

# The R2PI Spectroscopy of Tyrosine: A Vibronic Analysis

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Based on an infrared spectrum in an atlas, and on a Raman spectrum that we acquired ourselves, we have made a frequency assignment for the vibrational modes of tyrosine. This assignment was aided by the results of a GAUSSIAN frequency calculation that we performed at the Hartree–Fock level, using the 3-21G basis set. We have made a vibronic assignment of the bands in a jet-cooled LD-R2PI spectrum that we obtained for tyrosine, using the aforementioned ground-state analysis as a guide. By UV hole burning, we have verified which of the low-frequency R2PI peaks are origins, assigning the others as torsions. We have assigned the various origin bands, with their associated bands to higher energy, to configurations in which the amino acid backbone is either *gauche* or *anti* to the ring. © 2002 Elsevier Science (USA)

**Key Words:** amino acid; assignment; conformer; infrared; IR; jet cooling; *p*-alkylphenols; Raman; REMPI; resonance-enhanced multiphoton ionization; R2PI; resonant two-photon ionization; spectroscopy; tyrosine; UV; ultraviolet; vibration; vibronic; vibronic analysis.

## INTRODUCTION

Tyrosine, one of the building blocks of proteins, is especially important for its role as a precursor to dopamine, a neurotransmitter, which is, in turn, a precursor to the neurotransmitters epinephrine and norepinephrine. With the goal of identifying some of the physical properties that cause these neurotransmitters to exhibit their interesting biological behavior, we have been studying the vibronic spectroscopy of families of structurally related compounds. The spectroscopy of tyrosine has been studied fairly extensively, both in the ground state (1, 2) and for electronic transitions (3–5). As far as we can tell, however, no one has yet made a complete assignment for the ground-state vibrations or for the vibronic transitions between the ground and first excited electronic states. Martinez (5) has studied in detail the origin ( $v' = 0 \leftarrow v'' = 0$ ) region of the vibronic spectrum of tyrosine, particularly with an eye toward the possible lowest energy conformations tyrosine may adopt. We have also been studying the question of what the stable conformations are for tyrosine and how this affects its vibronic spectroscopy and that of small peptide chains that contain tyrosine on either end. Of particular interest is the possibility that the carboxyl group in tyrosine, in some conformations, may interact with the  $\pi$  electron system of the benzene ring. In a separate paper (6), we have described our work concerning the conformers of tyrosine, and we have compared the spectra obtained for various tyrosine-containing peptides with each other and with that obtained for tyrosine. In this paper we give a ground-state vibrational assignment for tyrosine, and we present a resonant two-photon ionization (R2PI) spectrum for tyrosine with a vibronic assignment.

## THEORY AND METHODS

The goal of this work was to understand the R2PI spectrum of tyrosine, and primarily to make assignments for as many bands as possible. While one would normally expect some differences between the excited-state and ground-state vibrations of a molecule, ground-state vibrational data and assignments can often serve as a useful reference for analyzing the R2PI spectrum. First, selection rules dictate that in general, bands that are intense in the Raman spectrum also appear strongly in the R2PI spectrum. Intense IR bands, if they are not also intense in the Raman, do not, and the vibrations that give rise to them exhibit weak R2PI bands or appear in double quanta. In addition, unless the molecule changes shape significantly upon excitation, in most cases one would expect the molecule to expand slightly, the force field to become correspondingly weaker, and all the vibrational frequencies to decrease slightly. Thus, if used judiciously, IR and Raman data can greatly assist the interpretation of the R2PI spectrum. To this end we analyzed IR and Raman data to obtain a ground-state vibrational assignment. The theory and rationale behind this assignment are discussed in considerable detail elsewhere (7–9), but we note here a few useful points.

Tyrosine is essentially a *para*-alkylphenol, albeit with a somewhat complicated alkyl chain, whose main structural feature is a benzene ring. One may therefore reasonably expect to observe benzene-like vibrations and, in addition, vibrations arising from the substituent chain and the hydroxyl group. In fact, even when the benzene ring has polyatomic substituents, if they are not too rigidly attached, and if their motions do not couple too strongly to those of the ring, then as far as the ring vibrations are concerned, they may be treated as point masses. In this case, the symmetry

of the molecule with respect to the benzene ring may be taken as that which would obtain if the substituents were single atoms (8, 10). The ring modes of all *p*-alkylphenols would thus transform according to  $C_{2v}$  symmetry, with the principal symmetry axis running through the two substituted carbon atoms. In fact, and as we will show in this paper for tyrosine, in their vibronic spectra the *p*-alkylphenols exhibit symmetry that is probably at least as great as  $C_s$ .

Studies of the infrared spectroscopy of substituted benzenes date back to the early 1930s with the work of Freymann (11), Kohlrausch and Pongratz (12), Barchewitz (13) and LeComte (14–16). Since then, much work has been done concerning both the ground-state and excited-state spectroscopy of benzenes substituted in various ways (7, 8, 17–23). The only systematic study of the ground-state spectroscopy of *para*-substituted phenols, however, appears to be that of Jakobsen and Brewer (24). Cabana and Sandorfy (20) did study a group of *para*-substituted phenols, but only with regard to the OH stretching mode. Jakobsen made a complete ground-state assignment for *p*-cresol and several deuterated *p*-cresols (25). This was followed by a normal coordinate analysis for a similar group of compounds by Takeuchi *et al.* (26). Green *et al.* extended Jakobsen's work to the *para*-halogenated phenols (27). A ground-state assignment for tyrosine does not appear to be available in the literature, although a partial assignment may be found in the work of Rava and Spiro (1) and that of Takeuchi *et al.* (2).

The patterns in the spectra of benzene derivatives that have the same substituent arrangements, as well as the behavior described above regarding polyatomic substituents, allowed Varsanyi to describe in a systematic way the spectroscopy of substituted benzenes (7), and to compile an atlas comprising tables of IR and Raman data, with assignments for 700 benzene derivatives (8). It also allowed us, using Varsanyi's work as a starting point, to analyze the tyrosine spectrum by analogy with the spectra for several other *p*-alkylphenols, using data from the literature cited above as well as data that we acquired ourselves.

To provide a further guide for the assignments, we performed *ab initio* frequency calculations for several *p*-alkylphenols, including tyrosine. For each molecule we visualized each vibrational mode, and were thus able to arrive at a theoretical assignment. For the work described here, we made the calculation for only one stable conformer of tyrosine. We describe the methods we used to do this in the next section.

## EXPERIMENTAL

### Ground-State Data and Experiments

As there are no published IR or Raman data for tyrosine, at least for a frequency range that encompasses all its vibrational modes, we used the IR spectrum from the *Aldrich Library of Infrared Spectra* (28). We measured the bands in this spectrum, at their maximum intensities, according to the chart grid. With this spectrum, calibrated frequencies are given for the nine most intense bands. For these bands most of the measured values agreed

with the calibrated values to within  $\pm 2 \text{ cm}^{-1}$ , and none differed by more than  $\pm 5 \text{ cm}^{-1}$ . As this spectrum was obtained with a Nujol mull, we removed the bands arising from Nujol itself (29, 30). We obtained the Raman spectrum in house, from tyrosine powder. The instrument we used has been described in the literature (31), and we will not describe it here. Nonetheless, we must note several things. The 532-nm output of a doubled Nd:YAG laser provided the excitation. For calibration, we obtained emission spectra of neon and krypton. The wavelength scale was then fit to the neon and krypton lines in the range from 540.06 to 671.7 nm by means of a least-squares curvilinear regression. The calibration covers the range from about  $280 \text{ cm}^{-1}$  to about  $3909 \text{ cm}^{-1}$  in Raman shift. As may be obvious from the calibration wavelengths, the acquired spectrum comprised the Stokes lines.

### The R2PI Experiments

The technique we used to obtain the R2PI spectrum of tyrosine was laser-desorption/jet-cooled resonant two-photon ionization with time-of-flight mass spectrometric detection (LD/R2PI/TOF-MS). The instrument we used to perform this work has been described elsewhere (32). We therefore note here only a few important technical details.

