Observation of Rotational Isomers I: A ZEKE and Hole-Burning Spectroscopy Study of 3-Methoxyphenol

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Three rotational isomers of 3-methoxyphenol have been studied using two-color resonance-enhanced multiphoton ionization (REMPI) and zero kinetic energy (ZEKE) photoelectron spectroscopy. Hole-burning spectroscopy was employed to confirm the presence of three isomers in the REMPI spectrum (S_1 band origins were identified at 35 974, 36 034 and 36 202 ± 1 cm^{-1} for isomers I, IV, and III, respectively). ZEKE spectra recorded via the S_1 states of the isomers provide adiabatic ionization energies of 65 228, 64 741, and 65 648 ± 5 cm^{-1}, respectively. The isomers are assigned with the aid of HF/cc-pVDZ, MP2/cc-pVDZ, and B3LYP/cc-pVDZ ab initio and density functional theory calculations. We discuss the characteristics of the 3-methoxyphenol rotational isomers by comparing the REMPI and ZEKE spectra with those of other substituted benzenes.

I. Introduction

In the low-temperature environment of a supersonic jet expansion, conformational isomers can be isolated and spectroscopically characterized when the barrier for interconversion between isomers is sufficiently high.[1−8] In studies of such systems, a general problem arises, since it can be difficult to identify isomers which display similar spectroscopic features. While microwave spectroscopy provides detailed information that can lead to a definitive structural assignment, less abundant isomers are difficult to detect using this method.[9] A combination of resonance-enhanced multiphoton ionization (REMPI) and zero electron kinetic energy (ZEKE) spectroscopy can prove useful in such cases.[10−13] REMPI spectroscopy is a sensitive technique for indicating the existence of minor components, and ZEKE spectra (obtained via different S_1 states) provide additional high-resolution spectral information to aid the identification of different isomers.[14,15] In addition, hole-burning spectroscopy can be applied to confirm the presence of multiple isomers.[16]

In this paper, we apply two-color (1 + 1′) REMPI, hole-burning and ZEKE spectroscopy to characterize the rotational isomers of 3-methoxyphenol (3MP), which are illustrated in Figure 1. Ab initio and density functional theory (DFT) calculations are performed to aid the spectral assignment. This work is an important preliminary to the following paper, which presents a study of 3MP·H_2O clusters.[17] Therefore, the central aims of this study are to (a) confirm the number and identity of rotational isomers in the REMPI spectrum and (b) identify prominent vibronic features in the REMPI and ZEKE spectra of the 3MP isomers, which may also be present in the spectra of the 3MP·H_2O complexes.

There have been two previous spectroscopic studies of 3MP. Caminati et al. detected a single C_s symmetry isomer of 3MP (isomer I) using microwave spectroscopy.[9] The barrier to methoxy group rotation was found to be ∼1050 cm^{-1}. More recently, Fujimaki et al.[18] obtained a one-color (1 + 1) REMPI spectrum of 3MP and detected two isomers (I and IV) using autoionization-detected infrared spectroscopy. However, the assignment given in that work remains tentative, since the OH stretching vibrations of the two isomers are too similar (3584 and 3589 cm^{-1}) to allow a definitive assignment from comparison with relatively low level ab initio calculations.

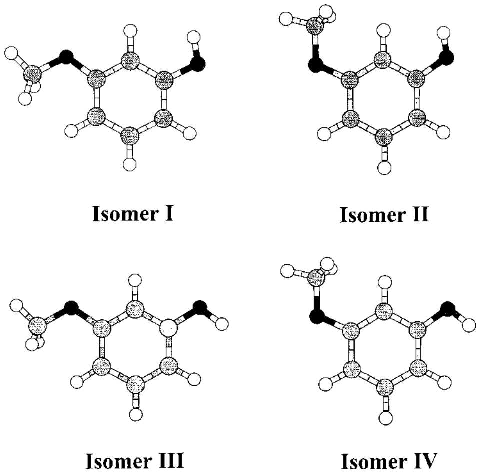

Figure 1. Four rotational isomers of 3-methoxyphenol. (Labeling follows ref 18.)

