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Methyl Group Rotational Dynamics in *o*-, *m*-, and *p*-Xylene Cations from Pulsed Field Ionization Zero-Kinetic-Energy Spectroscopy

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The pulsed field ionization zero-kinetic-energy (PFI-ZEKE) spectra of *o*-, *m*- and *p*-xylene have been recorded and analyzed. These clearly demonstrate neighboring methyl groups to be interacting and further apart groups to be noninteracting. The spectra show well-resolved features, typically within 150 cm^{-1} of the $S_1 \rightarrow$ ion origins, which are assigned to transitions associated with the internal rotations of the ring methyl groups. The observed transitions are fit using a one-dimensional periodic potential with a free rotor basis. The results of the analysis show that the potential barrier to methyl rotation in the xylene ion increases in the order para < meta < ortho and that the barriers differ from those determined for the S_0 and S_1 neutral state in significant ways. This is particularly true for the interacting groups of *o*-xylene. The two methyl groups of *p*- and *m*-xylene are determined to be noninteracting whereas the methyl groups of *o*-xylene interact strongly. The ionization potentials for *o*-, *m*-, and *p*-xylene are also derived from the PFI-ZEKE spectra.

Introduction

The internal rotation of a methyl group is a unique large-amplitude motion in that the energy levels associated with the rotation can range anywhere from those of a one-dimensional near free rotor (low barrier) to those of restricted torsional motion (high barrier). Internal rotation is a kind of molecular vibration that cannot be described by a normal coordinate. Since the internal rotation is a largely anharmonic motion, it has a special importance in relaxation processes. The anharmonic coupling of vibrational modes to methyl rotations is the origin of chemically significant processes such as intramolecular vibrational relaxation (IVR).[1] These processes can be dramatically accelerated by the internal rotational motion. Electronic relaxations can also be accelerated due to increases in the nonoptical Franck−Condon factor by the large anharmonicity.[2]

Internal methyl rotation is often restricted by steric hindrances that are associated with the local environment in proximity to the methyl group. Changes in molecular geometry are therefore expected to be reflected in changes in the methyl group rotational barrier. When the steric hindrance of the methyl rotation is small, the rotational barrier is primarily due to interactions with neighboring electron density. The internal rotations of methyl groups can therefore be used as sensitive probes to the structural and electronic properties of molecules and their changes upon electronic excitation and ionization. The internal rotation of toluene has been studied in the ground neutral S_0 state,[3,4] the excited neutral S_1 state,[4−6] and the ground ionic state.[7] Here the rotation of the methyl group is sterically unhindered and depends only on the electronic properties of the benzene ring. The barrier to rotation was found to be small in all three states, the methyl group being a near free rotor. The effect of substituents to the benzene ring of toluene on methyl rotation has been recently addressed by several groups.[4,5,8−13] The addition of a substituent group to the toluene ring results in methyl potential barrier increases in the order para < meta < ortho. The barriers in the ionic ground states of several substituted toluenes were determined by Ito et al.[9,14] to increase dramatically compared to those in the neutral ground state. Substituting an additional methyl group to the toluene ring (xylene) presents an additional interesting aspect in that the methyl substituents could interact with one another. The internal rotational barriers for *o*-, *m*-, and *p*-xylene in the ground electronic state (S_0) of the neutral were determined via heat capacity measurements[15] and more recently by Breen et al.,[4] using dispersed emission (DE) and time-of-flight mass spectroscopy (TOFMS) for the S_0 ground and S_1 excited states. Their results show dramatic changes in the barrier heights for internal rotation with electronic excitation. In *m*-xylene, for example, the methyl group is nearly a free rotor in S_0 but becomes greatly hindered in S_1. Similar results have been reported for related molecules.[8−13] The two rotors in *o*-, *m*-, and *p*-xylene in the S_0 state and *m*- and *p*-xylene in the S_1 state were found to be completely uncoupled; however, the two rotors of *o*-xylene in S_1 interact strongly. The dramatic and interesting changes and interactions that have been shown to occur within *o*-, *m*-, and *p*-xylene upon electronic excitation have inspired us to investigate the molecules in the ground ionic state.

