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Evidence for fast intramolecular vibrational relaxation within the  $1\ E\ 1u$  state**

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# Resonant multiphoton ionization photoelectron spectroscopic study of benzene. Evidence for fast intramolecular vibrational relaxation within the ${}^1E_{1u}$ state

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Resonant multiphoton ionization photoelectron measurements were carried out for benzene under collision-free conditions in such a way that the benzene molecule is ionized by four photons through various two-photon allowed vibronic levels of the  ${}^1B_{2u}$  excited state. As a result, single prominent, somewhat broad photoelectron bands were observed in the 0.14–0.36 eV region, arising from  $\Delta v = 0$  ionization transitions. The prominent peak is shifted with increasing photon energy by  $K = h\nu_i - C$ , where  $K$  is the photoelectron energy,  $h\nu_i$  the photon energy, and  $C$  a constant. This relationship strongly indicates that the third photon is resonant with a real intermediate excited state. Therefore, the overall ionization process is expressed by  $(2 + 1 + 1)$ . It is concluded that fast intramolecular vibrational relaxation occurs at the third-photon states within the  ${}^1E_{1u}$  ( $\pi\pi^*$ ) state and subsequent ionization takes place from vibrationally relaxed levels. The relaxation within the  ${}^1E_{1u}$  state is supported from the 0–0 energy which was evaluated here for the ionized states from the photoelectron data. It is also suggested that the lifetime of the vibrationally relaxed  ${}^1E_{1u}$  states is the order of  $10^{-11}$ – $10^{-12}$  s or longer.

## I. INTRODUCTION

Intramolecular vibrational relaxation in electronic excited states of molecules under collision-free conditions is of considerable current interest from the experimental and theoretical points of view, and much attention has been placed on phenomena concerning vibrational randomization of energy and phase in excited molecules in supersonic nozzle beams.<sup>1–4</sup>

The recent development of laser and supersonic nozzle beam techniques has made it possible to obtain valuable information about intramolecular vibrational randomization. Laser fluorescence spectroscopy is a powerful method for relaxation decay measurements. However, molecules which do not fluoresce cannot be studied by this method. Multiphoton ionization technique recently developed by Johnson *et al.*<sup>5,6</sup> is also powerful for studying electronically excited states including nonfluorescent states.

Very recently, resonantly enhanced multiphoton ionization photoelectron spectroscopy for molecules has been developed in this laboratory<sup>7–11</sup> and by other groups,<sup>12–19</sup> providing information about identification and characterization of resonant intermediate excited states and their ionic states. One of the most striking features of this method is that any electronically excited state that can be ionized by a laser may be studied.

The present work was originally initiated to clarify the mechanism of laser-induced ionic photofragmentation of benzene.<sup>20,21</sup> In our preliminary work,<sup>8</sup> it has been indicated that the parent benzene cation is initially formed by four-photon ionization through two-photon resonant  ${}^1B_{2u}$  vibronic levels. In the course of our laser photoelectron study, we have found that the third photon of such four-photon ionization of benzene should be resonant with its  ${}^1E_{1u}$  excited state. In this paper we report photoelectron spectra attributable to the  ${}^1E_{1u}$  vibronic states of benzene as well as evidences for intra-

molecular relaxation within the  ${}^1E_{1u}$  state for the first time.

Very recently, Murakami *et al.*<sup>22</sup> and Aron *et al.*<sup>23</sup> have reported assignments of two-photon allowed  ${}^1B_{2u}$  vibronic states of benzene in their multiphoton ionization ion-current spectroscopic studies. Their assignments of the  ${}^1B_{2u}$  vibronic levels of benzene are prerequisite to interpretation of our laser photoelectron spectra.

Since the up-pumping ionization transition from resonant intermediate states should in principle compete with intramolecular relaxation processes, it will be possible to study rapid picosecond vibrational relaxation processes with a conventional nanosecond pulsed laser under suitable laser power conditions. In the present work, we have obtained the first example that shows photoelectron spectra attributable to vibrationally relaxed states of an electronically excited state.