II. Experimental Section

Figure 2 illustrates the experimental setup used to perform the REMPI, ZEKE, and hole-burning experiments described below. 3MP was heated to 140 °C in a sample reservoir located directly behind the valve (General Valve Series 9, 500 μm nozzle) and seeded in neon gas at 0.5−2.5 bar. The skimmed supersonic beam was intersected 20 cm downstream by two coaxial, counterpropagating synchronously pumped dye lasers. The ion/electron optics, molecular beam, and laser beams are arranged in a mutually perpendicular fashion. The pulse sequences, timings, and field strengths are identical to those described previously.[19]

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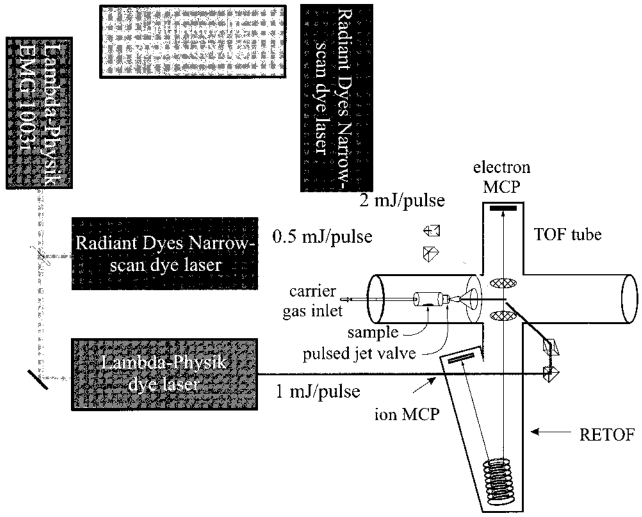

Figure 2. Schematic diagram of the experimental apparatus showing the laser configuration employed in the two-color REMPI, ZEKE, and hole-burning experiments.

The two-color laser system used for REMPI and ZEKE spectroscopy comprises an Excimer laser (Lambda-Physik EMG 1003i) synchronously pumping two frequency-doubled dye lasers (Radiant Dyes Narrowscan to promote $S_1 \leftarrow S_0$ excitation and Lambda Physik FL 3002 to effect ionization). Hole-burning experiments were performed using a Nd:YAG (Continuum Precision PL 8020) pumped dye laser (Radiant Narrowscan with an additional axicon amplification stage) which was set to the respective $S_1 \leftarrow S_0$ transition. The excimer-pumped Radiant Narrowscan laser was then employed as the probe laser. It was necessary to employ hole-burning with two-color REMPI spectroscopy to obtain good quality spectra, since 3MP readily fragments with one-color ionization. Therefore, the two Narrowscan dye-laser beams were spatially overlapped using a beam splitter. The probe laser was fired 400−600 ns after the hole-burning laser, and ions were retrieved by a 305 V/cm pulsed electrical field commencing 1 μs before the burn laser. A time gate discriminates the hole-burning signal from the probe signal.

All spectra were calibrated by simultaneously recording the iodine absorption spectrum to ensure a laser accuracy of ±0.02 cm^{-1}.[20] The spectra presented are single scans (with the data being smoothed by a three-point compression) and were normalized to dye laser intensity, although the laser profiles are reasonably flat over the range studied. Quoted laser photon energies were corrected from air to vacuum, and ionization energies were extrapolated to zero field to account for the effect of field ionization.[21]

