Volume 3, Number 6 ACTA PHYSICA SINICA June, 1994
1004-423X/94/03060401-05 (Overseas Edition) © 1994 Science Press

STUDY OF THE POLARIZATION SPECTROSCOPY OF 3p RYDBERG STATES OF m-DIMETHYLBENZENE*

LIU YAO-MING(刘耀明), LIN MEI-RONG(林美荣), ZHANG BAO-ZHENG(张包铮),
ZHAO QING-CHUN(赵青春), and CHEN WEN-JU(陈文驹)
Institute of Modern Optics, Nankai University, Tianjin 300071, China

(Received 6 August 1993)

A polarization-selected three-photon resonant multiphoton ionization investigation of the 3p Rydberg region of the spectra of m-dimethylbenzene has been conducted. Several vibronic states have been discovered and also assigned for the first time.

PACC: 3380K

I. INTRODUCTION

With the advent of high peak powered, pulsed tunable dye layers, the field of multiphoton ionization (MPI) spectroscopy has developed rapidly. The technique of multiphoton ionization is rapidly gaining popularity in molecular spectroscopy and in chemical analysis because of its high sensitivity, based on the detection of charged species.[1-5] As a spectroscopic tool, MPI allows accessment of states forbidden in single photon excitation, makes more accessible states that could only be reached by VUY excitation, and permits the study of molecular systems having low fluorescence yields. As an analytical tool, MPI provides selective ionization of one species in a mixture in which the fragment distribution may be controlled by laser power and wavelength.

The dependence of resonance-enhanced multiphoton ionization (REMPI) signals on the polarization of the resonantly absorbed photons provides a powerful tool for the analysis of vibronic spectra. This approach has been successfully applied to state assignments of numerous molecules.[6,7-11] The theoretical basis for these measurements in two- and three-photon resonant absorptions has been elegantly described by several investigators.[12-16] For polyatomic molecules containing more than three atoms, separate rotational branches of a given vibronic transition are often unresolvable. In this case, the value of the measured ratio Ω of the integrated band intensity for circularly polarized to that for linearly polarized light provides vital information concerning the symmetries of initial and final states. For a two-photon resonances, transitions to states which belong to the totally symmetric irreducible representation are predicted to have a band intensity ratio for circularly to linearly polarized light of $\Omega < 3/2$, while for transitions to states of different symmetry a value of $\Omega = 3/2$ is

*Project supported by the National Natural Science Foundation of China.

expected. In three-photon resonances, there is a similarly characteristic polarization ratio if $\Omega = 5/2$. By measuring the polarization ratio for three-photon resonance, we have studied the spectra of m-dimethylbenzene.

Due to the importance of benzene as a testing ground of various theories of molecular structure and dynamics, it has received extensive studies on its structure and electronic states. In contrast, less work has been performed on the excited states of methyl-substituted benzenes. Methylbenzenes have a similar π-electron structure to that of benzene, but their symmetries are lower than that of benzene. Some forbidden transitions of benzene may become allowed for methylbenzene. Studies on methylbenzenes may help to understand the electronic states of benzene. For these reasons, in this paper, we present the three-photon resonant four-photon ionization spectra of m-methylbenzene excited by polarized light. Several 3p Rydberg transitions are discovered and analyzed for their symmetry assignments.

II. EXPERIMENT

The experimental apparatus is depicted schematically in Fig. 1. A pulsed Nd : YAG laser (Quantel) pumps a dye laser (TDL50) with pulse duration 10ns and 10Hz repetition rate. The dye is Rhodamine 6G. The output light of the dye laser is first split by S and received by photodiode P. D. as a trigger signal and for power monitoring. The other part of the beam is focused into an ionization cell C through quartz window by convergent lens L. In the cell there is 6 Torr of m-dimethylbenzene gas. The sample has been purified by vacuum distillation. Since the sample is in the gas phase, the cell is connected to a vacuum system, which is pumped down to 10^{-5} Torr before the cell is filled with the sample. In the cell, we also add 6 Torr buffer gas-Ar.

Inside the cell, there is a parallel plate electrode, biased at 200V, which allows the collection of ions produced in the ionization process. The ion current signal is first transferred to a preamplifier (EG&G 115) for amplification, then to one channel of a boxcar averager (EG&G 162/165). The second channel of the averager is used to record laser intensity detected by a photodiode. The signal from the two channels is simultaneously converted to digital form by an A/D converter (HY6070) interfaced with an IBM PC computer. At the same time, the laser wavelength scan is controlled by the computer through a standard RS-232 input/output interface.

Circularly polarized light is obtained by passing the linearly polarized output of the dye laser through a Fresnel rhombus. In order to measure the polarization ratio, Ω, the intensities of the linearly and circularly polarized light are carefully adjusted to be approximately equal at each given wavelength setting of the dye laser.

