

## Remarks on the Absorption Spectra of Phenylalanine and Tyrosine in Connection with the Absorption in Toluene and Paracresol

H. Sponer

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## Remarks on the Absorption Spectra of Phenylalanine and Tyrosine in Connection with the Absorption in Toluene and Paracresol

H. SPONER

*Department of Physics, Duke University, Durham, North Carolina*

(Received August 22, 1942)

The absorption spectra of phenylalanine and tyrosine in the near ultraviolet are compared with those of toluene and paracresol and an interpretation of the individual bands is proposed.

### INTRODUCTION

IT is generally recognized that the selective absorption in the near ultraviolet (2900–2400Å) of the amino acids<sup>1</sup> phenylalanine, tyrosine, and tryptophane must be attributed to their aromatic groups. Very rough comparisons have been made between these absorptions and that of benzene, phenol, and indol, respectively, from low dispersion spectrograms.<sup>2</sup> If one makes use of the recent developments in the interpretation of the spectra of benzene<sup>3</sup> and its derivatives,<sup>4</sup> a better understanding of the spectra of the aromatic amino acids may be obtained.

To apply the results achieved for the benzenes we will consider phenylalanine as a toluene molecule in which one H of the CH<sub>3</sub> group has been substituted by the CH(NH<sub>2</sub>)COOH group. Accordingly, the tyrosine must be considered as a substituted paracresol.

The near ultraviolet absorption spectra of toluene and paracresol represent, like those of other mono- and disubstituted benzenes, allowed transitions. This means, that they have strong 0,0 bands and that the majority of bands is caused by excitation of totally symmetrical vibrations and  $\nu$ - $\nu$  (mostly 1–1) transitions of non-totally symmetrical vibrations. If molecules are not completely unsymmetrical, there may appear in addition "forbidden" bands, that is, bands which according to electronic selection rules alone are forbidden but which appear when an unsym-

metrical vibration of proper symmetry is excited with one quantum. The benzene spectrum consists only of such forbidden bands. Paracresol has no symmetry in the strict sense, hence only allowed bands will occur. Toluene has one symmetry element, namely, a plane perpendicular to the ring plane and going through one of the H atoms of the CH<sub>3</sub> group. Its spectrum should mainly have allowed bands and may contain some forbidden bands. It is therefore obvious, that the allowed spectrum of phenylalanine is better compared with the allowed spectrum of toluene than with the forbidden benzene spectrum.

The mentioned theoretical statements have been obtained for spectra in the vapor phase but can, with proper caution, be extended to solution spectra. Although in solutions selection rules are more likely to break down, the general appearance will be that of the gas spectrum. For example, there is no 0,0 band in the benzene vapor spectrum but it may appear weakly in solutions, while there is a strong 0,0 band in toluene in the vapor and in solution as well. But, of course, the bands are shifted in solutions with respect to the bands in the gas; also the finer structure of the vapor spectrum disappears in solutions, giving rise only to broad bands which in the vapor represent whole groups of narrower bands. Changes in polar solvents are greater than in non-polar ones.

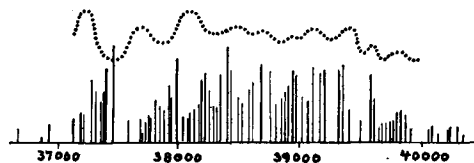


FIG. 1. Schematic representation of the absorption spectrum of toluene vapor. The curve represents the absorption in hexane solution [taken from J. Savard, *Ann. de Chimie* 11, 287 (1929)].

<sup>1</sup> See for detailed literature references J. R. Loofbrouow, *Rev. Mod. Phys.* 12, 267 (1940).

<sup>2</sup> K. Feraud, M. S. Dunn, and J. Kaplan, *J. Biol. Chem.* 112, 323 (1935).

<sup>3</sup> A. L. Sklar, *J. Chem. Phys.* 5, 669 (1937); H. Spöner, G. Nordheim, A. L. Sklar, and E. Teller, *J. Chem. Phys.* 7, 207 (1939).

<sup>4</sup> H. Spöner and S. H. Wollman, *J. Chem. Phys.* 9, 816 (1941); I. Walerstein, *Phys. Rev.* 59, 924A (1941); K. Asagoe and Y. Ikemoto, *Proc. Phys. Math. Soc. Japan* 22, 677 (1940); furthermore unpublished results.