III. Results and Discussion

A. Ab Initio and Density Functional Theory Calculations of 3-Methoxyphenol. Geometric structures of the neutral (S_0) and cationic (D_0) ground-states of 3MP were obtained from ab initio and DFT calculations using GAUSSIAN 98.[22] The cc-pVDZ basis set was used for all calculations, since it has been shown to produce reliable results for clusters containing water molecules,[10,23] and it will be used for the 3MP·H_2O clusters.[17] Ab initio calculations were performed at the HF and MP2 levels of theory to facilitate comparison with related systems. Harmonic vibrational frequencies were calculated to confirm that optimized structures correspond to local minima and to determine zero-point energy (ZPE) corrections. Reported vibrational frequencies are not scaled, and no scaling factor was applied when calculating the ZPE corrections due to uncertainty in the appropriate scaling factors for cations. Spin-unrestricted orbitals were employed in the D_0 state calculations. In the HF and MP2 calculations, the expectation value of the S^2 operator was substantial (0.9290−0.9380 and 0.915−0.922, respectively), leading us to view these results with some caution. The DFT calculations do not suffer from this limitation.[24]

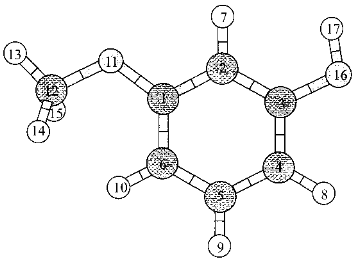

Figure 3. Definition of the labeling scheme for the structural parameters of 3-methoxyphenol.

TABLE 1: Relative Energies of the S_0 and D_0 States of the Rotational Isomers of 3MP Obtained from HF/cc-pVDZ, MP2/cc-pVDZ, and B3LYP/cc-pVDZ Calculations[a,b]

	S_0 relative energy (cm^{-1})			D_0 relative energy (cm^{-1})		
	HF	MP2	DFT	HF	MP2	DFT
isomer I	14	36	42	895	875	779
	(18)	(44)	(40)	(830)	(860)	(709)
isomer II	266	228	204	0	0	0
	(244)	(208)	(189)	(0)	(0)	(0)
isomer III	146	146	131	1730	1662	1397
	(124)	(122)	(98)	(1561)	(1634)	(1243)
Isomer IV	0	0	0	426	301	247
	(0)	(0)	(0)	(374)	(285)	(209)

[a] Zero-point energy-corrected values are given in parentheses. The absolute energies of the S_0 state of isomer IV are −419.477 882 (−419.331 239), −420.766 617 (−420.628 648), and −422.018 339 (−421.881 627) Hartrees in the HF, MP2, and B3LYP calculations, respectively. ZPE corrected values are given in parentheses. [b] The absolute energies of the D_0 state of isomer II are −419.240 600 (−419.094 819), −420.470 813 8 (−420.331 658), and −421.740 178 (−421.603 389) Hartrees in the HF, MP2, and B3LYP calculations, respectively. ZPE corrected values are given in parentheses.

Four local minima, C_s symmetry structures were obtained corresponding to the rotational isomers displayed in Figure 1. Structural parameters for the four isomers are available in the additional material, and the atom labeling scheme is defined in Figure 3. The bond lengths increase from the HF to the MP2 level of theory, with the DFT results lying between the HF and MP2 values. The calculations indicate that only modest geometric changes occur between the neutral and the ion. We note that the C_1-O_{11} and C_3-O_{16} bond lengths decrease in the ion, presumably due to a shift of electron density from the oxygen atom to the positively charged aromatic ring. This geometry change is accompanied by an increase in the C_1-C_6 and C_3-C_4 bond lengths, implying that the ionic state has more keto character than the S_0 ground state. In addition, the $O_{11}-C_{12}$ and $O_{16}-H_{17}$ bonds elongate, with both the hydroxy and methoxy groups straightening out. A similar pattern has been observed by Gerhards et al. in calculations of resorcinol monomers.[25]

Table 1 displays the relative energies of the S_0 states of the rotational isomers along with the ZPE-corrected values. In the three sets of calculations, isomer IV represents the lowest-energy isomer, with isomer I appearing at a slightly higher energy. As in resorcinol, the most sterically hindered structure (isomer II) represents the highest-energy conformation. It is notable that the relative energy differences between the isomers are reason-