## II. EXPERIMENTAL

The photoelectron spectrometer used here is the same as previously used in this laboratory.<sup>7–11</sup> A gaseous sample of benzene was introduced into the ionization region through a 100  $\mu\phi$  nozzle. The stagnation pressure in the sample source was about 150 Torr.

Laser irradiation experiments were carried out with a Nd-YAG pumped dye laser (Quanta-Ray DCR-1A, PDL-1) and the laser light was focused into the ionization region with a 25 cm focal length lens. Prior to photoelectron measurements, MPI ion current measurements were carried out for benzene in the 471–513 nm region, in order to check the available MPI spectrum. Photoelectron measurements were then carried out at 12 laser wavelengths which correspond to two-photon absorption  ${}^1B_{2u}$  vibronic levels shown in Table I.

Photoelectron spectra were measured with a time-of-

TABLE I. Experimental and calculated kinetic energies of photoelectrons produced by four-photon ionization of benzene in the gas phase. The laser wavelengths were selected so as to excite benzene molecule initially to vibronic levels of the  ${}^1B_{2u}$  state by two photons.

${}^1B_{2u}$ Vibronic level <sup>a</sup>	$\lambda_l$ (nm)	Photoelectron kinetic energy (eV)		
		$h\nu_l$ (eV)	$K_{\text{expt}}$	$K_{\text{calc}}$ <sup>b</sup>
$18_0^1$	512.5	2.419	0.145	0.142
$14_0^1 16_2^2$	508.4	2.438	0.155	0.161
$14_0^1 16_1^1$	506.3	2.449	0.166	0.172
$14_0^1$	504.2	2.459	0.181	0.182
$18_0^1 1_0^1$	500.7	2.476	0.195	0.199
$14_0^1 1_1^1 16_1^1$	494.8	2.506	0.225	0.229
$14_0^1 1_0^1$	492.7	2.516	0.238	0.239
$14_0^1 10_0^2$	489.8	2.531	0.256	0.254
$18_0^1 1_2^2$	489.4	2.534	0.261	0.257
$14_0^1 1_2^2 16_1^1$	483.8	2.562	0.287	0.285
$14_0^1 1_0^2$	481.8	2.573	0.304	0.296
$14_0^1 1_0^3$	471.3	2.630	0.363	0.353

<sup>a</sup>Reference 24.

<sup>b</sup>Obtained from Eq. (5) with  $I_a = 9.247$  eV and  $E_{00} = 6.97$  eV. This  $E_{00}$  value was deduced by a least-squares fit of the  $K_{\text{expt}}$  values from Eq. (5).

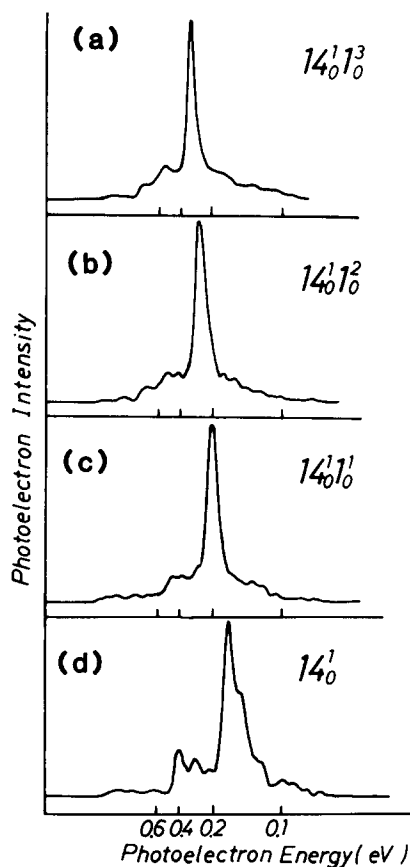


FIG. 1. Laser photoelectron spectra obtained at (a) 471.3 nm ( $14_0^1 1_0^3$ ), (b) 481.8 nm ( $14_0^1 1_0^2$ ), (c) 492.7 nm ( $14_0^1 1_0^1$ ) and (d) 504.2 nm ( $14_0^1$ ). The two-photon allowed  ${}^1B_{2u}$  vibronic levels are also shown.