With the exception of the work of Weisshaar and coworkers,[7,13] the study of internal methyl rotations in ions has until recently been limited by the low resolution of conventional ion spectroscopic techniques such as photoelectron spectroscopy (PES). These techniques are often unable to resolve the close level spacing between internal rotor levels. Here, we apply the high-resolution technique of zero kinetic energy (ZEKE) spectroscopy to resolve the methyl torsional bands of *o*-, *m*-, and *p*-xylene in the ground ionic state. To date, the only studies of this type concerning internal methyl rotations in the ionic state are those performed on toluene[7] and fluorotoluene[14] via ZEKE spectroscopy and cresol[9] via two-color ionization threshold spectroscopy. ZEKE spectroscopy has a particular advantage in the study of methyl rotations in that it resolves the rather weak signal which is lost using most other techniques. We demonstrate here how these weak features are critical in fitting methyl barrier potentials.

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ZEKE spectroscopy[16−18] and its applications have recently been reviewed in detail and are thus only briefly outlined here. ZEKE spectroscopy relies on ions produced through delayed pulsed field ionization of the narrow band of high-*n* Rydberg states that exist just below the ionization limit of each rotational, vibrational, and electronic ionic eigenstate. Using the unique properties of these weakly bound high-*n* Rydberg states below the ionization limit rather than the unbound states above the limit, as in PES, leads to the improvement in resolution of more than 2 orders of magnitude. Two unique properties of these high-*n* Rydberg states make ZEKE spectroscopy possible. First, an electron in a high-*n* Rydberg state is several thousand times further from the ionic molecular core than those electrons remaining in valence states. The electron−ionic core interactions are therefore strongly reduced. The core finds itself in an *ionic eigenstate*, the electron acting solely as a slowly orbiting spectator. This electron, once separated from the molecular core, is on the threshold of escaping the high Rydberg orbit with zero energy remaining. The selection of these states from completely ionized states depends on the fact that, despite their respective distances, the ionic core and the orbiting electron remain together as a neutral species. Second, high-*n* Rydberg states are very stable with respect to decay and thus live for a very long time.[19] Separation of these long-lived states from the fast decaying low-*n* Rydberg states is simply accomplished using a delay period. The long lifetimes, first observed by Reiser et al.[20] in 1988, were unanticipated since they deviate by nearly 2 orders of magnitude from what one would expect based on the lifetimes of lower-*n* Rydberg states by means of an n^3 scaling law. The stability of these states has only recently been discovered to be due to external perturbations (electric or magnetic fields, nearby ions, etc.) which operate only on the high-*n* Rydberg states, that is, those lying very close to the ionization threshold.[21−41] It has recently been demonstrated[42,43] that a mass-selected version of ZEKE (mass-analyzed ZEKE), where ions are detected instead of electrons, produces equivalent spectra at the same resolution with the added advantage of complete mass discrimination.

In this paper we use the high resolution provided by ZEKE spectroscopy to observe the internal rotational levels of the ground-state cations of *o*-, *m*-, and *p*-xylene. Using the measured torsional transitions to the cation, we determine the potential barriers for the internal rotation of the methyl group(s). A potential for internal rotation that includes 3-fold (V_3) and 6-fold (V_6) periodic terms and interaction terms allows us to calculate not only the potential barriers to methyl rotation but also interactions between the two methyl groups. In addition, we have determined accurate ionization potentials for each of the three isomers of xylene.

Experimental Section

The experimental apparatus used to measure the reported PFI-ZEKE spectra has been described in detail elsewhere[44] and is only briefly reviewed here. Room temperature spectra grade xylene is seeded into 4.5 bar of He and expanded into a pulsed supersonic jet. Having passed though two skimmers, the beam enters the ion optics region where it interacts with two counterpropagating lasers. The first laser excites the molecules into a selected intermediate state while the second is scanned through the Rydberg manifold. The absolute frequencies of the lasers are determined using a high-resolution wavemeter. The relative frequencies are calibrated by comparison with a simultaneously recorded iodine spectrum. A small electric "spoiling" field of 1 V/cm is applied 50 ns after laser excitation and is maintained up until the point of pulsed field ionization. During the 24 μs delay period between laser excitation and pulsed field ionization, the prompt ions produced directly through two-photon, one-color ionization or by autoionization are retarded with respect to the high-*n* Rydberg "ZEKE" neutrals. The stable ZEKE states which exist in a narrow band just below each eigenstate of the ion are now isolated from all prompt ions. Lower-*n* states decay during the delay time and are thus not detected. Pulsed field ionization is performed using a fast rising positive extraction pulse which produces a field of 200 V/cm. The field ionizes the neutrals, which are then extracted into a reflectron time-of-flight (RETOF) mass spectrometer. The observed ion signal arises solely from the field ionized Rydberg states which are stable enough to survive the relatively long drift time through the ion optics. Resonance-enhanced multiphoton ionization (REMPI) spectra are obtained in the same apparatus but with no applied spoiling field.