TABLE 2: Ionization Energies and Relative Ionization Energies of the Rotational Isomers of 3MP Obtained from HF/cc-pVDZ, MP2/cc-pVDZ, and B3LYP/cc-pVDZ Calculations[a]

	ionization energy (cm^{-1})			relative ionization energy (cm^{-1})		
	HF	MP2	DFT	HF	MP2	DFT
isomer I	52 956	65 756	61 782	455	538	490
	(52 698)	(65 994)	(61 731)	(439)	(531)	(459)
isomer II	51 809	64 690	60 842	−692	−528	−450
	(51 641)	(64 970)	(60 874)	(−618)	(−493)	(−398)
isomer III	53 657	66 433	62 312	1156	1215	1020
	(53 322)	(66 690)	(62 207)	(1063)	(1227)	(935)
isomer IV	52 501	65 218	61 292	0	0	0
	(52 259)	(65 463)	(61 272)	(0)	(0)	(0)

[a] Zero-point energy-corrected values are given in parentheses.

ably consistent for the three sets of calculations. The absolute energies of the D_0 states of the rotational isomers are also displayed in Table 1. In contrast to the S_0 results, isomer II is the most stable structure in the ion. This result reflects the situation for the resorcinol monomer, where the least stable neutral monomer is the most stable cation. The calculated adiabatic ionization energies (IEs) are displayed in Table 2 and represent differences between the total energy of the optimized neutral and corresponding optimized cation. Calculated relative ionization energies are also included in Table 2 to facilitate comparison with the experimental IEs. While it has been shown that calculations consistently underestimate the IE, the relative IEs of the isomers should be reliable. We again note that the relative ionization energies are consistent for the three sets of calculations.

The harmonic vibrational frequencies of the 12 lowest-frequency modes of isomers I, III, and IV of 3MP are presented in Table 3. Mode assignments are included to facilitate comparison with the spectral data.

B. REMPI Spectroscopy of 3-Methoxyphenol. The two-color (1 + 1′) REMPI spectrum of 3MP displayed in Figure 4 was recorded with the ionization laser set to 33 600 cm^{-1} to avoid fragmentation of higher clusters into the 3MP mass channel. The prominent bands at 35 974 and 36 034 ± 1 cm^{-1}, were assigned to the S_1 band origins of two isomers and appear to be in good agreement with the results of Fujimaki et al. (35 974 and 36 035 cm^{-1}).[18] However, the higher-energy region of our (1 + 1′) REMPI spectrum is considerably simplified compared to the earlier (1+1) spectrum, allowing us to identify a third S_1 band origin at 36 202 ± 1 cm^{-1}.

TABLE 3: Ab Initio Harmonic Frequencies (in cm^{-1}) of the 12 Lowest Frequency Modes in the S_0 and D_0 States of the Rotational Isomers of 3MP[a]