TABLE I. Comparison between spectra of toluene and phenylalanine.

Toluene vapor (ref. 5)	Assignment	Toluene in hexane (ref. 5)	Toluene in heptane (ref. 6)	Phenylalanine aqueous (ref. 2)	Phenylalanine aqueous (ref. 7)	Assignment
37473 vst	0,0	37260 st	37160 st	37370	36835 vw	0-600
37938 st	0+466 }				37428 w	0,0
37999 st	0+527 }	37720 m	37650 m	37825	37939 m	0+500
38401 vst	0+930 }	38100 st	38220 st		38361 w	0+930
38435 st	0+963 }	39480 vw				
38665 st	0+1193 }					
38929 m	0+527+930 }	38700 vw		38808	38838 st	0+500+900
38962 m	0+527+963 }					
39191 m	0+527+1193 }	38930 vw				
39332 m	0+2×930 }	39110 w				
39365 m	0+930+963 }					
39397 m-w	0+2×963 }					
39593 m	0+930+1193 }	39400 w	39390 st			
39628 m	0+963+1193 }					
		39600 w				
		39815 w		39592	39718 m	0+500+2×900
40296 w	0+2×930+963 }		40250 m			
40329 w	0+930+2×963 }			40605	40539 w	0+500+3×900
			41150 w	41481	41344 vw	0+500+4×900
				42540	42252 vw	0+500+5×900

#### COMPARISON BETWEEN TOLUENE AND PHENYLALANINE

The main results of the analyses of the spectra of toluene and phenylalanine are contained in Table I. A very rough intensity classification of the bands has been added. (vst=very strong, st=strong, m=medium, w=weak, vw=very weak.) To facilitate the understanding, the toluene spectrum has been reproduced schematically in Fig. 1. The 0,0 band at<sup>5</sup> 37473 is the strongest band of the first group in the spectrum and lies on the short wave-length side of that group. In solutions the group is smeared out, its maximum lying at 37260 cm<sup>-1</sup> in hexane<sup>5</sup> and at 37160 cm<sup>-1</sup> in heptane solution.<sup>6</sup> If our comparison is correct these broad bands correspond to one at 2671A=37428 cm<sup>-1</sup> in phenylalanine in aqueous solution.<sup>1,7</sup>

The next group of bands in toluene vapor consists mainly of the two strong bands 466 and 527 cm<sup>-1</sup> distant from the 0,0 band towards the violet end of the spectrum. Assigning *C<sub>s</sub>* symmetry to toluene the second band, at 38000 cm<sup>-1</sup>,

is in analogy to other substituted benzenes, best interpreted as forbidden transition made allowed by the excitation of a vibration antisymmetric to the plane defined before. This vibration corresponds to the one whose excitation (frequency value 518 cm<sup>-1</sup>) is responsible for the existence of the near ultraviolet benzene spectrum. In other monosubstituted benzenes belonging to *C<sub>2v</sub>* symmetry, the analogous vibration has a frequency of 521 in monochlorobenzene, 519 in monobromobenzene, possibly 517 in monofluorobenzene, all values referring to the excited state. In the ground state this vibration has a value of about 606-622 in all these substances because the substituent partakes only slightly in the motion. The vibration is degenerate in benzene and splits into two components in the above-mentioned monoderivatives. Besides the just discussed unsymmetrical component there is a symmetrical one of lower frequency. Although it is tempting to interpret the toluene band at 37938 cm<sup>-1</sup> as caused by the excitation of this vibration the explanation is rendered doubtful because most of the strong bands have companions on the red side displaced by about 62 cm<sup>-1</sup> (527-466=61).

The two discussed bands merge into one broad band in solutions. Now in phenylalanine there occurs a corresponding broad band at 2635A = 37939 cm<sup>-1</sup> giving a distance of 511 from the

<sup>5</sup> J. Savard, Ann. de Chimie 21, 287 (1929); there given as 37484 because the wave numbers have not been reduced to vacuum.

<sup>6</sup> K. L. Wolf and W. Herold, Zeits. f. physik. Chemie B13, 201 (1931).