Results and Discussion

Before presenting the experimental results, the notation and selection rules for the internal rotational levels of a methyl group should be summarized briefly. The internal rotational levels are denoted by the combination of rotational quantum number *m* of a one-dimensional free rotor and the symmetry species of the permutation inversion group.[45] The toluene molecule, for example, contains a single methyl rotor and belongs to the G12 permutation inversion group which is isomorphous to the C_{3v} point group. The internal rotational level has a_1 symmetry for $m = 0$, a_1 or a_2 for $m = 3n$ ($n > 1$), and e for others because of the 3-fold symmetry. The levels are thus denoted $0a'_1$, $1e''$, $2e'$, $3a''_2$, $3a''_1$, etc. The simplest method for symmetry labeling the double rotor energy levels of *o*-, *m*-, and *p*-xylene is to consider the internal rotational states of each rotor separately and thus use the symmetry labels and selection rules for toluene. An *o*-, *m*-, or *p*-xylene molecule with one rotor in its $0a'_1$ state and the other in its $1e''$ state is thereby said to be in the $0a'_11e''$ state. The selection rules for electronic transitions are $a_1 \leftrightarrow a_1$, $a_2 \leftrightarrow a_2$, and $e \leftrightarrow e$ in accordance with the molecular symmetry groups of *o*-, *m*-, and *p*-xylene. The $0a'_11e''$ form of symmetry labeling is used here because it clarifies the levels of each individual methyl rotor and reveals which transition takes place on which rotor. The approximation of separate noninteracting rotors is assumed for this discussion.

***p*-Xylene.** The PFI-ZEKE spectrum of *p*-xylene is compared to the PFI-ZEKE spectrum of toluene in Figure 1. The ionization potential (IP) determined from the spectrum and corrected to account for the field shift[46] is 68 186(2) cm^{-1}. While the IP for *p*-xylene is ∼3000 cm^{-1} lower than the IP of toluene, the spectra are very similar in that features are found in both spectra at ∼14, 45, and 76 cm^{-1} to higher energy of the origin band. The relative frequency, with respect to the origin, for each internal rotor transition is listed above the spectrum in Figure 1. Since a two-rotor system (e.g., xylene) has many more levels than a one-rotor system (e.g., toluene), the PFI-ZEKE spectrum of *p*-xylene should have more features than that of toluene. The fact that the spectra, in the origin region, are nearly identical suggests that the two rotors of *p*-xylene are uncoupled and independent and that the methyl rotor potential barriers are similar. On the basis of the similarities between the spectrum of toluene and *p*-xylene, we are able to assign a number of the transitions in the PFI spectrum of *p*-xylene to torsional states with excitation localized on one methyl group. The symmetry assignments are listed in Table 1.

To confirm these assignments, we have fit the transition energies by calculating the energies of the internal rotational

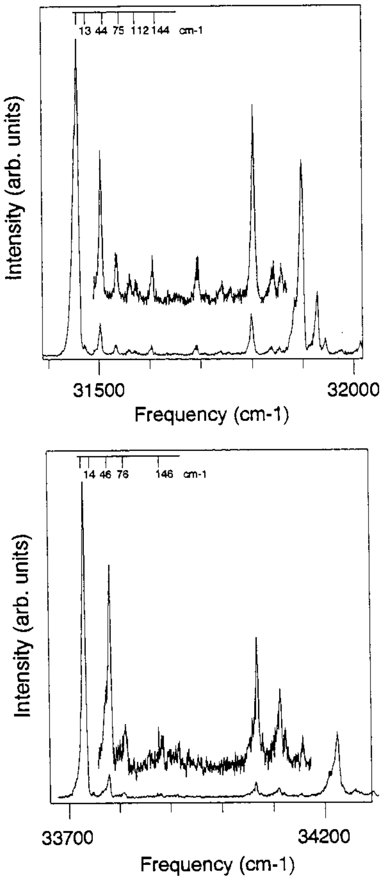

Figure 1. Mass analyzed ZEKE spectra of *p*-xylene (upper) and toluene (lower). The weak features to higher energy of the origin are due to methyl torsions. The labeled frequencies are those of internal rotor transitions and are relative to the origin at 31 458 cm^{-1}. Assignments are given in Table 1.