	S_0			D_0		
mode	HF	MP2	DFT	HF	MP2	DFT
			Isomer I			
a″ (CH_3 bend)	82	84	88	106	103	102
a″ (CH_3 torsion)	228	214	208	176	179	160
a′ (OCH_3 bend)	253	233	237	219 (*a*″)	220	206 (*a*″)
a″	257	242	237	239	231	229 (*a*′)
a″ (CH_3 torsion)	294	293	275	245 (*a*′)	237	230 (*a*′)
a″ (OH torsion)	361	339	366 (*a*′)	398 (*a*′)	374	230
a′ (OCH_3 and OH stretch)	393	368	373 (*a*″)	420 (*a*″)	413	372
a″ (ring)	509	453	466	468 (*a*′)	440	408
a′ (ring)	509	467	472	520	484	441
a′ (ring)	568	523	527	583 (*a*″)	544	487
a′ (ring)	632	584	587	611	575	541 (*a*″)
a″ (ring)	710	619	638	651	594	574 (*a*′)
			Isomer III			
a″	80	82	85	106	100	101
a″	227	213	206	174	178	157
a′	254	231 (*a*″)	236 (*a*″)	217 (*a*″)	214 (*a*″)	203 (*a*″)
a″	255	243 (*a*′)	237 (*a*′)	237	229	228 (*a*′)
a″	295	292	274	244 (*a*′)	237 (*a*′)	228
a″	338	321	358	398 (*a*′)	374 (*a*′)	371 (*a*′)
a′	394	368	366	421 (*a*″)	414 (*a*″)	409 (*a*″)
a″	505 (*a*′)	456	469	449 (*a*′)	443 (*a*′)	429 (*a*′)
a′	511 (*a*″)	463	470	490 (*a*″)	477 (*a*″)	475 (*a*″)
a′	570	525	529	517	494	485
a′	629	582	585	609	571	573
a″	710	619	638	640	586	603
			Isomer IV			
a″	90	92	98	125	122	121
a″	220	206	202	181	177	170
a′	236	225	220	218 (*a*″)	217	208 (*a*″)
a″	262	237	240	227 (*a*′)	222	211 (*a*′)
a″	294	293	276	251	251	246
a″	355	330	369	426 (*a*′)	397 (*a*′)	400 (*a*′)
a′	431	401	401	427	420 (*a*″)	418 (*a*″)
a″	508	453	468	482	452 (*a*′)	455 (*a*′)
a′	509	473	474	532	502	500
a′	574	525	534	534 (*a*″)	512 (*a*″)	510 (*a*″)
a′	600	582	559	589	549	549
a″	707	619	637	656	605	621

[a] Where a symmetry label is shown in parentheses, the ordering of the modes has changed relative to the assignment given in column 1.

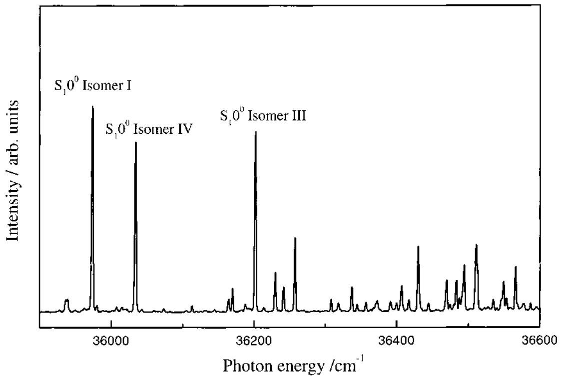

Figure 4. Two-color (1 + 1′) REMPI spectrum of 3-methoxyphenol, recorded with the ionizing laser set to 33 600 cm^{-1}.

TABLE 4: Frequencies of Vibronic Features Observed in the REMPI Spectrum of 3-Methoxyphenol[a]

no.	$E(S_1 \leftarrow S_0)$ (cm^{-1})	no.	$E(S_1 \leftarrow S_0)$ (cm^{-1})	no.	$E(S_1 \leftarrow S_0)$ (cm^{-1})
1	35974s I (S_10^0)	11	36319w	21	36445w
2	36034s IV (S_10^0)	12	36338w	22	36470w
3	36115w I	13	36345w	23	36484w IV (2A′)
4	36165w IV	14	36358w	24	36495m I ($6a^1$)
5	36170w I	15	36373w	25	36512m
6	36202s III	16	36392w	26	36535w
7	36230w I (*A*′)	17	36400w	27	36549w
8	36242w IV	18	36407w	28	36566m IV ($6a^1$)
9	36258m IV (*A*′)	19	36417w	29	36576w
10	36309w	20	36430m	30	36587w

[a] Intensities Are Denoted by s (strong), m (medium), and w (weak).