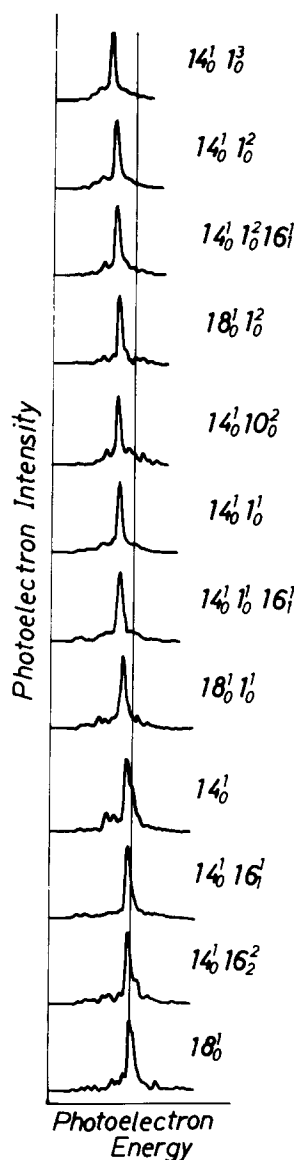


FIG. 2. A series of laser photoelectron spectra obtained by four-photon ionization via two-photon allowed  ${}^1B_{2u}$  vibronic levels, showing the photoelectron peak is shifted monotonically with the one-photon energy to the higher energy (left).

flight (TOF) electron energy analyzer which consists of a 10 cm long field-free drift tube and a channeltron at the end of this tube, a Biomation transient recorder (Model 6500, 2 ns/channel) being employed. Calibration for the photoelectron energy was carried out as in our previous work.<sup>9,10</sup> The overall energy resolutions for photoelectrons of 0.1 and 0.6 eV were about 10 and 50 meV, respectively.

### III. RESULTS

The MPI ion current spectrum obtained here for benzene in the 471–513 nm region is essentially the same as those already reported by Murakami *et al.*<sup>22</sup> and Aron *et al.*<sup>23</sup> The photoelectron spectra obtained here at four typical ion-current peaks are shown in Fig. 1: (a) 471.3 nm, (b) 481.8 nm, (c) 492.7 nm, and (d) 504.2 nm. All the photoelectron spectra obtained here are compared in Fig. 2, the peak intensities being normalized. The photoelectron kinetic energies ( $K_{\text{expt}}$ ) deduced from the prominent photoelectron peaks are summarized in Table I. As shown in Figs. 1 and 2, single

prominent peaks appear with almost the same bandwidths. The bandwidths, however, are considerably broader than those of single bands previously observed for (3+1) resonance MPI via Rydberg states of NO and NH<sub>3</sub>.<sup>11</sup>

#### IV. DISCUSSION

##### A. Photoelectron spectra

Under the present laser irradiation conditions, at least four photons are needed to produce the ground-state benzene cation. From the  $K_{\text{exp}}$  values in Table I, it is clearly indicated that under the present experimental conditions ionization takes place by four photons, i.e., the minimum number of photons. If one more photon is absorbed, the photoelectron kinetic energy should be larger by one-photon energy.

The two-photon resonant  $^1B_{2u}$  vibronic levels at which the photoelectron spectra were measured are interpreted in terms of the  $\nu_{14}(b_{2u})$  and  $\nu_{18}(e_{1u})$  vibrational modes.<sup>22,23</sup> These vibronic levels had been assigned originally by Wunsch *et al.*<sup>24</sup> by means of fluorescence spectroscopy. The energies and the characters of these vibronic levels are shown also in Table I.

