*J. Phys. Chem. A* **2005,** *109,* 9481−9487 **9481**

# Site-Specific H/D Exchange of *p*-Methoxyphenol Studied by Resonant Two-Photon Ionization and Mass-Analyzed Threshold Ionization Spectroscopy

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*Received: May 30, 2005; In Final Form: August 30, 2005*

The origin of the $S_1 \leftarrow S_0$ transition ($E_1$) and the adiabatic ionization energy (IE) of *cis*-*p*-methoxyphenol-$d_1$-OD are determined to be 33 660 and 62 302 cm$^{-1}$, whereas those of *cis*-*p*-methoxyphenol-$d_1$-OCH$_2$D are 33 669 and 62 323 cm$^{-1}$, respectively. Similarly, the $E_1$ and IE of *trans*-*p*-methoxyphenol-$d_1$-OD are determined to be 33 563 and 62 191 cm$^{-1}$ and those of *trans*-*p*-methoxyphenol-$d_1$-OCH$_2$D are 33 575 and 62 216 cm$^{-1}$, respectively. Comparing these data with those of *p*-methoxyphenol suggests that the H/D exchange on the OH substituent gives rise to a red shift in both the $E_1$ and IE, whereas that on the OCH$_3$ group yields a blue shift. The mass-analyzed threshold ionization spectra of the selected isomers can be used as the fingerprints for molecular identification. Analysis of these cation spectra shows that the substituent-sensitive in-plane C−OH and C−OCH$_3$ bending (mode 9b) and breathing (mode 1) vibrations are active for all of these isomeric cations.

## 1. Introduction

Isotope labeling is invaluable for the identification of spectral features resulting from some particular molecular motions.[1−3] It is known that heavier isotopomers have lower zero-point energy levels (ZPLs) than lighter ones. If the energy gap in the upper electronic state is different from that in the lower one, the electronic transition energies of the two isotopomers will be different. It has been reported that the adiabatic ionization energy (IE) of $C_6D_6$ is greater than that of $C_6H_6$ by 27 cm$^{-1}$,[4] whereas the IE of $C_6H_5OD$ is less than that of $C_6H_5OH$ by 15 cm$^{-1}$.[5] Since a hydrogen/deuterium (H/D) exchange only takes place in a particular part of a molecule, it is likely to relate to the active site of a chemical reaction. In addition, an H/D exchange can also be used to prove the site specification of an electronic transition.[6] However, recording spectra of a sample containing various isotopically substituted species without mass selection may suffer from band congestion and lead to misinterpretation of the data. Supersonic jet cooled resonance-enhanced multiphoton ionization (REMPI) in conjunction with time-of-flight mass spectrometry (TOFMS) has proved to be a powerful means to probe the photophysical and photochemical properties of polyatomic molecules and clusters.[2,3,6]

Methoxyphenols have OH and OCH$_3$ groups that may act as active sites for chemical reactions. Mikami and Wategaonkar and their co-corkers[7,8] have applied various spectroscopic techniques to study molecular properties of *p*-methoxyphenol and have proved the coexistence of the cis and trans conformers. To the best of our knowledge, detailed spectroscopic data of deuterium-substituted isotopomers of *p*-methoxyphenol are still not available in the literature. Since the origins of electronic transition ($E_1$ values) and the IE values of isotopomers may differ by only a few to a few hundred wavenumbers, high-resolution spectroscopic methods are needed for investigating the molecular properties of the selected deuterium-substituted species in the electronically excited $S_1$ and cationic ground $D_0$ states.[9] Both zero kinetic energy (ZEKE) photoelectron spectroscopy and mass-analyzed threshold ionization (MATI) spectroscopy with a resonant excitation scheme can give precise IE values and cation spectra of the selected isopotomers. Since the latter method detects ZEKE ions and provides mass information, it is more suitable for studies of isotopomers,[10] radicals,[11] and clusters.[12]

In this paper, we report one-color resonant two-photon ionization (1C-R2PI), two-color resonant two-photon ionization (2C-R2PI), and MATI spectra of selected isomers of deuterium-substituted *p*-methoxyphenol (*p*-methoxyphenol-$d_1$). It was found that H/D exchange only occurs in the OH and OCH$_3$ parts for both the cis and trans conformers. Comparison of the present experimental data of *p*-methoxyphenol-$d_1$ with those of *p*-methoxyphenol[7,8,13] allows us to learn the isotope effect on electronic transitions, ionization, and molecular vibrations. We have also performed ab initio calculations to provide a possible interpretation for our experimental findings.

## 2. Experimental Section

The experimental data presented in this paper were obtained by utilizing a time-of-flight (TOF) mass spectrometer equipped with two tunable UV lasers, as described in our previous publication.[14] The deuterium-substituted sample was prepared by mixing solid *p*-methoxyphenol (ACROS, 99% purity) and $D_2O$ (Andover, 99.96% purity) with a mole ratio of 1:2. The mixture was gently heated to about 60 °C in a high-temperature vacuum dryer for 1 1/2 h. This procedure was repeated four times. The deuterium-substituted solid *p*-methoxyphenol sample was heated to about 80 °C to have sufficient vapor pressure, seeded into 2 bar of helium, and expanded into the vacuum through a pulsed valve with a 0.15 mm diameter orifice. The

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10.1021/jp052850c CCC: $30.25

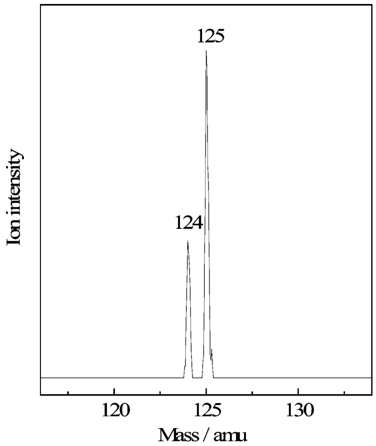

**Figure 1.** TOF mass spectrum of *p*-methoxyphenol mixture at excitation laser wavelength of 296.98 nm.

molecular beam was collimated by a skimmer located 15 mm downstream from the nozzle orifice. A delay/pulse generator (Stanford Research Systems, DG535) was used to control the two independent tunable UV lasers to initiate the two-color resonant two-photon excitation/ionization processes. A Fizeau-type wavemeter (New Focus 7711) was used to calibrate the wavelengths of both lasers. The two counterpropagating laser beams were then focused and intersected perpendicularly with the skimmed molecular beam at 50 mm downstream from the nozzle orifice.