Comparing the REMPI spectrum of 3MP with the spectrum of resorcinol allows us to begin to assign the rotational isomers. It is unlikely that isomer II represents one of the isomers present in the REMPI spectrum, since the analogous high-energy isomer was not observed for resorcinol.[10,11] The band at 36 202 cm^{-1} is assigned to isomer III because a similar energy gap (200–275 cm^{-1}) occurs between the analogous isomers of resorcinol. The remaining peaks at 35 974 and 36 034 cm^{-1} therefore represent isomers I and IV of 3MP. This assignment will be discussed in section III.D and is based on the ionization energies of the rotational isomers. It should be noted that this assignment differs from that of Fujimaki et al.,[18] although no explanation for the assignment was given in the earlier work.

The REMPI spectrum of 3MP displays a number of smaller-intensity features, which are listed in Table 4. Hole-burning spectroscopy (section III.C) allows us to associate several of these features with the band origins and reveals that for both isomers I and IV, three vibronic features appear at 141, 196, and 256 cm^{-1} and 131, 208, and 224 cm^{-1} above the S_10^0 transition, respectively. The isomer IV feature which lies 224 cm^{-1} above the origin is particularly intense.

Bernstein and co-workers have conducted a detailed study of the S_1-state spectra of methoxy-substituted benzenes to probe the effect of substitution on the barrier for methyl group rotation.[1] The $S_1 \leftarrow S_0$ spectrum of anisole was featureless except for the origin transition at 36 381.1 cm^{-1}. Upon further substitution by $-CH_3$ and $-OCH_3$ groups, however, additional features appear in the spectral region 200 cm^{-1} above the S_10^0 transition. Isotopic substitution led to the assignment of these features as internal rotational transitions of the substituent group. In *cis*-3-fluoromethoxybenzene, which should exhibit spectral characteristics similar to those of 3MP,[26] the $9a_1$ internal rotational transition at 219.7 cm^{-1} represents the most intense vibronic feature over this region of the REMPI spectrum, with an overtone at 441.7 cm^{-1}. It is possible, therefore, that the isomer I feature at 256 cm^{-1} and the isomer IV feature at 224 cm^{-1} represent the $9a_1$ transitions. (We note that it is unusual for the $9a_1$ transition to appear more intensely than internal rotor bands with smaller quantum numbers [2e, $3a_1$, etc.], but this pattern is observed in *cis*-3-fluoromethoxybenzene.[26]) Alternatively, these peaks could be assigned to the *a*′ symmetry mode corresponding to the in-plane bending motion of the $-OCH_3$ group. The HF calculations predict that this mode should occur at 253 and 236 cm^{-1}, respectively, for isomers I and IV. We currently favor assignment of the 256 and 224 cm^{-1} features to this $-OCH_3$ vibration (which we label *A*′), since it appears prominently in the REMPI and ZEKE spectra of the 3MP•H_2O complexes presented in the following paper.[17] The degree of excitation is greater for isomer IV than isomer I, possibly due to the hydrogen atoms of the methoxy group interacting with the oxygen atom of the OH group in this conformation.