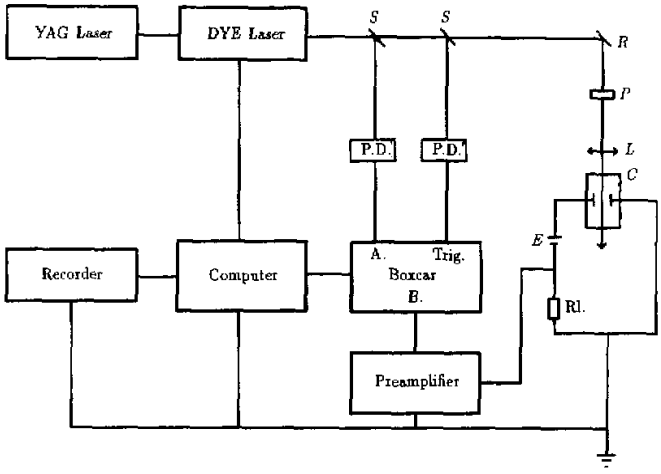

Fig. 1. The schematic diagram for experiment of three-photon resonance four-photon ionization spectrum of m-dimethylbenzene.

III. RESULTS AND DISCUSSION

The three-photon resonance ionization spectra of m-dimethylbenzene taken with both circularly and linearly polarized light are presented in Fig. 2. All spectral lines, position, vibrational frequency, polarization ratio and their assignments are listed in Table 1.

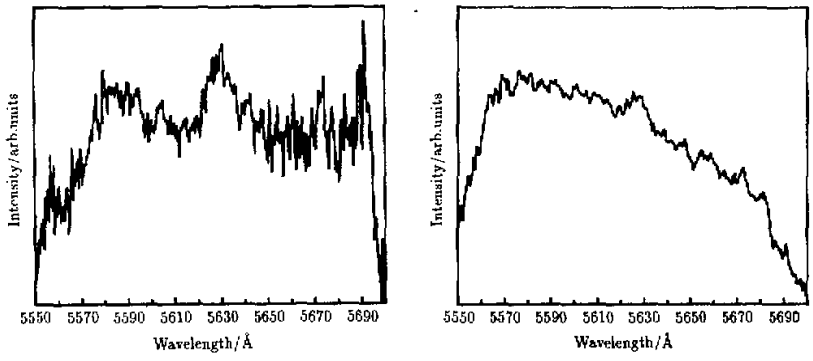

Fig. 2. The ionization spectrum of 3p Rydberg states of m-dimethylbenzene by three-photon resonance four-photon ionization (a) circularly polarized (b) linearly polarized.

The three-photon spectral region 5550–5700Å corresponds to the strongly allowed $^1E_{1u}$ state of benzene. VUV absorption spectra of m-dimethylbenzene[18,19] show that it is a broad diffuse absorption band in this region. There is no vibrational structure at all. Uneberg[20] studied this 3p Rydberg transition of methylbenzenes by two-photon resonance ionization

spectroscopy. They found several new vibronic states of toluene, p-xylene and o-xylene with the MPI technique. However for m-xylene, they could not obtain MPI spectra because of their diffuseness. So it is more difficult to detect the structure of m-dimethylbenzene than other methylbenzenes in this spectral range. We have studied this spectral region by polarization excitation with a three-photon resonance and discovered some new vibronic structure which have never been reported before. From Fig. 2, we can see that the spectral lines are clearer with excitation of circularly polarized light than by excitation with linearly polarized light.

Table 1. The assignments of 3-photon resonance MPI spectra for m-dimenthylbenzene.

Number	λ (Å)	3-photon energy (eV)	3-photon energy (cm^{-1})	$\Delta\nu(cm^{-1})$	ν''	Ω	Assignment
1	5556.0	6.708	53996	1119	1167	1.8	$9b_0^1, A_1$
2	5588.5	6.670	53682	805	874	1.56	$17b, A_1$
3	5631.5	6.618	53272	395	535	1.05	$6a_0^1, A_1$
4	5673.5	6.569	52877	0	0	0.79	0-0, A_1
5	5693.5	6.546	52692	−185	227	2.4	$10a_1^0, A_1$

ν'' : vibration frequency of ground state[17]

We will analyze the spectra of three-photon REMPI based on their symmetry, position, intensity and polarization behaviors.

First, we discuss the Rydberg character of the transitions, and the assignment of orbital angular momentum, with the Rydberg formula[12]

$$\nu_i^n = \epsilon_0 - \frac{R}{(n-\delta)^2}, \tag{1}$$

where $\epsilon_0 = 68819.8\text{cm}^{-1}$ is the first ionization potential[19], R is Rydberg constant, n is the principal quantum number and δ is quantum defect. The quantum defect value for this three-photon transitions is 0.3–0.4 for $n=3$. This supports the orbital angular momentum assignment of 3p Rydberg transitions.