The sample probe in our instrument is a graphite block that sits approximately 0.5 to 1.5 mm below the nozzle orifice, flush with the plate in which the orifice is drilled. This distance is adjusted for optimum signal at the beginning of each run. The nozzle orifice has a diameter of 1 mm. The desorption laser is a Nd:YAG laser whose output beam is focused to an  $\sim 0.5$ -mm-diameter spot, with a fluence of  $\sim 1 \text{ mJ/cm}^2$  or less,  $\sim 1 \text{ mm}$  downstream from the nozzle and in line with the jet axis. For the experiment reported here, the carrier gas was argon at a pressure of 5 atm. The graphite block is attached to a screw drive that pulls the sample across the jet axis, thus renewing the surface continuously during the run. The sample was prepared by mashing the tyrosine into a fine powder with the graphite block and thus grinding it into a thin layer on the surface of the block.

The mass spectrometer in this experiment is a reflectron instrument made by R. M. Jordan Company.

### *Ab Initio* Calculations

For the frequency calculations, we chose the GAUSSIAN series of molecular orbital programs, and for tyrosine the specific program we used was Gaussian 92 (33). We used the Hartree-Fock method with the 3-21G basis set. To perform this calculation we first optimized the geometry of the molecule, after which we did the frequency calculation. For each vibrational mode, along with the frequencies, GAUSSIAN gives the displacements from the equilibrium geometry, along the *x*-, *y*-, and *z*-axes, for each atom. By taking these displacements and adding them to, and subtracting them from, the coordinates in the equilibrium geometry, one can obtain the extremes of the various normal modes. By means of an Excel spreadsheet, we did this, and then we fed the resulting coordinates into a molecular editor

program (34), which allowed us to view both extremes of each normal mode on a computer terminal, and also to print them.

As tyrosine is a disubstituted benzene, we felt it was worthwhile to perform a calculation for benzene itself to be certain how GAUSSIAN represents its normal modes. Once we visualized the benzene modes according to the atom displacements calculated by GAUSSIAN, we could then match directly the corresponding modes in the set visualized for tyrosine.

## RESULTS AND DISCUSSION

### Ground-State Data

Table 1 lists the bands we observed in the IR and Raman spectra for tyrosine, with our assignments. First, we must make

a comment regarding the notation used in the assignments. For the benzene modes we use the Wilson notation (7, 8). When the benzene ring is substituted, some of the C–H modes become “C–X” modes, where X represents a substituent group. In a *para*-disubstituted benzene, two C–H stretches become C–X stretches, two in-plane C–H bends become C–X bends, and two out-of-plane C–H bends become C–X bends. One has considerable freedom in choosing which specific benzene modes become C–X modes. The only requirement, aside from frequency considerations, is that one choose pairs of stretches and bends that have opposite phasing for the motions of the substituents. Not only does the way these modes are designated vary from author to author, but in fact, the system Varsanyi uses in his atlas differs from the one he uses in his text. An additional problem arises because some modes have alternate designations. For example,

**TABLE 1**  
Observed Bands in the IR and Raman Spectra for Tyrosine, with Their Assignments: All IR and Raman Values Are in  $\text{cm}^{-1}$

IR, Nujol	Raman (rel. int.)	Assignment	IR, Nujol	Raman (rel. int.)	Assignment
	87 (19) <sup>b</sup>	Chain torsion	1176 (m)	1179 (37)	9a
	108 (42) <sup>b</sup>	HOOCNH <sub>2</sub> torsion	1196 (mw)	1200 (19)	
	122 (75) <sup>b</sup>	COOH torsion	1212 (mw, sh)	1213 (28)	7a
	140 (7) <sup>b</sup>	NH <sub>2</sub> torsion	1151 (m)	1153 (11)	
	163 (54)	11	1245 (s-vs)	1251 (19)	Ring OH ip bend
	255 (7) <sup>a</sup>	15	1268 (sh)	1263 (19)	14
	333 (7) <sup>a</sup>	10b	1328 (s-vs)	1329 (28)	13
	384 (7) <sup>a</sup>	9b		1370 (11)	Chain CH bend
	Calc. 416 <sup>c</sup>	16a	1415 (m)		Chain CH bend
434 (w)	427 (11)	6a	1437 (sh)	1437 (20)	19b
498 (m)		Chain bend	1513 (s)		19a
535 (m-s)		16b	1532 (vw, sh) <sup>d</sup>		
558 (vw)		Chain bend	1588 (s-vs, t)	1598 (16) <sup>a</sup>	8b
576 (m-s)		Chain bend		1604 (18) <sup>a</sup>	
639 (vw, sh)	641 (26)	6b	1605 (mw, sh, t)	1616 (30)	8a
645 (m)			1628 (w, sh, t)		
	714 (9)	4	1900 (vw)		Combination
739 (m)		12	2092 (mw)		Combination
796 (vbw, sh)	797 (19)	NH <sub>2</sub> “wag”	2500 (vw)		Combination
807 (m)			2599 (vw, sh)		Combination
828 (vw, sh)	828 (93)	1	2643 (vw)		Combination
	Calc. 841 <sup>c</sup>	1	2739 (w)		Combination
841 (m-s)	845 (26)	2 × 16a		2933 (67)	Chain C–H stretch
878 (m)		Chain C–C stretch	2955	2955 (30) <sup>a</sup>	Chain C–H stretch
899 (w)		Chain asym. stretch		2963 (77)	Chain C–H stretch
939 (w)		5		2966 (73)	7b
	971 (9) <sup>a</sup>	17a	3019	3020 (26)	20b
982 (w)	982 (17)	Chain CH <sub>2</sub> “rocks”	3036	3046 (23)	20a
989 (vw-w, d) <sup>d</sup>	989 (17)	Chain CH <sub>2</sub> “rocks”		3065 (100)	2
1016 (vw)		18a	3113	3137 (23)	NH <sub>2</sub> sym. stretch
1045 (m)	1046 (17) <sup>a</sup>	(Chain) C–N stretch		3167 (14) <sup>a</sup>	NH <sub>2</sub> asym. stretch
1099 (mw, d)		Chain C–O stretch	3206 (m-s)	3208 (14) <sup>a</sup>	O–H stretch (COOH)
1110 (m-s, d)		18b		3336 (10) <sup>a</sup>	O–H stretch (ring)

<sup>a</sup> Peak is difficult to discern.

<sup>b</sup> May be in the “tail” of the filter that removes Rayleigh scattering.

<sup>c</sup> Frequencies calculated from Fermi doublet by frequency-intensity relation given by Lord and Siamwiza. (36)

<sup>d</sup> Not in D-tyrosine spectrum.

Numbered assignments denote benzene ring modes, in Wilson notation. w-weak; m-medium; s-strong; v-very; d-part of a doublet; t-part of a triplet; sh-shoulder; ip-in-plane.

some authors designate benzene mode 13, in which the motion of the substituents is in opposite phase to that in mode 7a, as 7a'. In this work, we use the scheme from Varsanyi's atlas. For reference, in an Appendix we have included diagrams of the ring vibrations, numbered according to the Wilson notation, modeled after those given by Brodersen and Langseth (35).

It would be somewhat impractical to describe these assignments band by band, but there are several important points to note. We assume that the most intense peak in the Raman spectrum, in the region between 800 and 900  $\text{cm}^{-1}$ , is the ring "breathing" mode. In *para*-substituted benzenes, including tyrosine and other *para*-alkylphenols, a Fermi resonance occurs between the breathing mode and the second overtone of mode 16a (36). Lord and Siamwiza (37) give the mathematical expression relating the energy difference between the unperturbed modes, the energy difference between the perturbed modes, and the intensity ratio of the Raman bands. From this relation we calculated frequencies for the unperturbed modes 1 and 16a, which are listed, with the notation "Calc.," along with the observed bands. We assigned the OH bend according to the frequency shift it exhibits when the molecule changes between vapor and condensed phases. This behavior is well documented for *p*-cresol (25, 27).

Another thing we took into account in making our assignments was the relative variation in frequency of the vibrational modes as the nature of the substituents changes. Some modes exhibit considerable variation and are known as "X-sensitive." For other modes, called "X-insensitive," the frequency remains essentially constant for a variety of substituents. By fitting the frequencies calculated by Gaussian to those observed for the best-known X-insensitive modes, we were able to improve the confidence with which we could make the various assignments. Tables of the calculated vibrational frequencies for tyrosine and of the calculated frequencies for the ring vibrations of the other *p*-alkylphenols are presented in an Appendix.