<sup>7</sup> C. B. Coulter, F. M. Stone, and E. A. Kabat, J. Gen. Physiol. 19, 739 (1936).

TABLE II. Comparison between the spectra of paracresol and tyrosine.

Paracresol vapor (ref. 5)	Assignment	Paracresol in hexane (ref. 5)	Paracresol in heptane (ref. 6)	Tyrosine aqueous (ref. 2)      (ref. 7)		Assign- ment
35329 vst	0,0	35000 st	35950 st	35450 st	35501 m	0,0
35748 w	0+419					
36137 vst	0+808	35750 st	36880 st	36221 st	36393 st	0+820
36516 m	0+1187	36200 st				
36944 m	0+2×808	36600 m	37450 st			
37323 m-w	0+1187+808	37000 m		37302 m	37414 w	0+1900
37752	0+3×808	37400 w	38550 m			

0,0 band. It is suggestive to assume that it represents the analogue to the above-mentioned vibrations. The only difference is that the vibration is here symmetric because phenylalanine has no symmetry element.

In this connection there should be mentioned an extremely faint band in phenylalanine<sup>7</sup> at  $2714A = 36835 \text{ cm}^{-1}$ . It lies  $595 \text{ cm}^{-1}$  to the red from the 0,0 band. It seems plausible to interpret it as coming from the same vibration in the lower state which has the frequency value of 511 in the upper state. From comparison with benzene and the aforementioned monosubstituted benzenes this frequency should be about 600 and indeed, a medium strong Raman line<sup>8</sup> has been reported at  $622 \text{ cm}^{-1}$ .

Coming back to the vapor spectrum of toluene one finds that progressions with differences<sup>9</sup> of 930, 962, and  $1192 \text{ cm}^{-1}$  appear superimposed on the first two groups. These differences have to be interpreted as frequencies of symmetrical vibrations in which mainly the carbon atoms of the ring are involved. The occurrence of harmonics and combination bands of these frequencies causes the groups to come closer together toward the violet end of the spectrum and therefore they appear less distinct. This will be more the case in solutions where, due to the overlapping of such groups, irregular separations may result. Thus, in heptane solution broad bands have been reported at 38220, 39390, 40250, and  $41150 \text{ cm}^{-1}$ , involving differences be-

tween 1170 and  $860 \text{ cm}^{-1}$ . In hexane solution<sup>5</sup> more bands have been reported, the first three being strong and distinct while the others are not.

In phenylalanine broad bands have been found by Coulter, Stone, and Kabat at  $2574A = 38838 \text{ cm}^{-1}$ ,  $2517A = 39718 \text{ cm}^{-1}$ ,  $2466A = 40539 \text{ cm}^{-1}$ ,  $2418A = 41344 \text{ cm}^{-1}$ , and  $2366A = 42252 \text{ cm}^{-1}$ , while Feraud, Dunn, and Kaplan give for the same bands (in aqueous solution)  $2576A = 38808 \text{ cm}^{-1}$ ,  $2525A = 39592 \text{ cm}^{-1}$ ,  $2462A = 40605 \text{ cm}^{-1}$ ,  $2410A = 41481 \text{ cm}^{-1}$ , and  $2350A = 42540 \text{ cm}^{-1}$ . Their wave-lengths have been fairly well confirmed by Anslow and Nassar.<sup>10</sup> These bands may be interpreted as a progression of totally symmetric vibrations ( $900\text{--}1000 \text{ cm}^{-1}$ ) superimposed on the transition 0+500. It seems surprising that they do not appear also as superposition on the 0,0 band. One would particularly expect a band at 0,0+about 900 because this is a strong group in toluene. Now one can see from the microphotometer tracings<sup>7,10</sup> that the band at 38838 is the strongest band of the spectrum; it is also quite broad so that the 0,0+900 may fall within its range. In favor of this explanation is the report of Coulter, Stone, and Kabat of a band at  $2606A = 38361 \text{ cm}^{-1}$  which appears in the right place and which evidently shows up very indistinctly. The frequencies involved in the progression correspond most probably to the strong Raman lines<sup>8</sup> observed at 1003 and 1032, and perhaps also to the line  $1211 \text{ cm}^{-1}$  in phenylalanine. It should be mentioned that the assignments added for the higher bands of phenylalanine contain only one possibility. It may be that in reality more vibrational transitions take

<sup>8</sup> N. Wright and W. C. Lee, *Nature* **139**, 551 (1937). Experimental condition: phenylalanine aqueous, 2 percent, 20 percent potassium iodide.