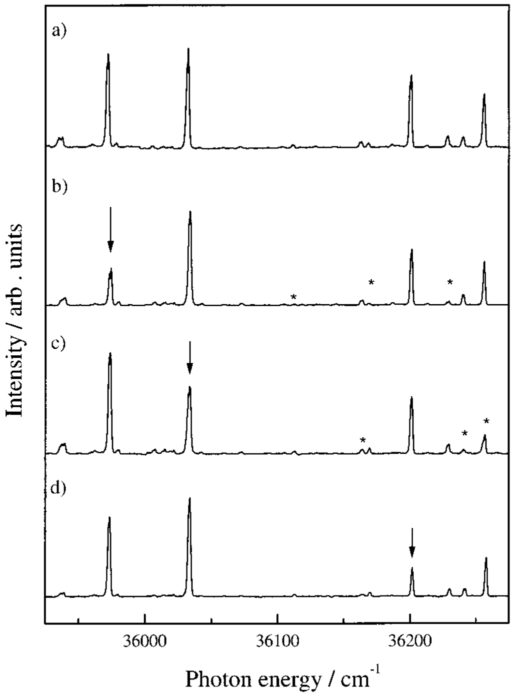

Figure 5. Hole-burning spectra of the two-color (1 + 1′) REMPI spectra of 3-methoxyphenol (a) without the hole-burning laser and (b) with the hole-burning laser set to the S_10^0 transition of isomer I, (c) isomer IV, and (d) isomer III. The arrows represent the positions of the hole-burning lasers, and the bands affected are marked with asterisks.

A number of features arising from the vibrations of the aromatic ring should appear in the region above 400 cm^{-1} from the origin transitions. For example, the $6a^1$ vibration occurs at 521.2 cm^{-1} in *cis*-3-fluoromethoxybenzene and at 514 cm^{-1} in phenol.[26,27] The medium-intensity features at 36 495 and 36 566 cm^{-1} may therefore represent the $6a^1$ transitions for isomers I and IV, respectively.

C. Hole-Burning Spectroscopy of 3-Methoxyphenol. Hole-burning spectra were recorded to confirm the presence of three rotational isomers of 3MP in the REMPI spectrum. For this molecule, it was essential to apply hole-burning with two-color (1 + 1′) REMPI excitation, since one-color (1 + 1) excitation resulted in extensive fragmentation. A two-color REMPI spectrum of 3MP is displayed in Figure 5a for comparison. Figure 5b presents the spectrum obtained with the burn laser set to the isomer I S_10^0 transition. Inspection of the spectrum reveals that the bands assigned to isomers IV and III are

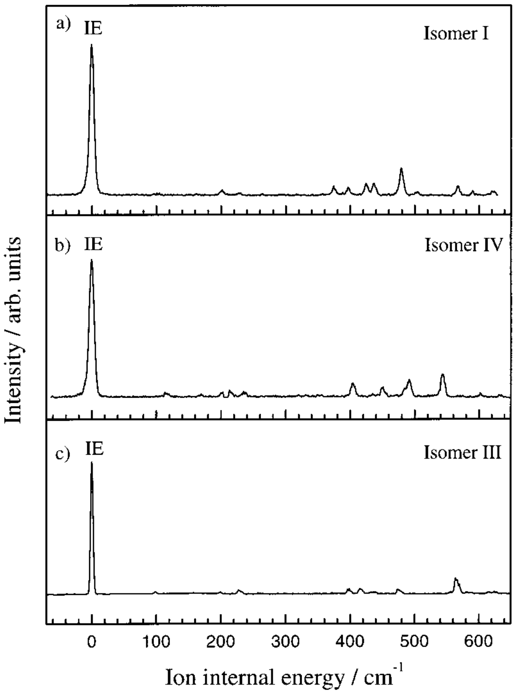

Figure 6. ZEKE spectra of 3-methoxyphenol recorded via the $S_1 0^o$ intermediate state of (a) isomer I, (b) isomer IV, and (c) isomer III. Each spectrum is displayed relative to the respective ionization energy.

unaffected by the burn laser, whereas the isomer I origin is clearly diminished, along with several smaller-intensity features. The hole-burning spectrum recorded with the burn laser set to the isomer IV $S_1 0^0$ transition (Figure 5c) shows that the isomer IV origin feature is depleted compared to the other isomer origin features, along with several vibronic features. Finally, Figure 5d displays the spectrum obtained with the hole-burning laser set to the isomer III origin band, illustrating that this feature does indeed represent a third isomer of 3MP. The hole-burning spectra exclude the existence of other isomers over this region of the spectrum, since all the significant spectral features can be associated with isomers I, IV, and III.