As shown in Fig. 2, the photoelectron peak is shifted to the higher kinetic energy with the increasing photon energy. Plots of the experimental photoelectron energies against the laser photon energies are shown in Fig. 3, indicating a linear relationship with a slope of 1.0. The solid line in Fig. 3 indicates a least-squares fit for the  $K_{\text{exp}}$  values. The linear relationship shown in Fig. 3 therefore may be expressed by

$$K = h\nu_1 - C, \quad (1)$$

where  $K$  is the photoelectron energy for the prominent peaks and  $h\nu_1$  the one-photon energy, and  $C$  a constant independent of the laser wavelength used.

The prominent peaks in Figs. 1 and 2 are considered due to  $\Delta v = 0$  ionization transitions. Similar prominent bands due to  $\Delta v = 0$  ionization transitions have recently been demonstrated in (3+1) ionization of NO and NH<sub>3</sub>,<sup>11</sup> (1+1) ionization of toluene,<sup>12(b)</sup> and (1+1) ionization of

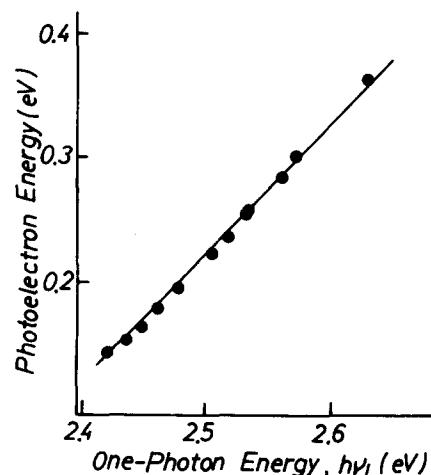


FIG. 3. Plots of the experimental photoelectron energies against the laser one-photon energies.

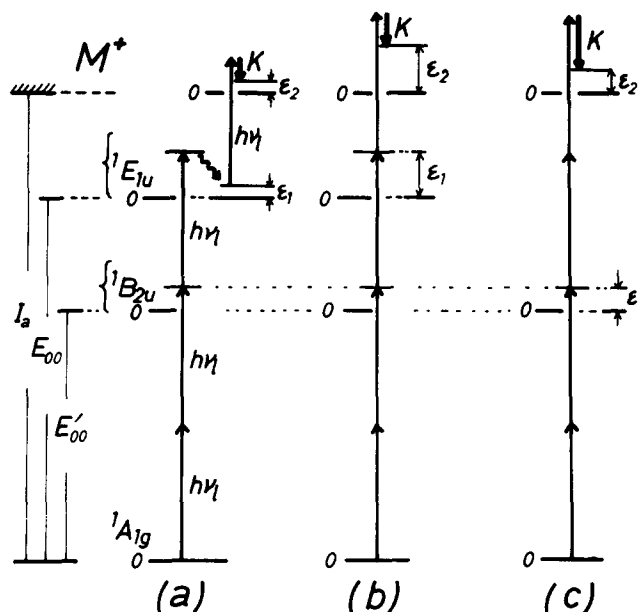


FIG. 4. Relevant energy level diagram for benzene and three kinds of ionization process. (a) The (2+1+1) ionization process including vibrational relaxation at the third-photon state. (b) The (2+1+1) ionization process. (c) The (2+2) ionization process.

chlorobenzene.<sup>19</sup> However, it should be mentioned that the photoelectron bands in Fig. 2 are considerably broader than those reported for the  $\Delta v = 0$  ionization transitions.<sup>11,12(b),19</sup> The broadening will be explained later in terms of vibrational relaxation at the third-photon states.