The transition at 52877cm^{-1} is labeled as the 0–0 transition. This agrees with the results of Bolovinos *et al.*[18] They gave the position of the 0–0 band at 52882cm^{-1}. From the polarization spectra of Fig. 2, we measured the polarization ratio $\Omega = 0.79$ at the 0–0 band. According to the three-photon polarization ratios for point group C_{2v}, this value of $\Omega = 0.79$ is located in the range of symmetry species A_1, 0.6–1.8.[22] So we assign this vibrationless 0–0 transition to an excited state of A_1 symmetry.

The vibration at 52692cm^{-1} is a hot band. From Table 1, the measured polarization ratio is 2.4. Only for the $A_2 \leftarrow A_1$ transition of C_{2v}, the three-photon polarization ratio is 2.5. So the total symmetry of final state should be A_2. Because the symmetry of electronic state is A_1, the vibrational symmetry must be a_2, therefore the total symmetry is $a_2 \times A_1 = A_2$. The

vibrational modes of symmetry a_2 are $10a$, $16a$, $17a$. Judging by the vibrational frequencies, the vibrational mode of this hot band is $10a$.

Vibration at 53996cm^{-1} corresponds to the degenerate vibration mode 9 of benzene, which splits into nondegenerate vibrations, $9a$ and $9d$ on lowering the symmetry. It is $C-X$ in-plane bending vibrations[17] (X is the carbon atom o-methyl substituent). According to its polarization character and vibration frequency, its symmetry species is b_2. From Table 1, vibrations 53272 and 53682cm^{-1} have symmetry of a_1 and b_1 respectively according to their polarization ratios. They are labeled as modes $6a$ and $17b$ respectively. From Fig. 2, we can see that the circular-polarized spectrum of $6a$ is clearer than linear-polarized spectrum.

IV. CONCLUSION

For the first time, several new 3p Rydberg states of m-dimethylbenzene have been discovered with the polarized three-photon resonance MPI technique. Based on the polarization character, vibrational frequency and intensity, the vibronic transitions are analyzed to obtain tentative excited state symmetries. These results can help understand the structure of m-dimethylbenzene in this region.

REFERENCES

[1] P. M. Johnson, M. Berman and D. Zakheim, *J. Chem. Phys.*, **62** (1975), 2500.
[2] P. M. Johnson, *J. Chem. Phys.*, **64** (1976), 4143, 4638.
[3] D. H. Parker, J. O. Berg and M. A. El-Sayed, in: Advances in Laser Chemistry, ed. A. H Zewail, (Springer, Berlin, 1978), p. 319.
[4] G. Petty, C. Tai and F. W. Dalby, *Phys. Rev. Lett.*, **34** (1975), 1207.
[5] M. B. Robin and N. A. Kuebler, *J. Chem. Phys.*, **69** (1978), 806.
[6] D. H. Parker, in: Ultrasensitive Laser Spectroscopy, ed. D. S. Kliger Academic, (New York, 1983), Chap. 4.
[7] J. O. Berg, D. H. Parker and M. A. El-Sayed, *J. Chem. Phys.*, **68** (1978), 5661.
[8] J. H. Glownia, S. J. Riley, S. D. Colson and G. C. Nieman, *J. Chem. Phys.*, **72** (1980), 5998.
[9] M. N. R. Ashfold, *Mol. Phys.*, **58** (1986), 1.
[10] P. H. Taylor, W. G. Mallard and K. C. Smyth, *J. Chem. Phys.*, **84** (1986), 1053.
[11] T. J. Cornish and T. Baer, *J. Am. Chem. Soc.*, **110** (1980), 3099.
[12] W. M. McClain and R. A. Harris, in: Excited States, ed. E. C. Lim, (Academic, New York, 1977), Vol. 3, p. 1.
[13] R. G. Bray and R. M. Hochstrasser, *Mol. Phys.*, **31** (1976), 1199.
[14] K. Chen and E. S. Yeung, *J. Chem. Phys.*, **69** (1977), 43.
[15] G. C. Nieman, *J. Chem. Phys.*, **75** (1981), 584.
[16] D. L. Andrews and W. A. Ghoul, *J. Chem. Phys.*, **75** (1981), 530.
[17] G. Varsanyi, Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives, (Academic, New York, 1974).
[18] A. Bolovinos, J. Philis, E. Pantos, P. Tsekeris, and G. Andritsopoulos, *J. Mol. Spectrosc.*, **94** (1982), 55.
[19] A. Bolovinos, J. Philis, E. Pantos, P. Tsekeris, and G. Andritsopoulos, *J. Chem. Phys.*, **75** (1981), 4343.
[20] Gene O. Uneberg, Pamela A. Campo, and Philip Johnson, *J. Chem. Phys.*, **73** (1980), 1110.
[21] Robin M. B., Higher Excited States of Polyatomic Molecules, (Academic, New York, 1974) Vol. 1.
[22] Lin Meirong, Liu Yaoming, Zhang Baozheng, Pan Xiaoning and Chen Wenju, ACTA PHYSICA (overseas edition), **3** (1994), 255.