We note here that the R2PI data helped decide the assignment of at least two bands in the ground-state spectrum, which fall at about 1265 and 1330  $\text{cm}^{-1}$ .

### R2PI Data

In 1988, Li and Lubman obtained an R2PI spectrum in the origin region for tyrosine (3). This spectrum showed only a few intense peaks, the most intense being at about 35 624, 35 654, and 35 670  $\text{cm}^{-1}$ . Some time later, Martinez *et al.* obtained a fluorescence spectrum that clearly showed many more features than appeared in Li's (5). They assigned as origins those bands in this region whose relative intensities did not change with laser power. There were 10 such peaks, and they labeled them A through J, associating each with a different conformer of tyrosine. With the hope of examining the origin region further, and also for the purpose of performing a vibronic analysis for tyrosine, the Lubman group obtained a second spectrum for tyrosine that extended approximately 900  $\text{cm}^{-1}$  to the blue of the origin

region (9). The origin region of this spectrum showed similar features to those in the spectrum of Li and Lubman. We believe that the cooling for the spectra from the Lubman group was insufficient, and that the resulting background obscured many of the spectral bands. Figure 1 shows the LD-R2PI spectrum that we recently obtained for tyrosine in the de Vries group. We have made no correction for variation in the laser power. The features between about 35 450 and 35 700  $\text{cm}^{-1}$  agree quite well with peaks A through J in Martinez' work. What appears as a low-frequency shoulder on peak E, however, appears in our spectrum as a separate peak. By means of a hole-burning experiment, which we described in our earlier paper mentioned above (6), we found pairs of bands within this region that were associated with each other. We thus found that J is actually not an origin, but rather a low-frequency mode built on origin D. The spacing between these two peaks is 48  $\text{cm}^{-1}$ , which we assign as a torsion of the entire side chain about the bond at the 4-position on the benzene ring. This work confirmed, however, that peaks A through I are indeed origins.

In our earlier paper (6) we also proposed that the pairs of origins separated by about 5  $\text{cm}^{-1}$  belong to conformers of tyrosine that differ only in the orientation of the -OH group on the ring. We thus arrived at a labeling scheme slightly different from that of Martinez, calling peaks A through I, respectively, A, B, B', C, D', F, G, E, and E', with an additional peak, D, 3  $\text{cm}^{-1}$  to the red of D'. We continue to use this nomenclature here. The establishment of which peaks in the origin region are truly origins and which arise from torsions greatly increased the confidence with which we could assign the bands in the rest of the spectrum.

In Fig. 1, we see that the spectrum contains clusters of peaks, the most intense of which appear at the origin and at about 800  $\text{cm}^{-1}$  to higher energy. There are another moderately intense cluster about 1200  $\text{cm}^{-1}$  from the origin and a group of somewhat weaker bands between the first two clusters. If the molecule does not change shape drastically upon excitation, so that the ground state and excited state have the same symmetry, odd overtones of totally symmetric vibrations are allowed, but forbidden for non-totally-symmetric vibrations, and even overtones for non-totally-symmetric vibrations are allowed, but expected to be weak. In such a case, the origin is usually also intense. The lower the symmetry of the molecule, the greater the number of vibrations that contain the totally symmetric representation. While oscillator strengths vary and not all allowed transitions necessarily yield intense bands, this would lead us to expect considerable vibronic activity, and thus a congested spectrum, for a molecule with little or no symmetry. Conversely, we would expect much less vibronic activity, and a much less crowded spectrum, for a molecule possessing high symmetry. Given that the spectrum in Fig. 1 represents, essentially, the overlap of 10 individual spectra, one for each origin, the relative lack of vibronic activity is remarkable, and it shows that despite the presence of the bulky amino acid side chain at the 4-position, the benzene chromophore behaves as if it has retained considerable symmetry.

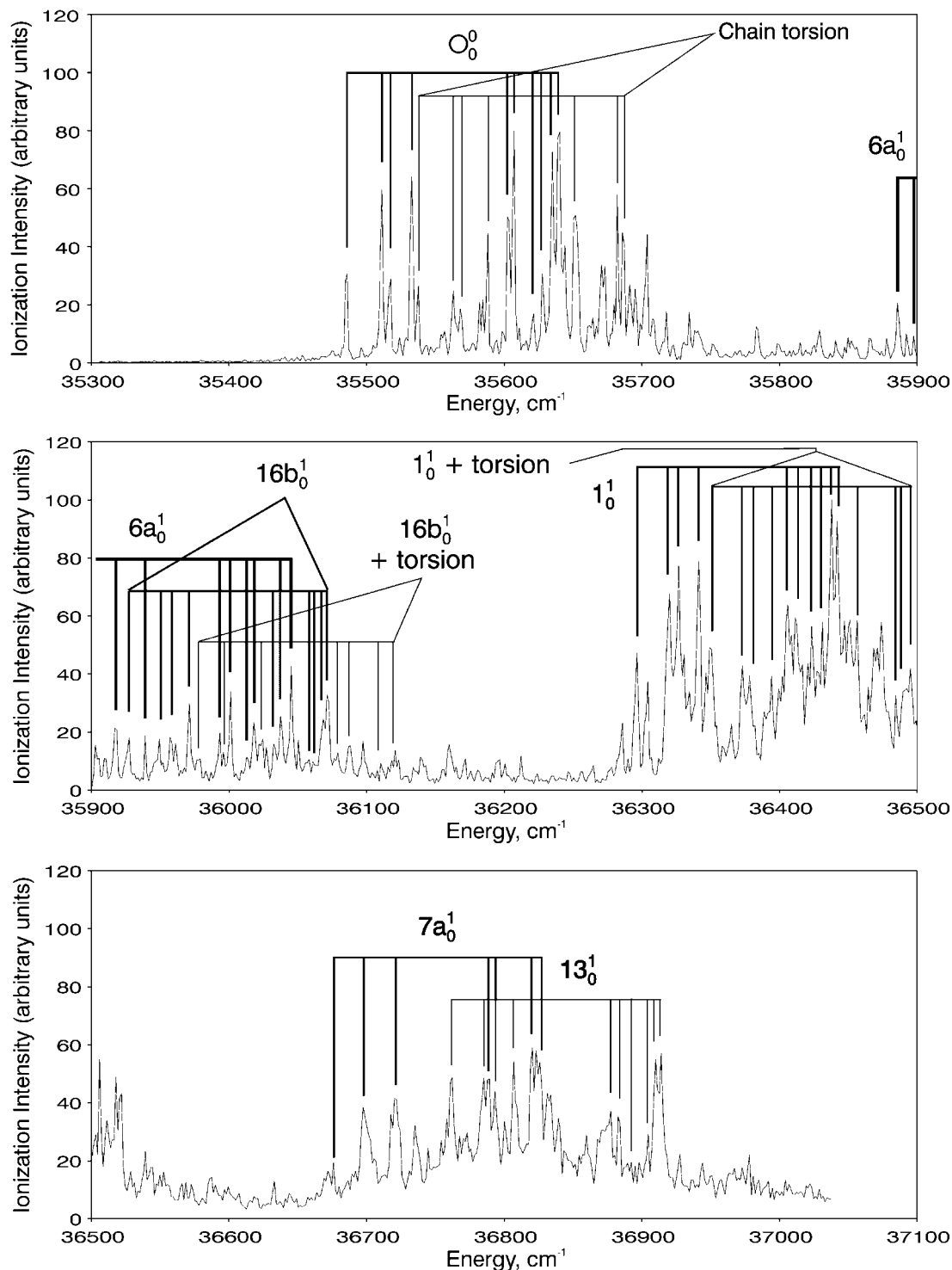


FIG. 1. LD-R2PI spectrum of tyrosine obtained in the de Vries group.