levels for the S$_1$ and cation states. The potential for internal rotation used in the calculation is

$$\begin{aligned} V(\phi) = (V_3/2)[1 - \cos(3\phi_1)] + (V_3/2)[1 - \cos(3\phi_2)] + \\ (V_6/2)[1 - \cos(6\phi_1)] + (V_6/2)[1 - \cos(6\phi_2)] + \\ V_{12} \cos 3\phi_1 \cos 3\phi_2 + V'_{12} \sin 3\phi_1 \sin 3\phi_2 \quad (1) \end{aligned}$$

where ϕ_1 and ϕ_2 are the torsional angles between the methyl groups and the benzene ring, V_3 and V_6 are the 3-fold and 6-fold potentials to methyl rotation, and V_{12} and V'_{12} are potentials that describe rotor−rotor interactions. The Hamiltonian is expressed by

$$H = -B\, d^2/d\phi^2 + V(\phi) \qquad (2)$$

where B is the reduced rotational constant of the methyl rotor about the methyl top axis, and ϕ is described in the basis set of free uncoupled rotor wave function $\phi = \phi_{1n}\phi_{2m} = (2\pi)^{-1}e^{\pm in\phi}e^{\pm im\phi}$. The eigenvalues can be obtained by diagonalizing the Hamiltonian. The eigenvalues for a single rotor were calculated following the method given by Lewis et al.[47] where the basis set of even and odd basis functions was used. The degenerate odd 3a$''_1$ and even 3a$''_2$ levels are split in a 6-fold periodic potential, and the a$_1$ level is above the a$_2$ level for a positive V_6 and below a$_2$ for a negative V_6. The calculation of the coupled rotor levels was then performed according to Tan et al.[48,49] A good fit to our experimental line positions is reached when $V_3 = 0$ cm^{-1} and $V_6 = 25$ cm^{-1} for the S$_1$ state[4] and $V_3 = 0$ cm^{-1} and $V_6 = -16$ cm^{-1} for the ion. The B value is fixed at 5.2 cm^{-1} in both states. The V_3 potential is zero due to the high symmetry of *p*-xylene with respect to both rotors. Including the cross potential interaction terms in the calculation does not improve the fit and is thus determined to be zero. This is consistent with our earlier assumption that the methyl rotors do not interact. The calculated transitions are compared with the observed PFI transitions in Table 1. The agreement remains reasonable within 10% of the potential parameters. The V_6 barrier determined here for the cation of *p*-xylene is close to the reported V_6 values for *p*-xylene[4] in the S$_0$ (10 cm^{-1}) and S$_1$ (25 cm^{-1}) state and those of toluene in the S$_0$ (10 cm^{-1}),[4] S$_1$ (25 cm^{-1}),[4] and ionic (−16 cm^{-1})[7] states. The very low V_6 internal rotational barriers indicate that the methyl groups in *p*-xylene and toluene are nearly free rotors.

***m*-Xylene.** The two-color REMPI spectrum of the *m*-xylene S$_1$ state is shown in Figure 2. The predominant feature in the spectrum is the intense triplet in the origin region with components at 36 944.1, 36 947.6, and 36 951.1 cm^{-1}. The triplet is the result of different nuclear spin states associated with the a and e levels which cannot be depopulated by supersonic expansion cooling. For xylene, three different states of the molecule exist which cannot interconvert: those of the 0a$'_1$0a$'_1$, 1e$''$0a$'_1$, and the 1e$''$1e$''$ internal rotational levels. The relative statistical weights for these states are 1:2:1, respectively. This ratio coincides with the observed relative intensities in Figure 2. Breen et al.[4] measured the dispersed emission spectra from each of the three levels in the origin region and assigned the highest energy component of the triplet as the true origin, i.e., the 0a$'_1$0a$'_1$ → 0a$'_1$0a$'_1$ transition. It follows then that the features shifted −3.5 and −7 cm^{-1} from the origin arise from the 1e$''$0a$'_1$ → 1e$''$0a$'_1$ and the 1e$''$1e$''$ → 1e$''$1e$''$ transitions, respectively. The energy levels in both ground S$_0$ and excited S$_1$ states were assigned, and potential barriers in each state were calculated.[4] The excited S$_1$ state barrier was found to be significantly higher than that in the ground state.[4] This again is consistent with the observed triplet feature. The red-shifted, hot band triplet components observed in our spectrum were not reported by Breen et al.[4] and show relative shifts of 12, 15, and 18 cm^{-1} from the 0a$'_1$0a$'_1$ origin. Hot bands are also observed to the red of the lowest torsional band at 36 985 cm^{-1}. The hot bands could not be fit to any combination of the methyl rotor transitions produced using the reported S$_0$ and S$_1$ torsional barriers. The hot transitions are therefore likely to arise from torsional band structure built on a low-energy vibration of *m*-xylene.