In the MATI experiments, a pulsed electric field of −2.0 V/cm was switched on about 700 ns after the occurrence of the laser pulses to reject the prompt ions. After a time delay of about 11.50 $\mu$s, a second pulsed electric field of +130 V/cm was applied to field ionize the Rydberg neutrals. These threshold ions were then accelerated and passed a 1.6 m field-free region before being detected by a microchannel plate particle detector. The ion signal from the detector was then collected and analyzed by a multichannel scaler/averager (Stanford Research Systems, SR430), interfaced to a personal computer. Each mass spectrum was accumulated at 2 $\mathrm{cm}^{-1}$ spacing for 300 laser shots.

## 3. Results

**3.1. TOF Mass Spectrum.** To record the R2PI and MATI spectra of the selected species in a mixture, a mass-gating technique was used.[15,16] For a better mass resolution, the channel width of our multichannel scaler was set at 5 ns. Figure 1 shows the TOF mass spectrum of the sample mixture at an excitation laser wavelength of 296.98 nm. The peaks corresponding to the ions of *p*-methoxyphenol (mass 124) and *p*-methoxyphenol-$d_1$ (mass 125) are clearly seen. Analysis of these peaks gives an estimated mass resolution $m/\Delta m$ of 700. This good resolvability warrants the success in recording the 2C-R2PI and MATI spectra of these isotopic species.

**3.2. Possible Isomers of *p*-Methoxyphenol-$d_1$.** Previous studies[7,8,13] have shown that the cis and trans conformers of *p*-methoxyphenol coexist. Under the experimental conditions involving supersonic expansion, the molecular conformation is preserved. In addition, the $E_1$'s of the trans and cis conformers of *p*-methoxyphenol appear at 33 572 and 33 667 $\mathrm{cm}^{-1}$, respectively. Concerning the possible location of the H/D exchange at room temperature, one expects that the deuterium substitution likely takes place at the OH and $OCH_3$ groups.

To search for possible isomers of *p*-methoxyphenol-$d_1$, we have performed ab initio and density functional theory (DFT) calculations. The optimized structures were confirmed by observing no imaginary frequency for vibrational modes. The calculated energies at different electronic states are used to deduce the electronic transition and ionization energies. Previous studies[17,18] show that the DFT methods give a better prediction for these transition energies than the ab initio approaches. However, both methods can predict a correct trend for the relative energies of these molecules. Due to the limitation of the length of this paper, only some results are given below to illustrate this point. To specify the position isomers resulting from the H/D exchange, we use *p*-methoxyphenol-$d_1$-OD and *p*-methoxyphenol-$d_1$-$OCH_2D$ to stand for these molecules. On the basis of the hybrid Becke three-parameter with PW91 correlation functional (B3PW91) calculation with the 6-311++G** basis set, the ZPLs of *cis*-*p*-methoxyphenol-$d_1$-OD and *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$ in the $S_0$ state are −421.810 145 and −421.810 098 hartrees and those of the corresponding trans species are −421.810 097 and −421.810 046 hartrees, respectively. This shows that in the $S_0$ state *cis*-*p*-methoxyphenol-$d_1$-OD is the most stable species, whereas *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$, *trans*-*p*-methoxyphenol-$d_1$-OD, and *trans*-*p*-methoxyphenol-$d_1$-$OCH_2D$ lie in higher energy levels of 10, 11, and 22 $\mathrm{cm}^{-1}$, respectively.

In contrast, restricted Hartree−Fock (RHF)/6-311++G** calculations give the corresponding electronic energies of −419.406 105, −419.406 035, −419.405 970, and −419.405 909 hartrees for these four isomers. This shows that *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$, *trans*-*p*-methoxyphenol-$d_1$-OD, and *trans*-*p*-methoxyphenol-$d_1$-$OCH_2D$ lie at higher energy levels than *cis*-*p*-methoxyphenol-$d_1$-OD by 15, 30, and 43 $\mathrm{cm}^{-1}$, respectively. Therefore, both DFT and ab initio methods prove that *cis*-*p*-methoxyphenol-$d_1$-OD is the most stable species and the other three isomers lie at higher energy levels by a few tens of wavenumbers. Since the difference in the energy levels of these species is so small, it is expected that they coexist in the sample.

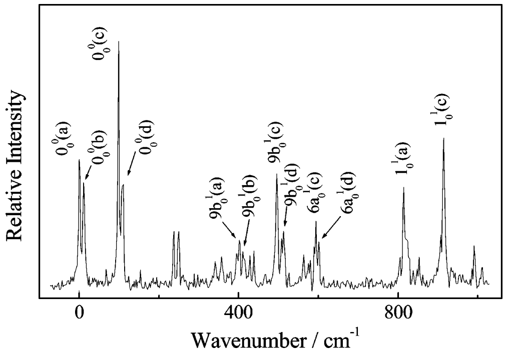

**Figure 2.** 1C-R2PI spectrum of *p*-methoxyphenol-$d_1$: a = *trans*-*p*-methoxyphenol-$d_1$-OD; b = *trans*-*p*-methoxyphenol-$d_1$-$OCH_2D$; c = *cis*-*p*-methoxyphenol-$d_1$-OD; d = *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$.