If the ring modes of tyrosine behaved according to  $C_{2v}$  symmetry, we would expect only those vibrations that transformed into the  $a_1$  symmetry species to appear with appreciable intensity. In the frequency range covered by our spectrum,

this would include modes 1, 6a, 7a, 9a, 12, 13, and 18a (8). If the molecule behaved according to  $C_s$  symmetry, transitions for all in-plane vibrational modes would be allowed, and we might expect, in addition, bands to appear from modes 6b, 9b, 14, 15,

TABLE 2  
Bands in the R2PI Spectrum of Tyrosine, with Their Proposed Assignments

$\bar{\nu}$ , cm <sup>-1</sup>	Int. <sup>a</sup>	Assignment	$\bar{\nu}$ , cm <sup>-1</sup>	Int. <sup>a</sup>	Assignment
35486	31	A <sub>0</sub> <sup>0</sup>	35949	18	B, 16b <sub>0</sub> <sup>1</sup>
35496	5		35957	18	B', 16b <sub>0</sub> <sup>1</sup>
35511	60	B <sub>0</sub> <sup>0</sup>	35961	16	
35518	29	B <sub>0</sub> <sup>0</sup>	35971	30	C, 16b <sub>0</sub> <sup>1</sup>
35524	9		35979	11	A, 16b <sub>0</sub> <sup>1</sup> + Chain torsion
35533	64	C <sub>0</sub> <sup>0</sup>	35993	20	D, 6a <sub>0</sub> <sup>1</sup>
35538	27	A <sub>0</sub> <sup>0</sup> + Chain torsion	35996	13	B, 16b <sub>0</sub> <sup>1</sup> + Chain torsion
35554	10		36001	34	D', 6a <sub>0</sub> <sup>1</sup>
35557	11		36013	11	F, 6a <sub>0</sub> <sup>1</sup>
35563	25	B <sub>0</sub> <sup>0</sup> + Chain torsion	36018	23	G, 6a <sub>0</sub> <sup>1</sup>
35568	19	B <sub>0</sub> <sup>0</sup> + Chain torsion	36024	18	C, 16b <sub>0</sub> <sup>1</sup> + Chain torsion
35582	21		36027	15	
35585	22	A <sub>0</sub> <sup>0</sup> + -COOH torsion	36032	16	D, 16b <sub>0</sub> <sup>1</sup>
35588	45	C <sub>0</sub> <sup>0</sup> + Chain torsion	36037	25	E, 6a <sub>0</sub> <sup>1</sup> /D', 16b <sub>0</sub> <sup>1</sup>
35604	49	D <sub>0</sub> <sup>0</sup>	36045	43	E', 6a <sub>0</sub> <sup>1</sup>
35607	80	D <sub>0</sub> <sup>0</sup>	36050	17	
35621	17	F <sub>0</sub> <sup>0</sup>	36058	10	F, 16b <sub>0</sub> <sup>1</sup>
35628	31	G <sub>0</sub> <sup>0</sup>	36061	10	G, 16b <sub>0</sub> <sup>1</sup>
35635	73	E <sub>0</sub> <sup>0</sup>	36069	24	E, 16b <sub>0</sub> <sup>1</sup>
35640	79	E <sub>0</sub> <sup>0</sup>	36072	33	E', 16b <sub>0</sub> <sup>1</sup>
35644	40		36076	11	
35652	51	D <sub>0</sub> <sup>0</sup> + Chain torsion	36079	13	D, 16b <sub>0</sub> <sup>1</sup> + Chain torsion
35662	13		36088	15	D', 16b <sub>0</sub> <sup>1</sup> + Chain torsion
35665	15		36097	17	
35671	34	F <sub>0</sub> <sup>0</sup> + Chain torsion	36108	7	
35674	33	G <sub>0</sub> <sup>0</sup> + Chain torsion	36110	9	E, 16b <sub>0</sub> <sup>1</sup> + Chain torsion
35680	20		36115	8	
35682	58	E <sub>0</sub> <sup>0</sup> + Chain torsion	36118	10	
35688	45	E <sub>0</sub> <sup>0</sup> + Chain torsion	36121	14	E', 16b <sub>0</sub> <sup>1</sup> + Chain torsion
35691	27		36123	10	
35695	25		36134	8	
35704	44	D <sub>0</sub> <sup>0</sup> + -COOH torsion	36139	11	
35709	15	D <sub>0</sub> <sup>0</sup> + -COOH torsion	36155	7	
35718	17		36160	16	
35723	6	F <sub>0</sub> <sup>0</sup> + -COOH torsion	36165	8	
35731	7	G <sub>0</sub> <sup>0</sup> + -COOH torsion	36172	11	A, 12 <sub>0</sub> <sup>1</sup>
35735	17	E <sub>0</sub> <sup>0</sup> + -COOH torsion	36176	6	
35738	11	E <sub>0</sub> <sup>0</sup> + -COOH torsion	36181	7	
35751	6	A, 10b <sub>0</sub> <sup>1</sup>	36195	10	B, 12 <sub>0</sub> <sup>1</sup>
35772	4		36200	9	B', 12 <sub>0</sub> <sup>1</sup>
35778	4	B, 10b <sub>0</sub> <sup>1</sup>	36212	12	C, 12 <sub>0</sub> <sup>1</sup>
35783	12	B', 10b <sub>0</sub> <sup>1</sup>	36246	6	
35800	6	C, 10b <sub>0</sub> <sup>1</sup>	36256	6	
35815	7		36265	8	
35829	11		36278	8	
35841	8		36286	23	D, 12 <sub>0</sub> <sup>1</sup>
35850	8		36290	11	D', 12 <sub>0</sub> <sup>1</sup>
35853	8		36296	47	A, 1 <sub>0</sub> <sup>1</sup>
35865	8	D, 10b <sub>0</sub> <sup>1</sup>	36304	37	
35878	8		36307	11, sh.	F, 12 <sub>0</sub> <sup>1</sup>
35886	21	A, 6a <sub>0</sub> <sup>1</sup> /F, 10b <sub>0</sub> <sup>1</sup>	36312	11	G, 12 <sub>0</sub> <sup>1</sup>
35892	10	G, 10b <sub>0</sub> <sup>1</sup>	36320	68	B, 1 <sub>0</sub> <sup>1</sup> /E, 12 <sub>0</sub> <sup>1</sup>
35898	9	E, 10b <sub>0</sub> <sup>1</sup>	36327	77	B', 1 <sub>0</sub> <sup>1</sup> /E', 12 <sub>0</sub> <sup>1</sup>
35903	16	E', 10b <sub>0</sub> <sup>1</sup>	36331	47	
35911	11		36335	34	
35918	21	B, 6a <sub>0</sub> <sup>1</sup>	36341	79	C, 1 <sub>0</sub> <sup>1</sup>
35927	18	A, 16b <sub>0</sub> <sup>1</sup>	36346	40	
35939	19	C, 6a <sub>0</sub> <sup>1</sup>	36349	49	A, 1 <sub>0</sub> <sup>1</sup> + Chain torsion

<sup>a</sup> Relative intensity (% relative to most intense peak); Numbers denote benzene ring modes in Wilson notation.

TABLE 2—Continued

$\bar{\nu}$ , $\text{cm}^{-1}$	Int. <sup>a</sup>	Assignment	$\bar{\nu}$ , $\text{cm}^{-1}$	Int. <sup>a</sup>	Assignment
36354	22		36518	49	
36358	15		36522	43	
36365	22		36539	23	
36373	43	B, $1_0^1$ + Chain torsion	36543	18	
36378	39	B', $1_0^1$ + Chain torsion	36587	14	
36381	22		36633	13	
36389	27		36672	16	
36394	39	C, $1_0^1$ + Chain torsion	36676	19	A, $7a_0^1$
36399	35		36697	38	B, $7a_0^1$
36402	39		36722	42	C, $7a_0^1$
36406	64	D, $1_0^1$	36735	32	
36409	53		36762	49	A, $13_0^1$
36411	59	D', $1_0^1$	36773	30	
36417	43		36785	48	B, $13_0^1$
36421	44		36789	48	D, $7a_0^1$
36423	56	F, $1_0^1$	36793	44	D', $7a_0^1$ /B', $13_0^1$
36427	41		36800	34	
36431	58	G, $1_0^1$	36807	54	C, $13_0^1$
36438	100	E, $1_0^1$	36820	59	E, $7a_0^1$
36442	92	E', $1_0^1$	36823	58	E', $7a_0^1$
36447	58		36826	54	
36451	58		36832	43	
36456	58	D, $1_0^1$ + Chain torsion	36839	34	
36464	35		36860	29	
36468	49		36870	31	
36471	49		36877	37	D, $13_0^1$
36474	58		36883	35	D', $13_0^1$
36479	27, sh	F, $1_0^1$ + Chain torsion	36898	hint, 20	F, $13_0^1$
36484	32	G, $1_0^1$ + Chain torsion	36904	29	G, $13_0^1$
36490	35	E, $1_0^1$ + Chain torsion	36910	55	E, $13_0^1$
36495	42	E', $1_0^1$ + Chain torsion	36914	57	E', $13_0^1$
36503	29		36928	22	
36506	55		36944	19	
36511	34		36978	22	

and 18b. For  $C_1$  symmetry, of course, all transitions become allowed.