<sup>9</sup> The corresponding frequency values in the ground state are in all probability the strong Raman frequencies 1005, 1030, and  $1212 \text{ cm}^{-1}$ . Taken from R. Ananthakrishnan, *Proc. Ind. Acad. Sci.* **A3**, 52 (1936).

<sup>10</sup> G. A. Anslow and S. C. Nassar, *J. Opt. Soc. Am.* **31**, 118 (1941).

place within the range of these bands but the one in the table seems to be the most prominent.

The intensity distribution of the bands is different in toluene and phenylalanine. This is partly connected with the fact that all bands in phenylalanine represent allowed transitions while in toluene some are "forbidden" bands.

#### COMPARISON BETWEEN PARACRESOL AND TYROSINE

As mentioned in the introduction we shall consider tyrosine as a substituted paracresol. The general results of the analyses of the two spectra<sup>11</sup> are exhibited in Table II which has been arranged in the same fashion as Table I for toluene and phenylalanine. Figure 2 shows the absorption spectrum of paracresol in schematic form. Starting again with paracresol in the vapor phase, the spectrum consists chiefly of a progression of bands with separations of  $808\text{ cm}^{-1}$  beginning with the 0,0 band at  $35329\text{ cm}^{-1}$ . The separation belongs to a totally symmetric vibration whose value in the ground state, taken from Raman measurements,<sup>12</sup> is very likely  $841\text{ cm}^{-1}$ . The first two groups (0,0 band and  $0+808$ ) of this progression are the strongest in the whole spectrum. Another group whose intensity is about the same as that of  $0+2\times 808$  lies about  $1187\text{ cm}^{-1}$  (this is the position of the most intense band at  $36516$ ) to the violet from the 0,0 band. Super-

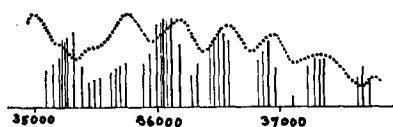


FIG. 2. Schematic representation of the absorption spectrum of paracresol vapor. The curve represents the absorption in hexane solution [taken from J. Savard, *Ann. de Chimie* 11, 287 (1929)].

imposed on it appear weaker bands with the  $808$  separation. The  $1187$  belongs to another symmetric vibration with a value of  $1213$  or  $1251$  in the ground state.<sup>12</sup> A weak band at  $35748$  indicates a vibrational frequency of  $419\text{ cm}^{-1}$  in the

upper state (probably  $464$  in the lower state<sup>12</sup>). From these remarks we see that the spectrum will have the appearance of groups with rough distances from the 0,0 band of  $800$ ,  $1200$ ,  $2\times 800$ ,  $1200+800$ ,  $3\times 800$ , the higher members being hardly observable. This characteristic is preserved in hexane solution<sup>5</sup> and to a lesser degree in heptane solution where only four groups have been reported.<sup>6</sup>

The fact that only three groups have been observed in the tyrosine spectrum is in favor of considering it a modified paracresol spectrum. The 0,0 band lies at  $35450\text{ cm}^{-1}$ . The distance between the first two bands is about  $820$  (average value) and in all probability corresponds to the strong Raman line<sup>13</sup> at  $844\text{ cm}^{-1}$ . The next group which is broader and weaker may contain two vibrational transitions, namely,  $2\times 800$  and  $0+820+1100$ . In fact, another strong Raman line<sup>13</sup> was found at  $1216\text{ cm}^{-1}$ . All transitions involve symmetric vibrations.

We may mention that the mechanism of the production of the spectra of simple substituted benzenes seems to be preserved to a large extent not only in solution spectra of the aromatic amino acids but also in proteins containing these substances.