**3.3. R2PI Spectrum of *p*-Methoxyphenol-$d_1$.** Figure 2 shows the 1C-R2PI spectrum of *p*-methoxyphenol-$d_1$ in the energy range near the $S_1 \leftarrow S_0$ electronic transitions. The distinct bands at 33 563, 33 575, 33 660, and 33 669 $\mathrm{cm}^{-1}$ are assigned to the transition origins of *trans*-*p*-methoxyphenol-$d_1$-OD, *trans*-*p*-methoxyphenol-$d_1$-$OCH_2D$, *cis*-*p*-methoxyphenol-$d_1$-OD, and *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$, respectively. Clearly, the $E_1$'s of the trans conformers of the two *p*-methoxyphenol-$d_1$ compounds are lower than those of the corresponding cis conformers by 94−97 $\mathrm{cm}^{-1}$. Similar observations have been reported for hydroquinone (by 35 $\mathrm{cm}^{-1}$),[8,19] *p*-dimethoxybenzene (by 221 $\mathrm{cm}^{-1}$),[20−22] and *p*-methoxyphenol (by 95 $\mathrm{cm}^{-1}$).[7,8,13] The intensity of a vibronic band is related to the molecular population in the ground state and the cross section of the vibronic transition. If the cross section of the vibronic transition is the same for these deuterium-substituted isomers, the observed band intensity can reflect the relative population of these isomeric species. The intensities of the observed origin bands in Figure 2 may be satisfactorily interpreted by the above argument.

It is known that $E_1$ may be estimated by various computational methods. In an ab initio approach, $E_1$ can be deduced from the energy difference of the ZPLs in the $S_1$ and $S_0$ states obtained by the configuration interaction singles (CIS) and RHF methods, respectively. With the 6-31G** basis set, this method predicts that the $E_1$'s of *trans*-*p*-methoxyphenol-$d_1$-OD, *trans*-*p*-methoxyphenol-$d_1$-$OCH_2D$, *cis*-*p*-methoxyphenol-$d_1$-OD, and *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$ are 44 290, 45 093, 45 175, and 45 180 $cm^{-1}$, respectively. These results correspond to an overestimation of about 34%. However, the ab initio approach predicts the same trend of the $E_1$'s of these isomeric species as those measured by the 1C-R2PI experiments stated above. When the 6-311++G** basis set is used, the corresponding values are 42 837, 42 807, 42 455, and 42 427 $cm^{-1}$, respectively, equivalent to a deviation of nearly 27%. Evidently, the $E_1$'s of the cis conformers are higher than those of the trans ones, as observed in the 1C-R2PI spectrum. These calculations also indicate that the $E_1$'s of the $OCH_2D$ isomers are less than those of the OD isomers. The discrepancy between the calculated and experimental results may be regarded as the limitation of the CIS calculations for estimating the electronic transition energy of deuterium-substituted *p*-methoxyphenols.

It is known that time-dependent (TD) DFT calculations can be used to compute the electronic excitation energy to a reasonably good accuracy.[23−26] The TD-B3PW91/6-311++G** calculations predicted that the $E_1$'s of the cis and trans conformers of *p*-methoxyphenol are predicted to be 34 755 and 34 519 $cm^{-1}$, which are higher than the measured values by about 3%. The TD-DFT methods in the current version of the Gaussian program package[27] do not take into consideration of zero-point correction for predicting the $E_1$'s. Thus, it is not yet possible to estimate the differences in the electronic transition energy among the deuterium-substituted species by using the TD-DFT methods.

The frequencies of the observed 1C-R2PI bands resulting from the vibronic transitions of these four isomers of *p*-methoxyphenol-$d_1$ are listed in Table 1, together with the calculated values. When a scaling factor of 0.9 is applied, the predicted vibrational frequencies from the CIS/6-311++G** calculations are reasonably close to the measured values. Comparing the experimental and calculated values of each mode of these four isomers as well as those of the undeuterated *p*-methoxyphenol[13] leads us to have confidence in the spectral assignment. The results show that the major spectral features result from the substituent-sensitive and in-plane ring vibrations. The $O-CH_3$ bending vibration has a frequency of 238 $cm^{-1}$, whereas mode 9b involving C−OH and $C-OCH_3$ bending vibrations appears at about 398 $cm^{-1}$. In addition, the bands corresponding to the in-plane ring deformation modes 6a and 1 are observed at 492 and 815 $cm^{-1}$, respectively.

**3.4. MATI Spectra of *p*-Methoxyphenol-$d_1$.** We have applied both the 2C-R2PI and MATI experiments to measure the IEs of the selected deuterium-substituted isomers of *p*-methoxyphenol-$d_1$. Analysis of the rising steps of the 2C-R2PI spectra (not shown) gives IEs of 62 185, 62 209, 62 302, and 62 309 $cm^{-1}$ with an uncertainty of about 20 $cm^{-1}$ for *trans*-*p*-methoxyphenol-$d_1$-OD, *trans*-*p*-methoxyphenol-$d_1$-$OCH_2D$, *cis*-*p*-methoxyphenol-$d_1$-OD, and *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$, respectively. In contrast to the 2C-R2PI method, the MATI technique gives rise to a sharp peak at the ionization threshold and thus yields a more definitive adiabatic IE.[6]