D. ZEKE Spectroscopy of 3-Methoxyphenol. ZEKE spectra recorded via the $S_1 0^0$ transitions of the rotational isomers of 3MP are displayed in Figure 6. The lowest-energy feature in each spectrum is assigned to the vibrational ground state of the cation, giving ionization energies, computed as the sum of the $S_1 0^0$ transition and the vibrationless $D_0 \leftarrow S_1$ transition, of 65 228, 64 741, and 65 648 ± 5 cm^{-1} for isomers I, IV, and III, respectively. The observation of three distinct IEs is a strong indication that three different isomeric species are present in the S_1 state spectrum and confirms the hole-burning results.

The assignment of the IEs is based on the relative values presented in Table 2. The DFT calculations predict that isomer IV should display the lowest IE, with the isomer I value being 460 cm^{-1} higher in energy and the isomer III value being 936 cm^{-1} higher. The relative IEs are in excellent agreement with the experimental values of 487 and 907 cm^{-1}. We note that the HF and MP2 calculated IEs also display a similar trend, although the agreement is not as good as that for the DFT calculations. The assignment presented will be reinforced by the assignment of the 3MP·H_2O isomers presented in the next paper,[17] which is based upon the monomer assignment. This again gives excellent agreement with the calculations. However, in subsequent work, it would be useful to obtain high-resolution REMPI spectra of the band origins to confirm the current assignment.[28]

The ZEKE spectra presented in Figure 6 are dominated by the IE feature, indicating that only a modest geometry change occurs upon ionization, which is in line with the calculations. Several smaller-intensity features are evident in the ZEKE spectra and are listed in Table 5. It is possible that the features in the region up to 250 cm^{-1} above the IE transition again correspond to the internal rotational transitions of the methyl group and the excitation of the A' mode, although their weak intensities make definitive assignment problematic. The relatively smaller amount of rovibronic features in the ZEKE spectra indicates that less excitation occurs for the $D_0 \leftarrow S_1$ transition compared to the $S_1 \leftarrow S_0$ transition. Other higher-energy features may correspond to intramolecular vibrations, but a definitive assignment is again complicated due to the number of vibrations over this spectral range (Table 3). A comprehensive assignment of the vibronic features would require extensive isotopic labeling and was considered to be beyond the scope of this study. In *cis*-3-fluoromethoxypheno,l[26] several transitions have been assigned, including 2e (118 cm^{-1}, weak intensity), $3a^1$ (162 cm^{-1}, weak), $9a_1$ (210 cm^{-1}, medium with an overtone at 416 cm^{-1}), $6b^1$ (481 cm^{-1}, medium), and $6a^1$ (554 cm^{-1}, strong), allowing some comparison with the vibrations listed in Table 5.

TABLE 5: Frequencies (in cm^{-1}) of Vibronic Features Observed in the ZEKE Spectra of the Rotational Isomers of 3MP Recorded via the Respective $S_1 0^0$ States.

	isomer I	
103vw	400w	566w
202w	424w	591vw
230vw	436w	
375w	479m	
	isomer IV	
115vw	213vw	451w
170vw	236vw	492m
203vw	405w	543m
	isomer III	
101vw	399vw	566w
201vw	416vw	
229vw	474vw	

[a] Frequencies are given relative to the ionization energies, and m denotes medium, w weak, and vw very weak.

IV. Concluding Remarks

Three rotational isomers of 3MP were identified in the S_1-state REMPI spectrum using a combination of hole-burning and ZEKE spectroscopy. The $S_1 0^0$ transition energy and IE were obtained for each of the rotational isomers, which will allow the calculation of spectral red-shifts for the 3MP·H_2O complexes in the following paper.[15] Vibronic features in the REMPI spectrum were assigned to the in-plane bend of the methoxy group. We anticipate that these features should also be present in the REMPI spectrum of 3MP·H_2O. Finally, the ZEKE spectra of the 3MP monomers display only low-intensity features over the spectral region up to 500 cm^{-1} above the IE transition, which will allow us to assign any dominant features over this region in the ZEKE spectra of 3MP·H_2O as intermolecular vibrations.

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