Table 2 gives a list of the bands in the spectrum in Fig. 1, along with our proposed assignments. Each origin band is labeled " $X_0^0$ ," where  $X$  is a letter denoting the conformer from which the given origin arises. The torsions are labeled as " $X_0^0$  + torsion," where, again,  $X$  stands for the origin with which the torsion is associated. All ring vibrations are designated as " $n_0^1$ ," where  $n$  is the number of the corresponding benzene mode in Wilson notation. These designations are preceded by the letter corresponding to the conformer with which the band is associated. Torsions combined with these modes are designated as they are for the origin bands. The numbers in the column labeled "Int." give the intensity of each peak in arbitrary units. These values have not been corrected for background.

As we mentioned above, the spectrum consists of clusters of peaks at certain common distances from the origin bands. On examining the spectrum we found that these clusters fell in

essentially the same pattern as the origin bands. We thus found that this apparently large number of peaks really represents only 11 vibrations. This greatly simplified the analysis of the spectrum.

We would expect the most intense features other than the origin bands to be those arising from the ring "breathing" mode, or mode 1, according to Wilson notation. The cluster of intense peaks approximately  $800 \text{ cm}^{-1}$  above the origin bands essentially follows the pattern of the origin bands, except that the first four peaks are approximately  $810 \text{ cm}^{-1}$  above their respective origins and the latter six are about  $802 \text{ cm}^{-1}$  above theirs. These are almost certainly due to the ring breathing mode, and we assign them accordingly. We also note that the frequency of the excited-state vibration is, on average, about 3% lower than that in the ground state. Thus, we would expect the frequencies of other in-plane stretches, at least those involving the ring, to be reduced to about the same extent in the excited state.

About  $50\text{ cm}^{-1}$  above both the origins and the bands from ring breathing appear two other clusters of peaks. We assign these as the torsion of the entire side chain about the bond at the 4-position of the ring. We designate them “chain torsion.” There is another, somewhat less intense, group of peaks about  $100\text{ cm}^{-1}$  above origins A, D, D', F, G, E, and E'. These are too low in frequency to be bending modes, and we assign them as the torsion of the  $-\text{COOH}$  group on the side chain.

The next most intense features are those at approximately  $1190$  and  $1280\text{ cm}^{-1}$  from their respective origins. This region is where we would expect modes 7a and 13 to appear. These are a pair of C–H stretches that become C–X stretches on substitution, and they represent movement of the substituents in opposite phases, 7a being the symmetric stretch, and 13 being the asymmetric stretch. The assignment for mode 7a was straightforward, as these bands are, on average,  $1186\text{ cm}^{-1}$  above their respective origins, which matches very well with the ground-state frequency of  $1212\text{ cm}^{-1}$ , being about 2% lower. The assignment for the other set of bands, however, was slightly more problematic. There are at least three bands that could appear in this region: benzene modes 13 and 14, the “Kekulé” C–C stretch, and the ring  $-\text{OH}$  in-plane bend. As noted above, we assigned the  $-\text{OH}$  bend in the ground state according to the work of Jakobsen, and of Green *et al.* to the band at about  $1248\text{ cm}^{-1}$ . This leaves the bands at approximately  $1266$  and  $1328\text{ cm}^{-1}$ , which most likely belong to benzene modes 13 and 14. Jakobsen and Brewer (24), on the basis of work by Mair and Hornig (38) and by Mecke and Rossmly (39), assign the band at  $1328\text{ cm}^{-1}$  to mode 14. They also support this assignment on the basis of an observed decrease in the frequency of this vibration when the spectrum was run for tyrosine in dilute  $\text{CS}_2$  solution. Originally, we adopted this assignment for the ground state. Our new R2PI data, however, indicate that this assignment is in error, and, in retrospect, so do the ground-state data. Based on the behavior of the other in-plane modes it is unlikely that the cluster at  $1280\text{ cm}^{-1}$  above the origin could belong to the band at  $1266\text{ cm}^{-1}$  in the ground-state spectra, as this represents a frequency increase of just over 1%. It is more likely that this set of bands is associated with the ground-state vibration at  $1328\text{ cm}^{-1}$ , being lower in frequency by about 4%. Based on symmetry considerations, mode 13 should appear preferentially over mode 14, and we would also expect the change in both dipole and polarizability that occur with mode 13 to be greater than that for mode 14. The band at  $1328\text{ cm}^{-1}$  is considerably more intense in both the IR and Raman than the band at  $1266\text{ cm}^{-1}$ . We therefore assign the ground state band at  $1266\text{ cm}^{-1}$  to benzene mode 14 and the one at  $1328\text{ cm}^{-1}$  to mode 13, and we assign the cluster of peaks in the R2PI spectrum at about  $1280\text{ cm}^{-1}$  above their respective origins to  $13_0^1$ .

We also observe a somewhat weak cluster of bands at about  $398\text{ cm}^{-1}$  from their origins, and another at about  $683\text{ cm}^{-1}$  above their origins. We assign these also to in-plane bends 6a and 12, respectively. These lie about 7% and 8%, respectively, below the corresponding ground-state frequencies.

The remaining bands that we were able to assign fall in clusters about  $264$ ,  $436$  and  $483\text{ cm}^{-1}$  above their respective origins. These are relatively weak, and we assign them to out-of-plane modes 10b and 16b, with the last cluster corresponding to a combination of 16b and torsion of the side chain.

Table 3 lists all the bands we assigned, grouped, as far as was possible, according to cluster, and showing which origin each is associated with and its distance above it. This is thus a table of excited-state vibrational frequencies for tyrosine. From this table, we can see clearly whether or not, or in what way, the frequencies of the different vibrations vary from conformer to conformer. As we noted earlier, with some conformers, the carboxyl group on the amino acid backbone might be able to interact with the phenol ring. If the degree of this interaction were to vary among the different conformers, one might expect this to have a corresponding effect on at least some of the vibrational frequencies.

We do not observe the low-frequency bands that would arise from hydrogen bonding. Exciplex formation, which could result from charge transfer between the side chain and the ring, would most likely change the Franck–Condon overlap to give rise to vibronic progressions, which we also do not observe. We may thus conclude that neither of these processes occurs to any significant extent in the gas phase. This does not, however, rule out some type of inductive interaction between the  $-\text{COOH}$  group and the  $\pi$  system of the ring, which we would expect to cause a shift in the frequencies of the origins for those conformers in which such an interaction could occur. The red-shifted origins we observed in the spectra of di- and tripeptides (6) suggest that this interaction in tyrosine gives rise to a red shift of the absorption. It is therefore tempting to think of the two groups of origins in the R2PI spectrum of tyrosine as belonging to two sets of conformers, the origins to the red corresponding to folded conformers (*gauche*) and the higher-energy origins corresponding to conformers in which the chain is extended away from the ring (*anti*). Indeed, several of the vibrational frequencies are distinctly different for the two groups, most notably those for mode 1 and its combination with the chain torsion, mode 16b and its combination with the chain torsion, and mode 10b. As it turns out, the situation is not nearly so simple.