**TABLE 1: Observed Bands in the 1C-R2PI Spectrum of *p*-Methoxyphenol-$d_1$ and Assignments**

| energy ($cm^{-1}$) | rel int | shift ($cm^{-1}$) | calcd[a] ($cm^{-1}$) | assignment[b] |
|---|---|---|---|---|
| | | | trans, OD | |
| 33 563 | 100 | 0 | | $0_0^0$ |
| 33 801 | 45 | 238 | 218 | $\beta(O-CH_3)$ |
| 33 965 | 38 | 402 | 409 | $9b_0^1$, $\beta(C-OH)/\beta(C-OCH_3)$ |
| 34 378 | 79 | 815 | 795 | $1_0^1$, breathing |
| | | | trans, $OCH_2D$ | |
| 33 575 | 100 | 0 | | ${0_0}^0$ |
| 33 813 | 55 | 238 | 212 | $\beta(O-CH_3)$ |
| 33 974 | 36 | 399 | 373 | $9b_0^1$, $\beta(C-OH)/\beta(C-OCH_3)$ |
| | | | cis, OD | |
| 33 660 | 100 | 0 | | $0_0^0$ |
| 33 902 | 12 | 242 | 218 | $\beta(O-CH_3)$ |
| 34 057 | 47 | 397 | 404 | $6a_0^1$, $\beta(CCC)$ |
| 34 154 | 28 | 494 | 504 | $9b_0^1$, $\beta(C-OH)/\beta(C-OCH_3)$ |
| 34 474 | 61 | 815 | 795 | $1_0^1$, breathing |
| | | | cis, $OCH_2D$ | |
| 33 669 | 100 | 0 | | ${0_0}^0$ |
| 33 918 | 32 | 249 | 212 | $\beta(O-CH_3)$ |
| 34 068 | 49 | 399 | 415 | $6a_0^1$, $\beta(CCC)$ |
| 34 161 | 46 | 492 | 500 | $9b_0^1$, $\beta(C-OH)/\beta(C-OCH_3)$ |

[a] At CIS/6-311++G** level of calculations, scaled by 0.9. [b] β, in-plane bending.

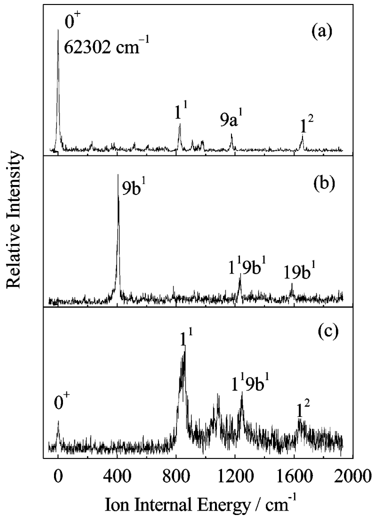

**Figure 3.** MATI spectra of *cis*-*p*-methoxyphenol-$d_1$-OD, recorded by ionizing via (a) $0^0$, (b) $9b^1$, and (c) $1^1$ levels in the $S_1$ state.

Figure 3 shows the MATI spectra of *cis*-*p*-methoxyphenol-$d_1$-OD recorded by ionizing via the vibrationless $0^0$ (33 660 $cm^{-1}$) and vibrational $9b^1$ (34 154 $cm^{-1}$) and $1^1$ (34 474 $cm^{-1}$) levels in the $S_1$ state. Analysis on the $0^+$ bands with consideration of the uncertainty in the laser photon energy, the spectral width, and the Stark effect yields the adiabatic IE of *cis*-*p*-methoxyphenol-$d_1$-OD to be 62 302 ± 5 $cm^{-1}$ (7.7245 ± 0.0006 eV). The frequencies of the MATI bands resulting from the cation vibrations are listed in Table 2, along with the calculated values. The frequencies of vibrational modes 9b, 1, and 9a of the *cis*-*p*-methoxyphenol-$d_1$-OD cation are measured to be 406, 828, and 1175 $cm^{-1}$, respectively. Figure 4 displays the MATI spectra of *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$ recorded by ionizing via the $S_1$ $0^0$ (33 669 $cm^{-1}$) and $S_1$ $9b^1$ (34 161 $cm^{-1}$) levels. All these MATI spectra seem to be dominated by one single transition, which indicates good Franck−Condon correspon-

**TABLE 2: Assignment of the Observed Bands (cm$^{-1}$) in the MATI Spectra of *cis-p*-Methoxyphenol-$d_1$-OD**[a]

| intermediate level in $S_1$ state | | | calcd | | assignment and approx description[b] |
|---|---|---|---|---|---|
| $0^0$ | $9b^1$ | $1^1$ | UHF | UB3 | |
| 230 | | | 223 | 219 | $\beta$(O−CH$_3$) |
| 379 | | | 375 | 376 | $15^1$, $\beta$(C−OH)/$\beta$(C−OCH$_3$) |
| | 406 | | 417 | 418 | $9b^1$, $\beta$(C−OH)/$\beta$(C−OCH$_3$) |
| 519 | | | 523 | 524 | $6a^1$, $\beta$(CCC) |
| | 782 | | 816 | 781 | $10a^1$, $\gamma$(CH) |
| 828 | | 838 | 823 | 839 | $1^1$, breathing |
| 910 | | | 934 | 920 | $\beta$(OD) |
| 980 | | | 986 | 987 | $18a^1$, $\beta$(CH) |
| | | 1086 | | | $1^1$, $\beta$(O−CH$_3$) |
| 1175 | | | 1218 | 1220 | $9a^1$, $\beta$(CH) |
| | 1237 | 1244 | | | $1^1 9b^1$ |
| | 1586 | | 1564 | 1540 | $19b^1$, $\nu$(CC) |
| 1654 | | 1655 | | | $1^2$ |

[a] The experimental values are shifts from 62 302 cm$^{-1}$, whereas the calculated ones are obtained from the UHF (scaled by 0.95) and UB3PW91 (without scaling) calculations using the 6-311++G** basis set. [b] $\nu$, stretching, $\beta$, in-plane bending, $\gamma$, out-of-plane bending.