The three components of the intense triplet in Figure 2 are sufficiently resolved that they can be selectively excited as intermediate states using a fixed narrow-band laser. A second laser is then scanned to produce PFI-ZEKE spectra where transitions are restricted by the selection rules governed by the symmetry of the populated S$_1$ intermediate state. PFI-ZEKE spectra produced through excitation via the 0a$'_1$0a$'_1$, 1e$''$0a$'_1$, and the 1e$''$1e$''$ levels of S$_1$ are shown in Figure 3, a, b, and c, respectively. The origin of the ground ionic state is assigned to the feature at 32 165 cm^{-1} found in each of the three PFI-ZEKE spectra. The ionization potential of *m*-xylene is thus determined to be 69 110(2) cm^{-1}. Several transitions comparing different pairs of spectra in Figure 3 are found at the same frequencies, suggesting the two methyl rotors groups of *m*-xylene cation are acting independently of each other. This conclusion is clarified by examining the symmetry labels of the transitions connected by the vertical lines in Figure 3 listed in Table 1. Here, for example, the 1e$''$1e$''$ → 1e$''$2e$'$ transition in Figure 3c is isoenergetic with the 1e$''$0a$'_1$ → 2e$'$0a$'$ transition

TABLE 1: Energies of Transitions between Internal Rotational Levels in the S_1 and Ground Ionic States of Xylene

	transition ($S_1 \rightarrow$ ion)	calcd (cm^{-1})	exptl (cm^{-1})
p-xylene	$0a'_1\,0a'_1 \rightarrow 0a'_1\,0a'_1$	0	0
$V''_3 = 0\ cm^{-1}$, $V''_6 = 10\ cm^{-1\,a,c}$	$0a'_1\,1e'' \rightarrow 0a'_1\,1e''$	0.03	0
$V'_3 = 0\ cm^{-1}$, $V'_6 = 25\ cm^{-1\,a,c}$	$1e''\,1e'' \rightarrow 1e''\,1e''$	0.06	0
$V_3 = 0\ cm^{-1}$, $V_6 = 16\ cm^{-1\,b,c}$	$0a'_1\,1e'' \rightarrow 0a'_1\,2e'$	15.5	13
	$1e''\,1e'' \rightarrow 1e''\,2e''$	15.5	13
	$0a'_1\,0a'_1 \rightarrow 0a'_1\,3a''_1$	42.9	44
	$1e''\,0a'_1 \rightarrow 1e''\,3a''_1$	42.9	44
	$0a'_1\,1e'' \rightarrow 0a'_1\,4e'$	78.4	75
	$1e''\,1e'' \rightarrow 1e''\,4e'$	78.4	75
	$0a'_1\,2e' \rightarrow 0a'_1\,5e''$	109.8	112
	$0a_1'\,2e' \rightarrow 3a''_1\,4e'$	108.0	112
	$3a''_1\,0a'_1 \rightarrow 6a'_1\,0a'$	146.2	144
m-xylene	$1e''\,1e'' \rightarrow 1e''\,1e''$	0	0
$V_3 = 0\ cm^{-1}$, $V''_6 = 25\ cm^{-1\,a,c}$	$1e''\,1e'' \rightarrow 1e'\,2e''$	70.3	73
$V_3 = 81\ cm^{-1}$, $V'_6 = 30\ cm^{-1\,a,c}$	$1e''\,1e'' \rightarrow 1e''\,5e''$	167.5	169
$V_3 = 125\ cm^{-1}$, $V_6 = 40\ cm^{-1\,b,c}$	$0a'_1\,1e'' \rightarrow 0a'_1\,1e''$	0	0
	$0a'_1\,1e'' \rightarrow 0a'_1\,2e'$	70.3	72
	$0a'_1\,1e'' \rightarrow 3a''_1\,1e''$	82.5	83
	$0a'_1\,1e'' \rightarrow 3a''_2\,1e''$	96.9	95
	$0a'_1\,1e'' \rightarrow 0a'_1\,5e''$	167.5	169
	$0a'_1\,0a'_1 \rightarrow 0a'_1\,0a'_1$	0	0
	$0a'_1\,0a'_1 \rightarrow 0a'_1\,3a''_2$	82.5	81
	$0a'_1\,0a'_1 \rightarrow 0a'_1\,3a''_1$	96.9	93
o-xylene	$0a'_1\,0a'_1 \rightarrow 0a'_1\,3a''_1$	195.0	195
$V''_3 = 425\ cm^{-1}$, $V''_6 = 18\ cm^{-1\,a,c}$	$0a'_1\,0a'_1 \rightarrow 0a'_1\,3a''_2$	216.0	210
$V'_3 = 166\ cm^{-1}$, $V'_3 = -25\ cm^{-1\,a,d}$	$0a'_1\,1e'' \rightarrow 3a''_1\,1e''$	218.4	224
$V'_6 = 0\ cm^{-1}$, $\chi = 0.72\ cm^{-1}$			
$V_3 = 425\ cm^{-1}$, $V_6 = 0\ cm^{-1\,b,d}$			
$V_{12} = 30\ cm^{-1}$, $V'_{12} = -90\ cm^{-1}$			