To assign the origins to their respective conformers with confidence, and to determine the exact shapes of the various conformers, it would be necessary to perform jet-cooled microwave spectroscopy and/or the type of analysis that Snoek *et al.*, recently performed for phenylalanine (40), in which they used a combination of UV hole-burning spectroscopy, resonant IR ion-dip spectroscopy, rotational band contour analysis, and *ab initio* calculations to assign the origins in the laser-induced fluorescence (LIF) spectrum of phenylalanine to its various conformers. Nonetheless, by using the results of this analysis for phenylalanine, which differs from tyrosine only in that it lacks a hydroxyl group on the ring, in combination with our earlier work (6), we may at least reasonably conclude which origins correspond to



TABLE 3  
Excited-State Vibrational Frequencies for Tyrosine, as Determined from the R2PI Spectrum

Assignment:	Origin: $\bar{\nu}$ , $\text{cm}^{-1}$	A 35486	B 35511	B' 35518	C 35533	D 35604	D' 35607	F 35621	G 35628	E 35635	E' 35640
Origin A	35486	0									
Origin B	35511		0								
Origin B'	35518			0							
Origin C	35533				0						
Chain torsion	35538	52									
Chain torsion	35563		52								
Chain torsion	35568			50							
-COOH tors.	35585	99									
Chain torsion	35588				55						
Origin D	35604					0					
Origin D'	35607						0				
Origin F	35621							0			
Origin G	35628								0		
Origin E	35635									0	
Origin E'	35640										0
Chain torsion	35652					48					
Chain torsion	35671							50			
Chain torsion	35674								46		
Chain torsion	35682									47	
Chain torsion	35688										48
-COOH tors.	35704					100					
-COOH tors.	35709						102				
-COOH tors.	35723							102			
-COOH tors.	35731								103		
-COOH tors.	35735									100	
-COOH tors.	35738										98
10b	35751	265									
10b	35778		267								
10b	35783			265							
10b	35800				267						
10b	35865					261					
6a	35886	400						(265, 10b)			
10b	35892								264		
10b	35898									263	
10b	35903										263
6a	35918		407								
16b	35927	441									
6a	35939				406						
16b	35949		438								
16b	35957			439							
16b	35971				438						
16b + torsion	35979	493									
6a	35993					389					
16b + torsion	35996		485								
6a	36001						394				
6a	36013							392			
6a	36018								390		
16b + torsion	36024				491						
16b	36032					428					
6a	36037						(430, 16b)			402	
6a	36045										405
16b	36058							437			
16b	36061								433		
16b	36069									434	
16b	36072										432
16b + torsion	36079					475					

The table gives the origins across the top, the assigned bands in the first two columns, and the frequency difference of each band from its respective origin.

TABLE 3—Continued

Assignment:	Origin: $\bar{\nu}$ , $\text{cm}^{-1}$	A 35486	B 35511	B' 35518	C 35533	D 35604	D' 35607	F 35621	G 35628	E 35635	E' 35640
16b + torsion	36088						481				
16b + torsion	36110									475	
16b + torsion	36121										481
12	36172	686									
12	36195		684								
12	36200			682							
12	36212				679						
12	36286					682					
12	36290						683				
1	36296	810									
12	36307							686			
12	36312								684		
1	36320		809							(685, 12)	
1	36327			809							(687, 12)
1	36341				808						
1 + torsion	36349	863									
1 + torsion	36373		862								
1 + torsion	36378			860							
1 + torsion	36394				861						
1	36406					802					
1	36411						804				
1	36423							802			
1	36431								803		
1	36438									803	
1	36442										802
1 + torsion	36456					852					
1 + torsion	36479							858			
1 + torsion	36484								856		
1 + torsion	36490									855	
1 + torsion	36495										855
7a	36676	1190									
7a	36697		1186								
7a	36722				1189						
13	36762	1276									
13	36785		1274								
7a	36789						1185				
7a	36793			(1275, 13)			1186				
13	36807				1274					1185	
7a	36820										
7a	36823										1183
13	36877					1273					
13	36883						1276				
13	36898							1277			
13	36904								1276		
13	36910									1275	
13	36914										1274

*gauche* structures and which correspond to conformers in which the  $-\text{COOH}$  group is *anti* to the ring.

The origin region of the LIF spectrum of phenylalanine is quite similar to that of the LIF and R2PI spectra of tyrosine (5, 40). The peaks are somewhat shifted relative to those in the tyrosine spectrum, and those that are doublets in the tyrosine spectrum because of the hydroxyl splitting, appear as single peaks. Still, there is a rough correspondence between the origins in the two spectra. Based on Snoeck's analysis, and also on the way the origins in the spectrum of ethyltyrosine differ from those for

tyrosine (6), we conclude that origins A, C, D, D', and probably also F and G arise from conformers in which the ring and  $-\text{COOH}$  group are *gauche* to each other, and that origins B, B', E, and E' correspond to *anti* conformers. In addition, we conclude that the pattern of vibrational frequencies associated with the various origins results from a combination of red-shifting due to interaction of the chain and the ring, and coupling of the chain motion to some of the ring vibrations. Thus, instead of observing a direct correlation between the vibrational frequencies and whether the conformers are *anti* or *gauche*, we observe a

range of frequencies for each set of conformers, such that they overlap as shown in Table 3.

## CONCLUSION

We have presented here a vibronic assignment for tyrosine, including a ground-state vibrational assignment as well. The relative intensities of the origins, i.e., that they are the most intense peaks in the spectrum, the intensities of the bands arising from the ring “breathing” mode, and the small change in frequency

of the in-plane stretches between the ground and excited state, all indicate that tyrosine does not drastically change shape upon electronic excitation, and that it expands slightly. The lack of vibronic activity in the R2PI spectrum shows that the molecule behaves as if the benzene ring retains a high degree of symmetry, even with an –OH group and a rather large side chain at its 1- and 4-positions. Based on the R2PI data, this symmetry could be as high as  $C_{2v}$ . In addition, we assign origins A, C, D, D', F, and G to conformers in which the ring and chain are *gauche* to each other and origins B, B', E, and E' to *anti* conformers.

## APPENDIX

TABLE A1  
Calculated Frequencies and Activities for the Vibrations of Tyrosine<sup>a</sup>

No.	$\bar{\nu}$ , cm <sup>-1</sup>	Activity	Mode
66	32.6338	R (3)	Torsion of entire side chain about C-ring bond
65	52.7152	IR (0)	Torsion of HOOCNH <sub>2</sub> HC-about chain C–C bond
64	68.0202	R (1)	11 (C–X oop bend, in-phase)
63	87.7599	R (1)	COOH torsion
62	163.1991	IR (11)	Amino torsion
61	199.0701	IR (0)	Distal chain C–C–C bend
60	210.2875	IR (1)	Proximal chain C–C–C bend
59	297.4854	IR (6)	O=C–C and H <sub>2</sub> N–C–C bends, in-phase
58	302.0848	IR (62)	Ring OH torsion
57	325.3877	IR (1)	15 (C–X ip (trigonal) bend)
56	393.7599	IR (2)	N–C–C bend (w/proximal C–C-pair)
55	434.7909	IR (7)	10b (C–X oop bend (C <sub>6</sub> libration))
54	461.2480	IR (3)	9b (C–X ip bend)
53	483.9847	IR (0)	16a (C–C–C oop bend)
52	518.7309	IR (8)	Carboxyl HO–C–C bend
51	559.9361	IR (2)	6a (C–C–C ip bend)
50	610.1379	IR (12)	16b (C–C–C oop bend)
49	627.9047	IR (58)	Carboxyl OH torsion
48	698.1358	IR (4)	O=C–O bend & in-phase proximal C–C–C bend/NH <sub>2</sub> wag
47	734.3613	R (3)	6b (C–C–C ip bend)
46	762.6694	IR (9)	O=C–OH “wag,” w/in-phase proximal C–C–C bend
45	778.7756	IR (100)	Amino “wag”
44	839.9250	R (2)	12 (C–C–C trigonal bend)
43	850.2198	IR (1)	4 (C–C–C puckering)
42	911.3925	IR (9)	1 (Ring “breathing”)
41	946.8168	IR (26)	Chain C–C stretch
40	963.4899	IR (5)	10a (C–H oop bend (C <sub>6</sub> libration))
39	972.7725	IR (4)	Distal C–C–C asymmetric stretch (chain)
38	1016.7885	IR (11)	17b (C–H oop bend)
37	1072.2822	IR (8)	Chain CH <sub>2</sub> “rock” w/out-of-phase NH <sub>2</sub> “rock”
36	1133.9119	IR (0)	18a (C–H ip bend)
35	1136.8002	IR (2)	5 (C–H oop trigonal bend)
34	1153.0060	IR (2)	17a (C–H oop bend)
33	1195.8264	IR (47)	C–N stretch & out-of-phase carboxyl C–OH stretch
32	1205.9550	IR (16)	CH <sub>2</sub> “twist” & NH <sub>2</sub> “rock,” w/ring C–O–H bend <sup>a</sup>
31	1226.4860	IR (54)	C–N stretch, w/in-phase carboxyl C–OH stretch
30	1228.5295	IR (1)	18b (C–H ip bend)
29	1267.8259	IR (68)	Ring C–O–H bend, w/CH <sub>2</sub> “twist” & NH <sub>2</sub> “rock” <sup>a</sup>
28	1315.0509	R (7)	7a (C–X stretch)
27	1325.6057	IR (8)	9a (C–H ip bend)
26	1346.3506	IR (23)	14 (C–C stretch, trigonal, or Kekulé)
25	1388.8179	IR (14)	13 (C–X stretch)