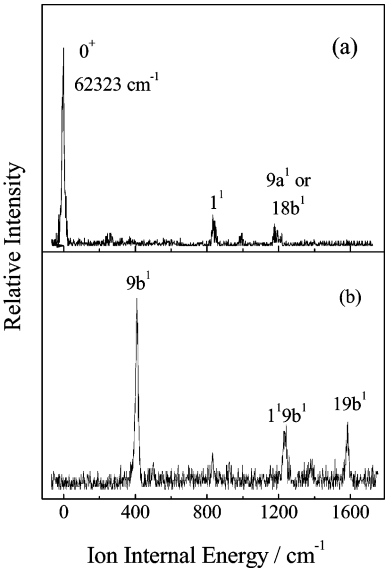

**Figure 4.** MATI spectra of *cis-p*-methoxyphenol-$d_1$-OCH$_2$D, recorded by ionizing via (a) $0^0$ and (b) $9b^1$ levels in the $S_1$ state.

dence between the $S_1$ and $D_0$ states. This result further demonstrates the similarity in molecular geometry between the two electronic states. The active vibrations of the cation observed are listed in Table 3. The adiabatic IE of *cis-p*-methoxyphenol-$d_1$-OCH$_2$D is measured to be 62 323 ± 5 cm$^{-1}$ (7.7271 ± 0.0006 eV).

It is noted that both modes 9a and 18b mainly involve in-plane ring CH bending vibrations.[28] Moreover, the frequency of mode 9a is slightly greater than that of mode 18b. It was reported that mode 9a was not active, whereas mode 18b was observed with the frequency of 1178 cm$^{-1}$ for the *cis-p*-methoxyphenol cation.[13] The frequencies of mode 18b for the *cis-p*-methoxyphenol, *cis-p*-methoxyphenol-$d_1$-OD, and *cis-p*-methoxyphenol-$d_1$-OCH$_2$D cations are predicted to be 1189, 1156, and 1189 cm$^{-1}$, whereas those of mode 9a are 1219, 1218, and 1220 cm$^{-1}$, respectively. This calculated result suggests that the band at 1175 cm$^{-1}$ in Figure 3 for *cis-p*-methoxyphenol-$d_1$-OD may be assigned to vibration 9a and the band at 1175 cm$^{-1}$ in Figure 4 for *cis-p*-methoxyphenol-$d_1$-OCH$_2$D may result from either vibration 18b or 9a. A similar consideration is taken in the spectral assignment for the deuterium-substituted *trans-p*-methoxyphenol-$d_1$ isomers.

The MATI spectra of *trans-p*-methoxyphenol-$d_1$-OD were recorded by ionizing through the $0^0$ (33 563 cm$^{-1}$), $9b^1$ (33 965 cm$^{-1}$), and $1^1$ (34 378 cm$^{-1}$) levels in the $S_1$ state as shown in Figure 5. The adiabatic IE of *trans-p*-methoxyphenol-$d_1$-OD is determined to be 62 191 ± 5 cm$^{-1}$ (7.7107 ± 0.0006 eV). The frequencies of the MATI bands resulting from the cation vibrations of *trans-p*-methoxyphenol-$d_1$-OD are listed in Table 4. The frequencies of modes $9b^1$, $1^1$, and $9a^1$ of this cation are measured to be 420, 830, and 1175 cm$^{-1}$, respectively. Figure 6 shows the MATI spectra of *trans-p*-methoxyphenol-$d_1$-OCH$_2$D recorded by ionizing via the $S_1$ $0^0$ (33 575 cm$^{-1}$) and $S_1$ $9b^1$ (33 974 cm$^{-1}$) levels. These experimental data give the adiabatic IE of this molecule as 62 216 ± 5 cm$^{-1}$ (7.7138 ± 0.0006 eV). The observed MATI bands at 421, 519, 828, 1175, and 1581 cm$^{-1}$ result from the $9b^1$, $6a^1$, $1^1$, $18b^1$ (or $9a^1$), and $19b^1$ vibrations of the *trans-p*-methoxyphenol-$d_1$-OCH$_2$D cation, as listed in Table 5.

It is noted that the bandwidth in Figures 3c and 5c is much broader than that in all other MATI spectra shown in the present paper. A similar finding has been observed in the MATI experiments of *p*-methylphenol[29] and *p*-*n*-propylphenol.[30] Since no fragment ions appeared in the mass spectrum, the observed broad band is not caused by dissociation of molecular ions. Wategaonkar and Doraiswamy[31] have studied the intramo-

**TABLE 3: Assignment of Observed Bands (cm$^{-1}$) in the MATI Spectra of *cis-p*-Methoxyphenol-$d_1$-OCH$_2$D**[a]

| intermediate level in $S_1$ state | | calcd | | assignment and approx description[b] |
|---|---|---|---|---|
| $0^0$ | $9b^1$ | UHF | UB3 | |
| 367 | | 385 | 387 | $15^1$, $\beta$(C−OH)/$\beta$(C−OCH$_3$) |
| | 409 | 428 | 428 | $9b^1$, $\beta$(C−OH)/$\beta$(C−OCH$_3$) |
| 833 | 832 | 819 | 841 | $1^1$, breathing |
| 1177 | | 1189 | 1131 | $18b^1$, $\beta$(CH) |
| 1177 | | 1220 | 1197 | $9a^1$, $\beta$(CH) |
| | 1233 | | | $1^1 9b^1$ |
| | 1586 | 1574 | 1547 | $19b^1$, $\nu$(CC) |

[a] The experimental values are shifts from 62 323 cm$^{-1}$, whereas the calculated ones are obtained from the UHF/6-311++G** (scaled by 0.95) and UB3PW91 (without scaling) calculations using the 6-311++G** basis set. [b] $\nu$, stretching, $\beta$, in-plane bending, $\gamma$, out-of-plane bending.