[a] S_0 state and S_1 state, ref 4. [b] Ion state, this work. [c] $V_{12} = 0$, $V'_{12} = 0$, $B = 5.2\ cm^{-1}$. [d] $B = 5.2\ cm^{-1}$.

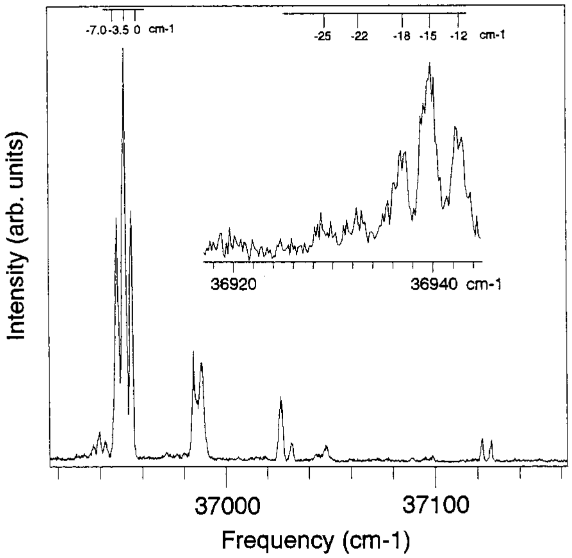

Figure 2. Two-color REMPI spectrum of the 0^0_0 region of *m*-xylene. The intense triplet corresponds to the three lowest levels in the S_1 state which cannot interconvert due to symmetry restrictions. The band at 36 951.1 cm^{-1} is assigned to the vibrationless and internal rotationless S_1 origin (ref 4.). The indicated frequencies are relative to this origin. The less intense, red-shifted triplet is expanded in the inset of the figure and is not due to hot torsional bands but rather a hot vibration.

in Figure 3b; hence, the excitation 2e′ must be localized on a single methyl group. Interactions between the two methyl groups would result in different transition energies to levels of different symmetry. Table 1 lists the calculated transitions between levels for internal rotations in the S_1 excited state for $V_3 = 81\ cm^{-1}$ and $V_6 = -30\ cm^{-1}$ and in the ionic state for $V_3 = 120\ cm^{-1}$ and $V_6 = 40\ cm^{-1}$. The B value is fixed at 5.2 cm^{-1} in both states. The fit of the calculated values to the spectrum is quite good and remains unchanged with 10% of the potential parameters. This again justifies the assumption that the two methyl groups are noninteracting.

The higher vibrational bands seen in the spectra are likely to be due to higher torsional bands coupled to low-lying vibrations. As such, no attempts were made to fit them using our potential. Several $a_1 \leftrightarrow a_2$ transitions are reported that fit well to our calculated transitions. These $a_1 \leftrightarrow a_2$ transitions are forbidden electronic transitions but are not strictly forbidden in photoelectron spectra.[50] These “forbidden” transitions are not observed in the $S_0 \rightarrow S_1$ spectrum of *m*-xylene nor are they observed in the $S_0 \rightarrow S_1$ or $S_1 \rightarrow$ ion spectrum of *p*-xylene. Coriolis type interactions are often invoked to explain the appearance of such forbidden transitions and may apply here as well. Ito et al.[14] observed similar forbidden transitions in the ZEKE-PFI spectrum of *m*-fluorotoluene and suggested an intensity borrowing scheme where forbidden transitions are induced by vibronic couplings between high Rydberg states through methyl rotational motions. Either explanation is plausible.