Note. These two modes have the C–O–H bend in opposite phase with respect to the chain motion.

<sup>a</sup> M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople. “Gaussian 92,” Revision C. Gaussian Inc., Pittsburgh, Pennsylvania, 1992 (reference 33 in the text).

TABLE A1—Continued

No.	$\bar{\nu}$ , $\text{cm}^{-1}$	Activity	Mode
24	1398.9712	R (3)	Aminomethylene C–H bend
23	1430.4031	R (5)	Carboxyl C–O–H bend (w/out-of-phase $\text{NH}_2$ rock)
22	1472.0006	IR (12)	Carboxyl C–O–H stretch (w/out-of-phase $\text{NH}_2$ rock)
21	1486.6402	R (17)	Chain $\text{CH}_2$ “wag”
20	1512.0128	IR (10)	3 (C–H ip bend, in-phase)
19	1532.9514	IR (2)	$\text{NH}_2\text{CH}$ C–H bend, w/out-of-phase $\text{NH}_2$ “rock”
18	1597.8065	IR (8)	19b (C–C stretch)
17	1658.7177	R (8)	Methylene C–H “scissor”
16	1691.8052	IR (27)	19a (C–C stretch)
15	1757.2554	IR (4)	8b (C–C stretch)
14	1794.1526	IR (14)	8a (C–C stretch)
13	1855.6330	IR (16)	$\text{NH}_2$ “scissor”
12	1958.4932	IR (97)	C=O stretch
11	3230.1418	R (43)	Methylene symmetric C–H stretch
10	3271.0598	R (36)	$\text{CH}_2$ asym. stretch w/out-of-phase C–H stretch
9	3286.4770	R (10)	$\text{CH}_2$ asym. stretch w/in-phase C–H stretch
8	3354.6395	R (28)	7b (C–H stretch)
7	3366.6124	R (25)	20a (C–H stretch)
6	3374.6444	R (46)	20b (C–H stretch)
5	3386.8167	R (86)	2 (C–H stretch, totally symmetric)
4	3688.4287	R (47)	$\text{NH}_2$ symmetric stretch
3	3787.4386	R (36)	$\text{NH}_2$ asymmetric stretch
2	3867.2145	R (100)	Carboxyl O–H stretch
1	3914.3418	R (84)	Ring O–H stretch

TABLE A2a

Calculated Frequencies for the In-Plane Ring Vibrations of Some *p*-Alkylphenols

Mode <sup>a</sup>	<i>p</i> -ethylphenol <sup>b</sup>		<i>p</i> -isopropylphenol <sup>b</sup>		Tyramine <sup>b</sup>		Tyrosine <sup>c</sup>	$\bar{x}$	$\sigma$	
	I	II	I	II	I	II				
15	339	301	274	275	282	294	283	293	22.68	(7.75%)
9b	402	401	376	376	399	401	405	394	12.62	(3.20%)
6a	490	469	516	517	483	505	494	496	17.6	(3.55%)
6b	649	652	648	648	651	651	651	650	1.63	(0.25%)
12	678	686	668	666	684	732	746	694	31.69	(4.57%)
1	805	805	800	800	802	814	810	805	5.24	(0.65%)
18a	1009	1010	1009	1009	1010	1010	1011	1010	0.76	(0.07%)
18b	1103	1093	1096	1092	1093	1094	1095	1095	3.72	(0.34%)
7a	1160	1174	1192	1190	1179	1171	1174	1177	11.11	(0.94%)
9a	1186	1182	1183	1183	1183	1183	1183	1183	1.25	(0.11%)
14	1206	1198	1200	1207	1228	1205	1201	1206	10.08	(0.84%)
13	1248	1244	1249	1245	1251	1246	1240	1246	3.63	(0.29%)
3	1358	1349	1363	1363	1350	1349	1351	1355	6.45	(0.48%)
19b	1424	1427	1428	1430	1428	1427	1428	1427	1.81	(0.13%)
19a	1516	1514	1515	1515	1513	1513	1513	1514	1.21	(0.08%)
8b	1570	1570	1570	1570	1569	1569	1571	1570	0.69	(0.04%)
8a	1606	1605	1605	1604	1605	1606	1605	1605	0.69	(0.04%)
7b	3002	3006	3009	2997	3010	3002	3010	3005	4.98	(0.17%)
20a	3000	2996	2999	3018	3010	3005	3020	3007	9.46	(0.31%)
20b	3041	3015	3022	3016	3028	3025	3028	3025	8.79	(0.29%)
2	3049	3049	3049	3049	3035	3036	3038	3044	6.83	(0.22%)

Frequencies are raw, rounded frequencies  $\times 0.9\text{--}10$ ,  $\text{cm}^{-1}$ .

<sup>a</sup> Wilson numbering.

<sup>b</sup> M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, J. A. Pople, “Gaussian 90,” Gaussian Inc., Pittsburgh, Pennsylvania, 1990.

<sup>c</sup> M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, “Gaussian 92,” Revision C. Gaussian Inc., Pittsburgh, Pennsylvania, 1992.

TABLE A2b  
Calculated Frequencies for the Out-of-Plane Ring Vibrations of Some *p*-Alkylphenols

Mode <sup>a</sup>	<i>p</i> -ethylphenol <sup>b</sup>		<i>p</i> -isopropylphenol <sup>b</sup>		Tyramine <sup>b</sup>		Tyrosine <sup>c</sup>	$\bar{x}$	$\sigma$	
	I	II	I	II	I	II				
11	152	126	122	122	107	103	88	117	20.38	(17.40%)
10b	342	384	414	414	356	378	382	381	26.90	(7.05%)
16a	422	422	422	423	423	422	422	422	0.49	(0.12%)
16b	508	536	539	539	544	536	522	532	12.58	(2.37%)
4	686	719	722	722	718	725	714	715	13.32	(1.86%)
10a	812	812	812	811	815	808	805	811	3.25	(0.40%)
17b	826	824	828	829	835	822	847	830	8.51	(1.03%)
5	942	942	948	944	944	937	943	943	3.29	(0.35%)
17a	961	959	958	962	959	965	957	960	2.73	(0.28%)

Frequencies are raw, rounded frequencies  $\times 0.8 + 34$ ,  $\text{cm}^{-1}$ .

<sup>a</sup> Wilson numbering.

<sup>b</sup> M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, J. A. Pople, "Gaussian 90," Gaussian Inc., Pittsburgh, Pennsylvania, 1990.

<sup>c</sup> M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, "Gaussian 92," Revision C. Gaussian Inc., Pittsburgh, Pennsylvania, 1992.