**TABLE 4: Assignment of Observed Bands ($cm^{-1}$) in the MATI Spectra of *trans-p*-Methoxyphenol-$d_1$-OD[a]**

| intermediate level in the $S_1$ state | | | calcd | | assignment and approx description[b] |
|---|---|---|---|---|---|
| $0^0$ | $9b^1$ | $1^1$ | UHF | UB3 | |
| 370 | | | 369 | 371 | $15^1$, $\beta(O-CH_3)/\beta(C-OH)$ |
| 424 | 420 | | 426 | 425 | $9b^1$, $\beta(C-OH)/\beta(C-OCH_3)$ |
| 520 | | | 519 | 522 | $6a^1$, $\beta(CCC)/\beta(O-CH_3)$ |
| 734 | | | 735 | 749 | $12^1$, $\beta(CCC)$ |
| 826 | 829 | 830 | 825 | 838 | $1^1$, breathing |
| 914 | | | 934 | 923 | $\beta(OD)$ |
| 984 | | | 987 | 988 | $18a^1$, $\beta(CH)$ |
| 1175 | | | 1214 | 1190 | $9a^1$, $\beta(CH)$ |
| 1244 | 1245 | 1254 | | | $1^19b^1$ |
| | 1591 | | 1570 | 1544 | $19b^1$, $\nu(CC)$ |
| 1651 | | 1684 | | | $1^2$ |

[a] The experimental values are shifts from 62 191 $cm^{-1}$, whereas the calculated ones are obtained from the UHF (scaled by 0.95) and UB3PW91 (without scaling) calculations using the 6-311++G** basis set. [d] $\nu$, stretching, $\beta$, in-plane bending.

**TABLE 5: Assignment of Observed Bands ($cm^{-1}$) in the MATI Spectra of *trans-p*-Methoxyphenol-$d_1$-$OCH_2D$[a]**

| intermediate level in the $S_1$ state | | calcd | | assignment and approx description[b] |
|---|---|---|---|---|
| $0^0$ | $9b^1$ | UHF | UB3 | |
| 385 | | 383 | 386 | $15^1$, $\beta(C\text{-}OH)/\beta(C-OCH_2D)$ |
| 421 | 421 | 428 | 427 | $9b^1$, $\beta(C-OH)/\beta(C-OCH_2D)$ |
| 519 | | 516 | 520 | $6a^1$, $\beta(CCC)/\beta(O-CH_2D)$ |
| 828 | 831 | 820 | 841 | $1^1$, breathing |
| 973 | 954 | 981 | 987 | $18a^1$, $\beta(CH)$ |
| 1175 | | 1188 | 1132 | $18b^1$, $\beta(CH)$ |
| 1175 | | 1219 | 1193 | $9a^1$, $\beta(CH)$ |
| | 1251 | | | $1^19b^1$ |
| | 1581 | 1570 | 1546 | $19b^1$, $\nu(CC)$ |
| 1646 | | | | $1^2$ |

[a] The experimental values are shifts from 62 216 $cm^{-1}$, whereas the calculated ones are obtained from the UHF (scaled by 0.95) and UB3PW91 (without scaling) calculations using the 6-311++G** basis set. [b] $\nu$, stretching, $\beta$, in-plane bending.

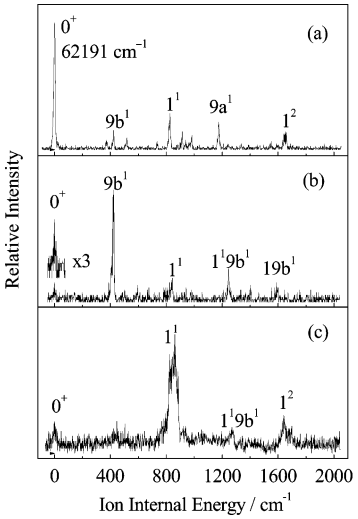

**Figure 5.** MATI spectra of *trans-p*-methoxyphenol-$d_1$-OD, recorded by ionizing via (a) $0^0$, (b) $9b^1$, and (c) $1^1$ levels in the $S_1$ state.

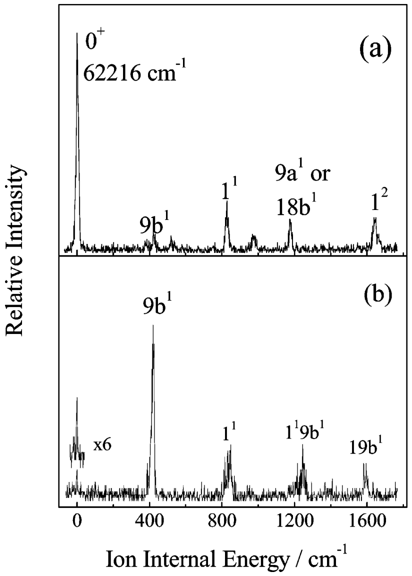

**Figure 6.** MATI spectra of *trans-p*-methoxyphenol-$d_1$-$OCH_2D$, recorded by ionizing via (a) $0^0$ and (b) $9b^1$ levels in the $S_1$ state.

lecular vibrational relaxation (IVR) dynamics in several *p*-alkoxyanilines by single vibronic level fluorescence spectroscopy. The onset of IVR was found to be about 821 $cm^{-1}$ for *p*-alkoxyanilines. Although the present MATI experiments involve monitoring threshold ions, the observed broad bandwidth in Figures 3c and 5c may imply that an IVR process occurs for the cis and trans conformers of *p*-methoxyphenol-$d_1$-OD in the electronically excited $S_1$ $1^1$ state (815 $cm^{-1}$).