***o*-Xylene.** The PFI-ZEKE spectrum of *o*-xylene is depicted in Figure 4. The intense single feature at 31 895 cm^{-1} is assigned to the origin band of the ground state of the ion. The ionization potential is thus 69 200(2) cm^{-1}. The assigned origin transition is followed by a ~200 cm^{-1} flat expanse from the origin to the first group of peaks which appear at ~32 100 cm^{-1}. The lack of structure at low frequencies immediately points to a rather high potential barrier to internal rotation, i.e., a strongly hindered rotor. Steric hindrance between the two adjacent methyl rotors of *o*-xylene is not entirely unexpected and has already been reported in the S_1 state.[4] The measured torsional bands were fit using the potential in (1) with $V_3 = 425\ cm^{-1}$, $V_{12} = 30\ cm^{-1}$, and $V'_{12} = -90\ cm^{-1}$ and the S_1 values reported in ref 4. The B values are fixed at 5.2 cm^{-1} in both states. Table 1 lists the calculated and experimental transitions along with their symmetry assignments. The V_{12} rotor−rotor interac-

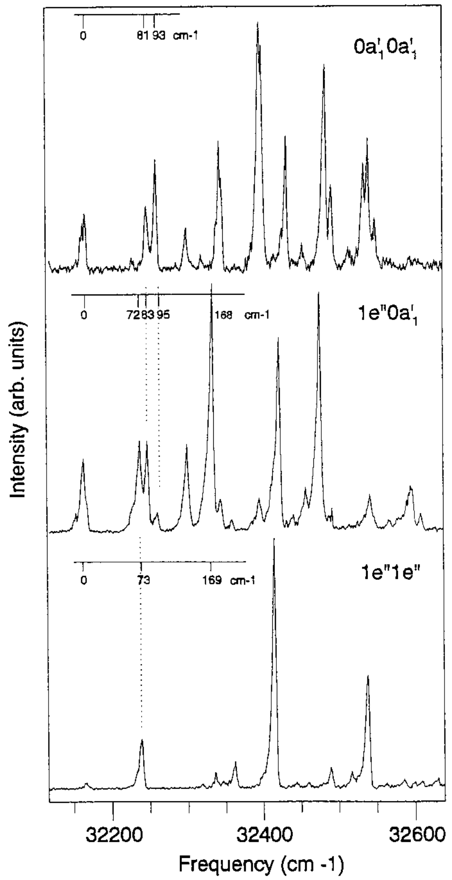

Figure 3. Mass analyzed ZEKE spectra of *m*-xylene obtained by the selective excitation of the components of the intense triplet shown in Figure 2. The upper (via 36 951.1 cm^{-1}), middle (via 36 947.6 cm^{-1}), and lower (via 36 944.1 cm^{-1}) spectra arise through the selective excitation of intermediate states of symmetry $0a'_1 0a'_1$, $1e''0a'_1$, and $1e''1e''$, respectively. The labeled internal rotor transitions frequencies are relative to the origin band at 32 165 cm^{-1}. Assignments are given in Table 1.

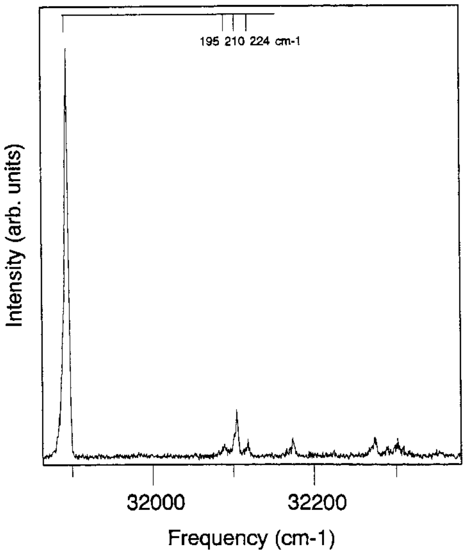

Figure 4. Mass analyzed ZEKE spectrum of *o*-xylene. The most intense band at 31 895.2 cm^{-1} is assigned to the origin. The weak features >200 cm^{-1} to higher energy of the origin are due to methyl rotations.

tion term must be included in the potential in order to best fit the experimental data. This indicates a strong interaction between the two rotors of the *o*-xylene cation, in contrast to the cations of *p*- and *m*-xylene. The higher effective barrier found for *o*-xylene is consistent with this rotor–rotor interaction.