In order to evaluate the photoelectron energies, let us consider three processes of ionization as shown schematically in Fig. 4: (a) The three-photon state is resonant and fast intramolecular vibrational relaxation occurs; (b) the three-photon state is resonant, but no vibrational relaxation occurs; and (c) the three-photon state is nonresonant. In the first two cases (a) and (b) in which the third-photon state is resonant, the photoelectron energy may be expressed by

$$K = h\nu_1 + E_{00} - I_a + \epsilon_1 - \epsilon_2, \quad (2)$$

where  $I_a$  is the adiabatic ionization energy of benzene,  $E_{00}$  is the 0-0 energy of the electronically excited state associated with the three-photon levels, and  $\epsilon_1$  and  $\epsilon_2$  are the internal energies of the initial excited and the final ionic state of ionization, respectively. In the third case (c) in which the third-photon state is nonresonant, we have

$$K = 2h\nu_1 + E'_{00} - I_a + \epsilon_1 - \epsilon_2 \quad (3)$$

in which  $E'_{00}$  is the 0-0 energy of the two-photon resonant  $^1B_{2u}$  state.

From Eq. (1) it is seen that  $\epsilon_1 - \epsilon_2$  should be constant, independent of the photon energy used. Since the prominent photoelectron peaks are considered due to  $\Delta v = 0$  ionization transitions as mentioned before, we may estimate that

$$\epsilon_1 - \epsilon_2 = 0. \quad (4)$$

In other words, the internal energy is unchanged upon ionization. If the prominent peaks are due to  $\Delta v = \pm 1$  ionization transitions, it follows that  $\epsilon_2 - \epsilon_1 = \pm h\nu_{1b}$ .

Using relationship (4), from Eq. (2) we have

$$K = h\nu_1 + E_{00} - I_a \quad (5)$$

in the cases (a) and (b) in Fig. 3. From Eq. (3) we have

$$K = 2h\nu_1 + E'_{00} - I_a \quad (6)$$

in the case (c) in which the third-photon state is non-resonant. With  $I_a = 9.247$  eV,<sup>25</sup> and the  $K_{\text{exp}}$  values, we have obtained an average value of  $E_{00} = 6.97$  eV from Eq. (5). Then, putting this average  $E_{00}$  value into Eq. (5), we have evaluated  $K$  at each photon energy. The photoelectron energies ( $K_{\text{calc}}$ ) thus obtained are shown in Table I for comparison, indicating excellent agreements with the corresponding experimental values. It should be mentioned that the experimental linear relationship with the slope of 1.0 in Fig. 3 cannot be explained by Eq. (6). Therefore, it may be concluded that the  $(2+1+1)$  ionization leading to Eq. (5) is important in the present experiments.

The weak satellite bands in Fig. 1 may arise from  $\Delta v = \pm 1$  ionization transitions. Since the laser photon energy is fixed in each photoelectron measurement,  $\Delta v = \pm 1$  ionization transitions may produce photoelectrons whose kinetic energies spread broadly in the higher and the lower energy region around the prominent peak.

### B. Assignments of the third-photon states

As mentioned in the previous section, the linear relationship shown in Fig. 3 indicates that ionization takes place at the third-photon resonant intermediate states of benzene. The three-photon energy levels lie above the third  $\pi\pi^*$ ,  $^1E_{1u}$  state. The  $E_{00}$  value obtained here from the experimental photoelectron energies is 6.97 eV, in reasonable agreement with the 0-0 energy of the  $^1E_{1u}$  state (6.87 eV) estimated earlier by Wilkinson<sup>25</sup> from a broad absorption band.

Since the overall symmetry characters of the  $\nu_{14}(b_{2u})$  and  $\nu_{18}(e_{1u})$  levels of the  $^1B_{2u}$  state are given by  $b_{2u} \times B_{2u} = A_{1g}$  and  $e_{1u} \times B_{2u} = E_{2g}$ , it is seen that one-photon transitions from these vibronic levels to the  $^1E_{1u}$  state can be allowed: that is,

$$A_{1g} \times E_{1u} = E_{1u}(x, y)$$

and

$$E_{2g} \times E_{1u} = B_{1u} + B_{2u} + E_{1u}(x, y).$$

Therefore, we have concluded that the third-photon states are assigned to the  $^1E_{1u}$  vibronic states.