## 4. Discussion

**4.1. Site-Specific H/D Exchange and Isotope Effect on the Transition Energy.** It is generally known that isotopomers have very little difference in the molecular structure and electron density. However, the heavier isotopomer may have a slightly lower ZPL than the lighter one in each electronic state, leading to different transition energies. A previous study[2] shows that the differences of the electronic transition energy and IE between the $^{35}Cl$ and $^{37}Cl$ isotopomers of chlorobenzene are not detectable by using a typical mass-resolved spectroscopic technique with an energy resolution of about 1 $cm^{-1}$. Similar results have been reported for the $^{35}Cl$ and $^{37}Cl$ isotopomers of *p*-chloroaniline[3] as well as the $^{79}Br$ and $^{81}Br$ isotopomers of *p*-bromoaniline.[32] Nevertheless, the energy differences among the deuterium-substituted isotopomers of aromatic molecules

**TABLE 6: Measured Transition Energies (in cm$^{-1}$) of *p*-Methoxyphenol, Phenol, and *o*-Dimethoxybenzene and Their Deuterium-Substituted Isotopomers**[a]

| molecule | $S_1 \leftarrow S_0$ | $\Delta E_1$ | $D_0 \leftarrow S_1$ | $\Delta E_2$ | IE | ΔIE |
|---|---|---|---|---|---|---|
| *cis*-*p*-methoxyphenol[b] | 33 667 | 0 | 28 646 | 0 | 62 313 | 0 |
| *cis*-*p*-methoxyphenol-$d_1$-OD[c] | 33 660 | −7 | 28 642 | −4 | 62 302 | −11 |
| *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$[c] | 33 669 | 2 | 28 654 | 8 | 62 323 | 10 |
| *trans*-*p*-methoxyphenol[b] | 33 572 | 0 | 28 638 | 0 | 62 210 | 0 |
| *trans*-*p*-methoxyphenol-$d_1$-OD[c] | 33 563 | −9 | 28 628 | −10 | 62 191 | −19 |
| *trans*-*p*-methoxyphenol-$d_1$-$OCH_2D$[c] | 33 575 | 3 | 28 641 | 3 | 62 216 | 6 |
| phenol[d] | 36 349 | 0 | 32 276 | 0 | 68 625 | 0 |
| phenol-$d_1$[d] | 36 346 | −3 | 32 264 | −12 | 68 610 | −15 |
| *o*-dimethoxybenzene[e] | 35 738 | 0 | | | | |
| *o*-di(methoxy-$d_6$)benzene[e] | 35 767 | 29 | | | | |

[a] $\Delta E_1$, $\Delta E_2$, and ΔIE are shifts of $S_1 \leftarrow S_0$, $D_0 \leftarrow S_1$, and IE for the deuterium-substituted species with respect to those of undeuterated molecules. [b] Reference 13. [c] This work. [d] Reference 5. [e] Reference 33.

**TABLE 7: Measured Frequencies (in cm$^{-1}$) of the Active Vibrations of *p*-Methoxyphenol and Its Deuterium-Substituted Isotopomers**

| | $S_1$ | | $D_0$ | |
|---|---|---|---|---|
| molecule | 9b | 1 | 9b | 1 |
| *cis*-*p*-methoxyphenol | 406 | 813 | 426 | 830 |
| *cis*-*p*-methoxyphenol-$d_1$-OD | 397 | 815 | 406 | 838 |
| *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$ | 397 | | 409 | 832 |
| *trans*-*p*-methoxyphenol | 401 | 813 | 425 | 831 |
| *trans*-*p*-methoxyphenol-$d_1$-OD | 401 | 815 | 420 | 830 |
| *trans*-*p*-methoxyphenol-$d_1$-$OCH_2D$ | 399 | | 421 | 830 |

may range from a few to a few tens of wavenumbers and can be measured with mass-resolved high-resolution spectroscopic methods.

Table 6 lists the measured electronic transition and ionization energies of *p*-methoxyphenol, phenol, and *o*-dimethoxybenzene and their deuterium-substituted isotopomers.[5,13,33] These values have been measured with an energy resolution of about 1−2 cm$^{-1}$ for $E_1$ by R2PI spectroscopy and about 5 cm$^{-1}$ for IE by MATI spectroscopy. The $E_1$'s of *cis*-*p*-methoxyphenol, *cis*-*p*-methoxyphenol-$d_1$-OD, and *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$ are measured to be 33 667, 33 660, and 33 669 cm$^{-1}$. This indicates that the H/D exchange on the OH substituent causes a red shift of 7 cm$^{-1}$, whereas that on the $OCH_3$ group gives a blue shift of 2 cm$^{-1}$. As seen in Table 6, the $E_1$ of phenol-$d_1$-OD is red shifted by 3 cm$^{-1}$ with respect to that of phenol.[5] In contrast, the $E_1$ of *o*-di(methoxy-$d_6$)benzene is blue shifted by 29 cm$^{-1}$ with respect to that of *o*-dimethoxybenzene.[33] Thus, the assignment for the four deuterium-substituted isomers of *p*-methoxyphenol is consistent with the previous experimental results. A similar trend in the energy of the $D_0 \leftarrow S_1$ transition ($E_2$) is also observed, as seen in Table 6. As a result, the IE of *cis*-*p*-methoxyphenol-$d_1$-OD is less than that of *cis*-*p*-methoxyphenol by 11 cm$^{-1}$, whereas that of *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$ is greater by 10 cm$^{-1}$. A similar result of the isotope effect is found for the isomers of *trans*-*p*-methoxyphenol. Therefore, one may conclude that deuteration on the OH substitutent gives rise to a red shift in the electronic excitation and ionization energies of *p*-methoxyphenol, whereas deuteration on the $OCH_3$ group yields a blue shift.