Summary and Conclusion

The measured PFI-ZEKE spectra of *o*-, *m*-, and *p*-xylene have been used to determine the potential barriers of methyl rotation in the ground ionic state. The potential barriers for the xylene cation are summarized in Table 1. The barrier height to internal rotation of the methyl groups of *p*-xylene correspond to the V_6 barrier, that of *m*-xylene to a $V_3 + V_6$ barrier, and that of *o*-xylene to a $V_3 + V_{12} + V'_{12}$ barrier. Table 1 also lists the potential barriers determined for the S_0 and S_1 neutral states.[4] A comparison of the data in Table 1 for the xylene cations and the data determined for neutral xylene[4] shows that the barrier heights are quite different for different states. For the neutral and ionic states of the xylenes, the methyl rotor potential barrier increases in the order para < meta < ortho and could be attributed simply to the increased steric hindrance between rotors in the series. One should note that the analogous series of fluorotoluenes shows the same trend,[14] and thus the hindrance in *o*-, *m*-, and *p*-xylenes is likely to arise from interactions between the average mass of the CH_3 group and not necessarily between individual methyl hydrogens. Trends in the methyl rotor barrier heights through the S_0 to S_1 to the ion state are less obvious. The barrier heights determined for *p*-xylene on going from S_0 to S_1 to the ion change very little while the barrier heights in the same series for *m*-xylene show significant increases. *o*-Xylene shows a decrease in *effective* barrier height in the ion state relative to S_0, and the barrier determined for S_1 is smaller than that in S_0 and the ion. In addition, the methyl group interactions, which are strong in the S_1 and in the ion state but are nonexistent in the S_0 state, are inconsistent with the effects one might expect on the rotor barrier; i.e., intuitively, an increase in the methyl group interactions would lead to an increase in the methyl rotor barrier height. The results determined in these experiments do not fit with the trend of increasing rotor barriers with ionization, determined for a small number of experimentally derived methyl barrier heights.[7,9,14] The interpretations often used to explain the restricted rotation of methyl groups, which include hyperconjugation and steric effects, should thus be cautiously reserved until more data on a number of different ionic systems are accumulated.

The approximation of noninteracting methyl rotors was shown to be valid for the ion state of *p*-xylene by comparing its PFI-ZEKE spectrum to the corresponding PFI-ZEKE spectrum of toluene. In addition, we were able to fit the methyl torsional potential using a double-rotor calculation which duplicated the experimental energies by calculating combinations of individual methyl group rotation states. The *m*-xylene cation was also shown to have two noninteracting methyl groups. Here, we compared three ZEKE spectra taken from different intermediate levels which form pairs of spectra with one methyl group of common symmetry. Again, as with *p*-xylene, we were able to fit the rotor transitions assuming no interactions between individual rotors. For *o*-xylene we do find strong coupling in the ionic state and were forced to fit the rotor transitions using a rotor–rotor cross term. The methyl group interactions found in *o*-xylene are consistent with those found in other ortho species.[4,49]

Finally, the correlation between the ionization potentials and the torsional barriers is worth mentioning. The IP determined for *p*-xylene is ~1000 cm^{-1} lower than the IP's determined for *o*- and *m*-xylene, and the effective methyl rotor barrier for *p*-xylene is also significantly lower compared to those of *o*-

and *m*-xylene. If the low barrier in *p*-xylene results from little steric hindrance and small electronic interactions, then one would assume very little hyperconjugation. If hyperconjugation plays a role in the higher methyl rotational barriers of *o*- and *m*-xylene, then one would expect a stabilization of the π-system due to this hyperconjugation and the higher ionization potentials measured here.

Laser supersonic molecular jet spectroscopy is a proven method for studying the properties of isolated cold molecules and clusters in their ground and excited electronic neutral states. ZEKE spectroscopy extends these studies to include the ionic states. ZEKE spectra (i.e., ion spectra) of a number of molecules have been recorded with vibrational and even rotational resolution.[16] The spectra of van der Waals ionic clusters and hydrogen-bonded ionic complexes have also been recorded using the ZEKE technique.[51,52]

The results of the work presented here represent a further demonstration of ZEKE spectroscopy as a technique to probe the properties and dynamics of molecular ions. Here we have used the high resolution offered by ZEKE spectroscopy to investigate the internal methyl rotations of xylene in the ground ionic state. Studies performed on the cresol[9] and fluorotoluene[14] ions constitute the only other work of this type to date. The internal rotor levels of such systems are closely spaced and thus necessitate a high-resolution spectroscopy to resolve the transitions. As demonstrated in this study and those referred to above, the properties of ionic species are often very different from those of their neutral counterparts. Hence, the facile extension of ZEKE spectroscopy to the investigation of the physical properties of ions with the same quality and ease of those performed using laser supersonic jet techniques for neutrals is very important. It demonstrates that these are subtle effects in the interactions between rotors in various electronic states that are clearly molecule specific. The results presented here will hopefully inspire a further extension of studies which have already been established in the neutral state to the ionic state.

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