It has been well known that the gas-phase absorption spectrum corresponding to the  $^1E_{1u} \leftarrow X$  transition of benzene shows a very broad, structureless band with a maximum at about 56 000  $\text{cm}^{-1}$ .<sup>27-30</sup> Several single vibronic bands attributed to the  $a_{1g}$  mode have been observed in rare-gas solids by Katz *et al.*<sup>30</sup> Even in a

4-K matrix the observed vibronic bands show a significant line broadening ( $\Delta\nu \approx 300 \text{ cm}^{-1}$ ).<sup>30</sup> Considering the broader absorption profile of the gas-phase  $^1E_{1u}$  band, it may be readily accepted that the third-photon states correspond to the vibronic levels of the  $^1E_{1u}$  state with excess energies of 3000–7000  $\text{cm}^{-1}$ . According to the abovementioned symmetry consideration, the  $a_{1g}$  mode should be excited in the third-photon  $^1E_{1u}$  excited state. The excess energies of the third-photon states (3000–7000  $\text{cm}^{-1}$ ) correspond to three to seven quanta of the  $a_{1g}$  mode.

Furthermore, it should be pointed out that the prominent photoelectron peak observed in each case in Fig. 3 corresponds to the ground-state benzene cation ( $^2E_{1g}$ ) which is formed by removal of an electron from the  $\pi_g^*$  or  $\pi_g^*$  orbital of the  $^1E_{1u}$  excited-state benzene.<sup>28</sup>

### C. Fast vibrational relaxation within the $^1E_{1u}$ state

There are two possible channels for ionization taking place from the third-photon  $^1E_{1u}$  states; one is the up pumping from the third-photon states, and the other is from their vibrationally relaxed states. The vibrational relaxation in principle should occur in competition with the up pumping. If the up-pumping rate at the three-photon states is much faster than the vibrational relaxation rates, ionization takes place mainly at the nonrelaxed vibronic states.

The intramolecular decay rate of the  $^1E_{1u}$  state has been reported to be the order of  $10^{14} \text{ s}^{-1}$  in the 4-K matrix by Katz *et al.*<sup>30</sup> from their absorption linewidths (300  $\text{cm}^{-1}$ ). Assuming an ionization cross section of the order of  $10^{-17} \text{ cm}^2$ , we may estimate the up-pumping rate to be the order of  $10^{10}$ – $10^{11} \text{ s}^{-1}$  for our laser intensity of  $10^8$ – $10^9 \text{ W/cm}^2$ . This up-pumping rate is three to four orders of magnitude smaller than the abovementioned intramolecular decay rate.

From the results of Murakami *et al.*<sup>22</sup> and the fact that ions produced by the ionization of the  $^1E_{1u}$  state can be detected, it seems reasonable to consider that the electronic relaxation rate should be at most ten times the ionization up-pumping rate,  $10^{10}$ – $10^{11} \text{ s}^{-1}$  estimated above. Therefore, the electronic relaxation rate should be less than  $10^{11}$ – $10^{12} \text{ s}^{-1}$ , i.e., the electronic relaxation lifetime of the vibrationally relaxed  $^1E_{1u}$  state to be longer than  $10^{-11}$ – $10^{-12} \text{ s}$ .