Recently, it has been reported that computational techniques can be used to predict IE to reasonably good accuracy.[34] We have applied the B3PW91 method with the 6-311++G** basis set to calculate the IEs of isomers of *p*-methoxyphenol-$d_1$. The IEs of *cis*-*p*-methoxyphenol, *cis*-*p*-methoxyphenol-$d_1$-OD, and *cis*-*p*-methoxyphenol-$d_1$-$OCH_2D$ are predicted to be 60 735, 60 715, and 60 731 cm$^{-1}$, whereas those of *trans*-*p*-methoxyphenol, *trans*-*p*-methoxyphenol-$d_1$-OD, and *trans*-*p*-methoxyphenol-$d_1$-$OCH_2D$ are predicted to be 60 622, 60 601, and 60 618 cm$^{-1}$, respectively. Comparing these calculated values with the measured ones listed in Table 6, one finds that these calculations underestimate the IEs by about 2.5%. In addition, the deuteration on the $OCH_3$ group leads to a slightly greater IE than that on OH group. This trend in the IEs predicted by the present B3PW91/6-311++G** calculations is in agreement with that measured by the experiments.

**4.2. Site-Specific H/D Exchange and Isotope Effect on the Molecular Vibration.** *p*-Methoxyphenol has 45 normal vibrations, which include 30 benzene-like, 3 OH, and 12 $OCH_3$ motions. Under the present experimental conditions, the substituent-sensitive C−OH/C−$OCH_3$ bending vibration (mode 9b) and the breathing motion (mode 1) are found to be active in both $S_1$ and $D_0$ states. Although deuteration may vary the frequencies of some normal modes, it does not change the intrinsic nature of molecular vibrations. Thus, modes 9b and 1 of various isomers of deuterium-substituted *p*-methoxyphenol are also active in both states.

Table 7 lists the measured frequencies of observed active vibrations 9b and 1 of *p*-methoxyphenol and its deuterium-substituted isomers. Comparing the frequencies of these two modes of the OD and $OCH_2D$ position isomers, one finds that site-specific H/D exchange has a negligible effect on the frequencies of these two active vibrational modes for both cis and trans conformers. Second, the frequencies of mode 9b of the cis conformers of *p*-methoxyphenol-$d_1$ in the cationic $D_0$ state are less than those of the corresponding trans species by 12−14 cm$^{-1}$. However, the frequencies of mode 1 of the cis and trans conformers are nearly same in both $S_1$ and $D_0$ states. This indicates that deuterium substitution can slightly affect the frequencies of substituent-sensitive bending vibrations (e.g., mode 9b) of a particular conformer (e.g., trans) in the cationic state. It is known that mode 9b mainly involves in-plane C−OH and C−$OCH_3$ bending vibrations and mode 1 represents breathing motion. Thus, frequency reduction resulting from deuterium substitution for mode 9b is greater than for mode 1. A third observation is that frequencies of these active vibrations in the $D_0$ state are greater than those in the $S_1$ state. One knows that frequency is proportional to the square root of the force constant for each vibration. Thus, the present finding indicates that *p*-methoxyphenol and *p*-methoxyphenol-$d_1$ are slightly more rigid in the cationic $D_0$ state than in the neutral $S_1$ state.

## 5. Conclusion

We have recorded the R2PI and MATI spectra of deuterium-substituted *p*-methoxyphenol to investigate the site-specific H/D exchange and isotope effect on transition energy and molecular vibration. The $E_1$'s and the adiabatic IEs of *cis*-*p*-methoxyphenol-$d_1$-OD are determined to be 33 660 and 62 302 cm$^{-1}$, which are less than those of *cis*-*p*-methoxyphenol by 7 and 11 cm$^{-1}$, respectively. The corresponding values of *cis*-*p*-methoxyphenol-$d_1$-OCH$_2$D are 33 669 and 62 323 cm$^{-1}$, which are greater than those of *cis*-*p*-methoxyphenol by 2 and 10 cm$^{-1}$, respectively. Similarly, the $E_1$'s and IEs of *trans*-*p*-methoxyphenol-$d_1$-OD are determined to be 33 563 and 62 191 cm$^{-1}$, which are less than those of *trans*-*p*-methoxyphenol by 9 and 19 cm$^{-1}$, respectively. In addition, the corresponding values of *trans*-*p*-methoxyphenol-$d_1$-OCH$_2$D are 33 575 and 62 216 cm$^{-1}$, which are greater than those of *trans*-*p*-methoxyphenol by 3 and 6 cm$^{-1}$, respectively. These experimental data indicate that H/D exchange on the OH substituent gives rise to a red shift in $E_1$ and IE, whereas H/D exchange on the OCH$_3$ group yields a blue shift.

Detailed examinations on the measured frequencies of observed active vibrations 9b and 1 of *p*-methoxyphenol and its deuterium-substituted isomers lead to the following conclusion. First, site-specific H/D exchange has a negligible effect on the vibrational frequencies of these two modes. Second, deuterium substitution may slightly influence the frequencies of substituent-sensitive bending vibrations of a particular isomer in the cationic state. Last, *p*-methoxyphenol and *p*-methoxyphenol-$d_1$ are slightly more rigid in the cationic $D_0$ state than in the neutral $S_1$ state.

**Acknowledgment.** We gratefully acknowledge financial support from the National Science Council of the Republic of China under Grant NSC-94-2113-M-001-009.

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