some vibrational states above I. P. belonging to E_{1u} , $n = 3$ Rydberg state. Table 1 lists three E_R and their possible assignments.

Table 1
 E_R and Their Possible Assigned Rydberg Vibrational States(cm^{-1})

E_R	Assigned Rydberg Vibrational States	Isoenergy States of Ion
347.5	$6^0 \quad 1^1$	$6^1\left(\frac{3}{2}\right)$
502.0	6^2	16^2
1026.0	$6^1 \quad 1^1$	$6^2\left(\frac{3}{2}\right)$

From Eq. (5), $\rho U_{RC}^2 = 3.18 \text{ cm}^{-1}$ is obtained. From Eq. (3) it measures the coupling of the zero-order states ϕ_R and ϕ_C .

Comparing the two spectra of $6_0^1 16_1^1$ and $6_1^0 16_1^1$ in Fig. 4, we found that the appearance of the peaks is very sensitive to the transitions we have chosen. The former shows very sharp peaks while the latter does not. This fact reflects the requirements of symmetry and transition strength (Franck-Condon factor). This is the characteristics which can be explored only by two-color laser resonance enhanced ionization spectroscopy. For example, photoelectron spectroscopy could not.

IV CONCLUSION

Resonance and antiresonance were not easily observed before with absorption spectroscopy method in polyatomic molecule. One reason may be the sensitivity of the absorption spectroscopy tool was not high enough. For large molecules like benzene, the interference effects within lowest continuum states are normally strong and complex, so resonance effect can be smeared out. By studying the resonance in continuum of small molecule or atoms of longer lifetime, one can bring new information of autoionization state. The appearance of resonance and antiresonance above the ionization potential shows again breakdown of Born-Oppenheimer Approximation (BOA) in high excited Rydberg state. Quantitative work on U_{RC} will be of much interest for investigating the mechanism of the breakdown of BOA.

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