It should also be mentioned that intramolecular relaxation below the  $14_0^1 1_0^3$  level of the  $^1B_{2u}$  state seems to be much slower than the up-pumping rate. Aron *et al.*<sup>23</sup> have shown remarkable broadening of MPI bands for the two-photon  $14_0^1 1_0^3$  states at  $n \geq 3$ . On the other hand, Murakami *et al.*<sup>22</sup> have suggested that in the four-photon ionization no significant depopulation of the  $^1B_{2u}$  state occurs below  $n = 3$ . According to the recent nanosecond and picosecond fluorescence decay measurements,<sup>31,32</sup> values of  $10^{10}$ – $10^{11} \text{ s}^{-1}$  are reported for the nonradiative rate for such highly vibronic levels of the  $^1B_{2u}$  state.

In Sec. IIIA, we have pointed out that the photoelectron spectrum shows a single prominent band with a bandwidth wider than those in the  $(3+1)$  MPI of  $\text{NH}_3$  and  $\text{NO}$ .<sup>11</sup> Ionization from different vibronic levels by

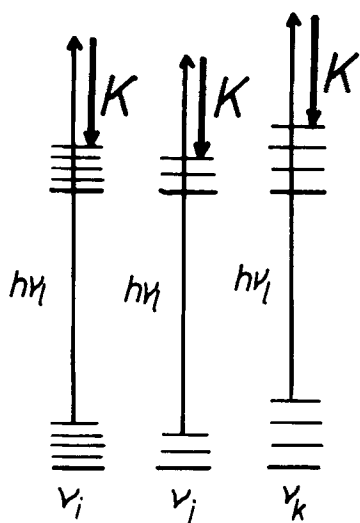


FIG. 5. Schematic drawing for vibrational energy levels of different vibrational modes and  $\Delta v = 0$  ionization transitions.

$\Delta v = 0$  transitions is schematically shown in Fig. 5. As can be seen from Fig. 5, the photoelectron kinetic energies would be identical, if  $\Delta v = 0$  ionization transitions take place without any change in the internal energies upon ionization. The fact that only the single, broad prominent bands appear in the photoelectron spectra indicates that there may be only slight changes in molecular geometry as well as in the fundamental frequencies between the  ${}^1E_{1u}$  and the ionic state. The observed broadening of the prominent photoelectron bands therefore may be explained in terms of an overlap of various  $\Delta v = 0$  transition bands starting from the vibrationally relaxed levels of the  ${}^1E_{1u}$  states.

With all these results in mind, we are led to the following conclusions. Excitation of benzene to the  ${}^1E_{1u}$  vibronic levels with internal energies of 3000–7000  $\text{cm}^{-1}$  gives rise to initial population of the optical active modes, and then rapid intramolecular vibrational energy distribution occurs within the same electronic state. This is one of the most important conclusions in the present work. If internal conversion occurs to the lower electronic states ( ${}^1B_{1u}$ ,  ${}^1B_{2u}$ , and  ${}^1A_{1g}$ ), the  $E_{00}$  value obtainable from experiment would differ from the 0–0 energy of the  ${}^1E_{1u}$  state.

## V. CONCLUSIONS

The following conclusions have been deduced from the present photoelectron spectroscopic study of the resonant multiphoton ionization of benzene via two-photon allowed vibronic levels of the  ${}^1B_{2u}$  state. (1) The single prominent photoelectron peaks observed here may be due to  $\Delta v = 0$  ionization transitions by a total of four photons i.e., the minimum number of photons to ionize the molecule. The number of photons absorbed in the process of multiphoton ionization may be directly determined from photoelectron kinetic energies. (2) A linear relationship with a slope of one has been found between the photoelectron energies and the laser one-photon energies. From this relationship, it has been concluded

that the third photon is resonant with a higher electronically excited state. (3) From the ionization and relaxation rate consideration, it has also been concluded that fast intramolecular vibrational relaxation takes place at the third-photon states. Therefore, the single broad photoelectron bands are considered due to an overlap of the  $\Delta v = 0$  ionization transitions from vibrationally relaxed levels. (4) From the 0–0 energy evaluated here from the relationship given by Eq. (5), we have indicated that the vibrational relaxation occurs within the  ${}^1E_{1u}(\pi\pi^*)$  excited state.

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