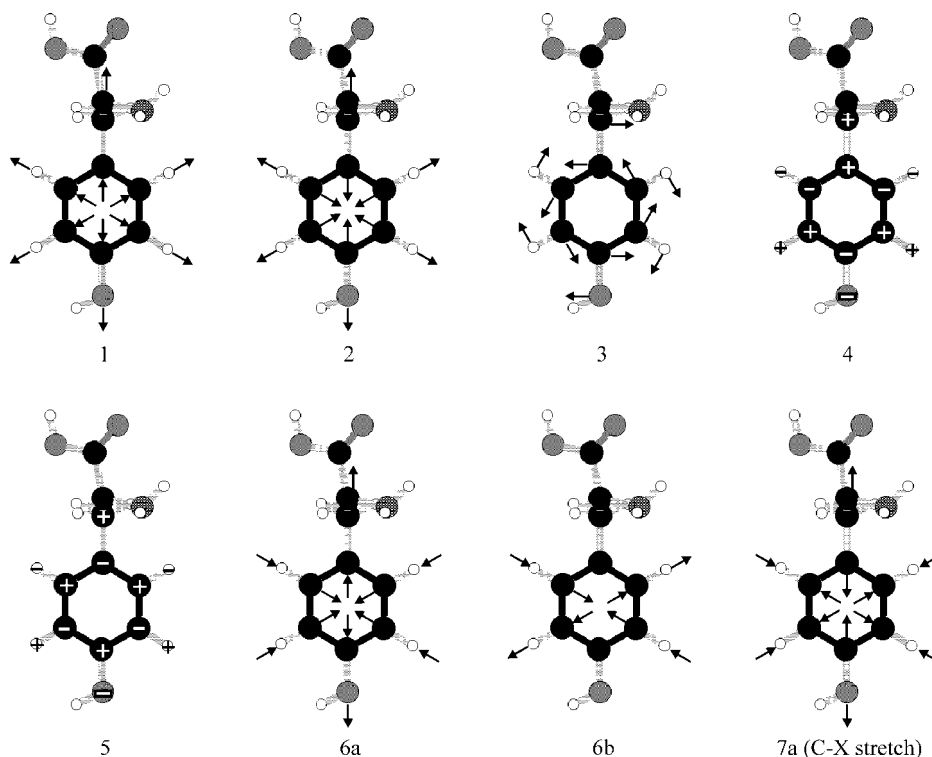


FIG. A1. Benzene ring vibrations for tyrosine, according to the Wilson numbering, after Brodersen and Langseth (reference 35 in the text).

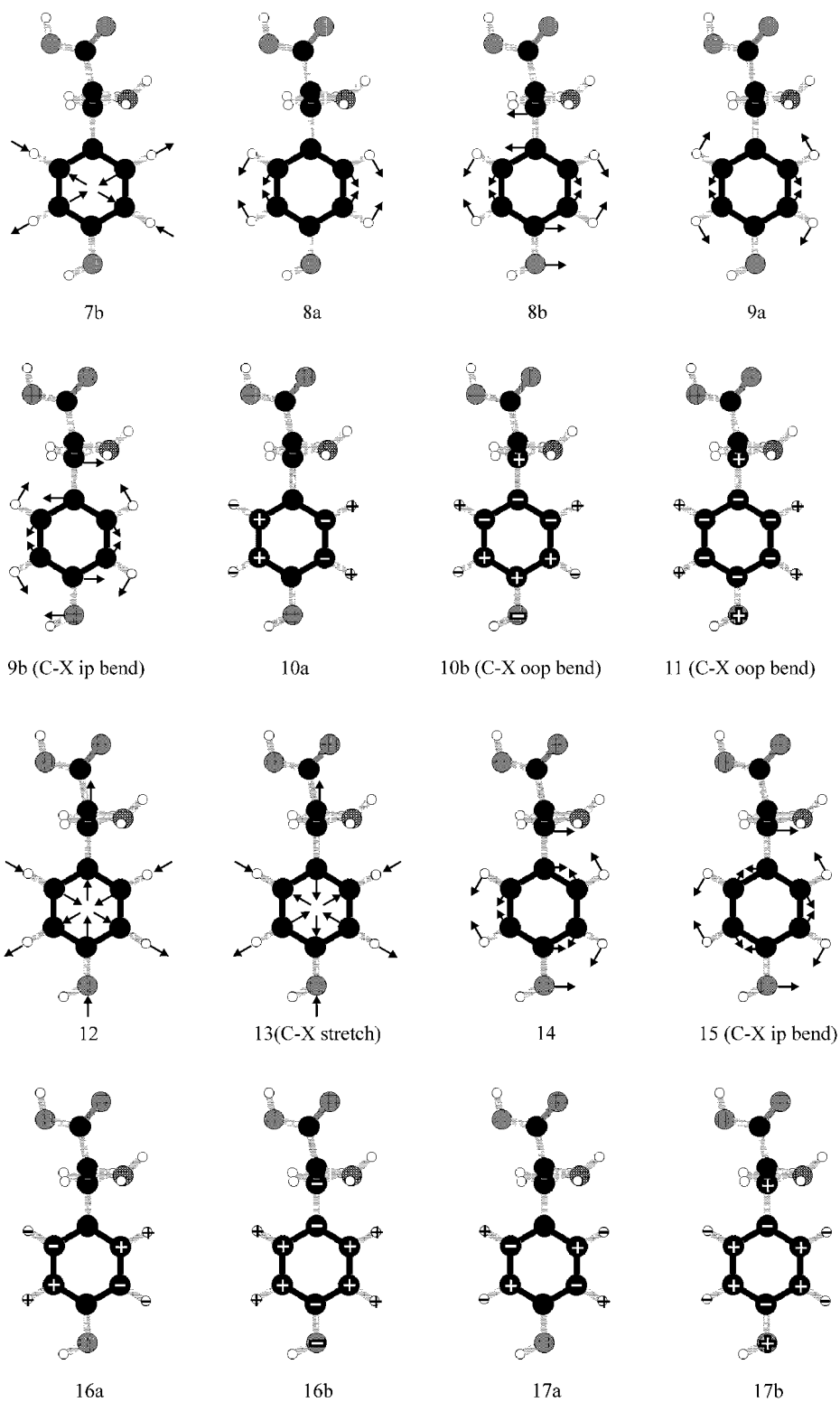


FIG. A1—Continued

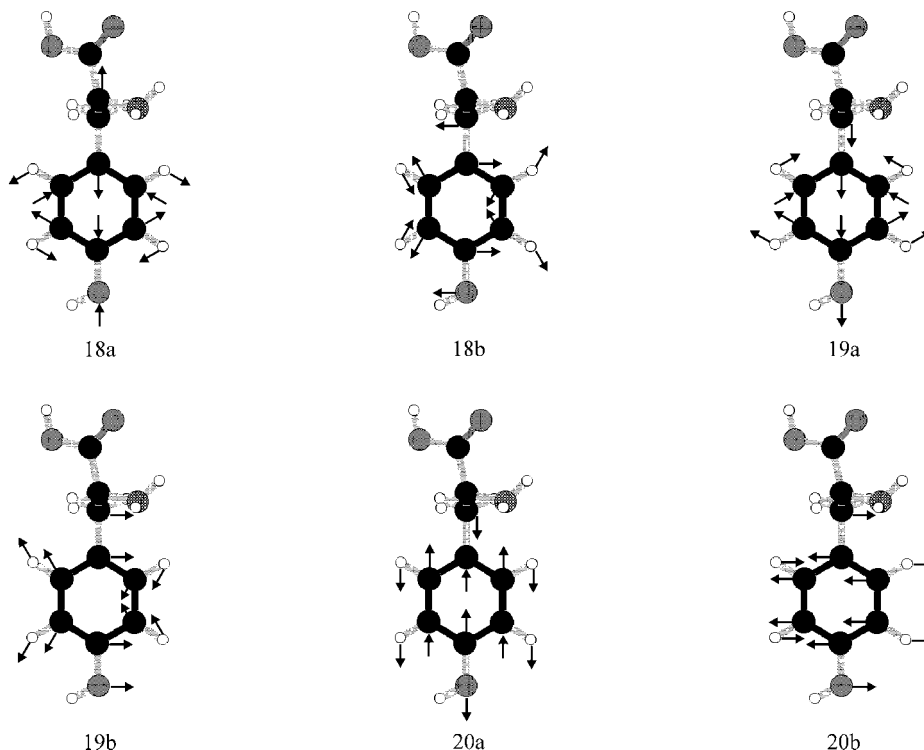


FIG. A1—Continued

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