Finally, some remarks may be made as to the sharpness of the different spectra. The toluene spectrum in the vapor state is much sharper than that of paracresol. The latter looks as if predissociation occurs over its total range while in toluene it sets in only toward the short wavelength end of the spectrum. This predissociation is characteristic for benzene and all known derivative spectra. In benzene it has been brought in connection with the rupture of one CH bond,<sup>14</sup> assuming that although the vibrational energy is mostly accumulated in the totally symmetric C-vibration, the oscillation energy may, on account of anharmonic forces, go over into the stretching of a C-H bond. In substituted benzenes there is in addition the possibility for the rupture of other bonds involved with other repulsive curves. If the comparison used here is correct, one might expect from the appearance

<sup>11</sup> The interpretation of the paracresol spectrum (and also of the toluene spectrum) differs, for most bands, from the one given by Savard, but is in agreement with the recent analyses of other monoderivatives of benzene.

<sup>12</sup> K. W. F. Kohlrausch and A. Pongratz, *Monats. f. Chem.* 63, 427 (1933).

<sup>13</sup> N. Wright and W. C. Lee, *Nature* 136, 300 (1935). (Tyrosine, 5 percent in 0.9*N* HCl.)

<sup>14</sup> G. Nordheim, H. Sponer, and E. Teller, *J. Chem. Phys.* 8, 455 (1940).

of the toluene and paracresol spectra that there is more tendency towards photo-decomposition in tyrosine than in phenylalanine.

The spectra of phenylalanine and of tyrosine beyond 2500Å are continuous. They consist of more than one absorption system. About 2200Å there is expected another absorption of the ring

which corresponds to the benzene absorption at 2000Å. Furthermore, the "end absorption" of all amino acids irrespective of an aromatic nucleus begins below 2500Å and is attributed to the amino group. Due to overlapping it will probably not be possible to separate these different absorptions.

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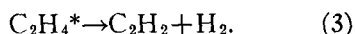
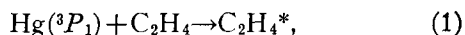
## The Mercury Photosensitized Reactions of Ethylene at High Temperatures\*

D. J. LEROY AND E. W. R. STEACIE  
National Research Laboratories, Ottawa, Canada  
(Received August 10, 1942)

The mercury ( $^3P_1$ ) photosensitized reactions of ethylene have been investigated over the temperature range 25°C to 350°C. In addition to those previously found at 25°C, the reaction  $\text{Hg}(^3P_1) + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_3 + \text{H} + \text{Hg}(^1S_0)$  is shown to occur. There was a considerable increase in the quantum yield at high temperatures and this is attributed to the hydrogen atom and vinyl radical sensitized polymerization of ethylene. The reactions of ethylene with  $\text{Na}(^2P)$ ,  $\text{Cd}(^3P_1)$ ,  $\text{Zn}(^3P_1)$ ,  $\text{Hg}(^3P_1)$ ,  $\text{Cd}(^1P_1)$ , and  $\text{Zn}(^1P_1)$  atoms are summarized and the latter three are shown to be closely related.

### INTRODUCTION

IN a number of recent papers it has been established with considerable certainty that in the mercury ( $^3P_1$ ) and cadmium ( $^3P_1$ ) photosensitized reactions of ethane<sup>1-3</sup> and propane<sup>4,5</sup> the initial step consists in the removal of a hydrogen atom with the production of the corresponding alkyl radical. In contrast with this behavior of the paraffins, that of ethylene is much more complex. The mercury photosensitized reactions of ethylene<sup>6</sup> have been shown to involve the steps



\* Contribution No. 1079 from the National Research Laboratories, Ottawa, Canada.

<sup>1</sup> E. W. R. Steacie and N. W. F. Phillips, *Can. J. Research* **B16**, 303 (1938).

<sup>2</sup> E. W. R. Steacie and R. L. Cunningham, *J. Chem. Phys.* **8**, 800 (1940).

<sup>3</sup> E. W. R. Steacie and R. Potvin, *J. Chem. Phys.* **7**, 782 (1939).

<sup>4</sup> E. W. R. Steacie and D. J. Dewar, *J. Chem. Phys.* **8**, 571 (1940).

<sup>5</sup> E. W. R. Steacie, D. J. LeRoy, and R. Potvin, *J. Chem. Phys.* **9**, 306 (1941).

<sup>6</sup> D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **9**, 829 (1941).

On the other hand, the initial step in the cadmium ( $^1P_1$ )<sup>7</sup> and zinc ( $^1P_1$ )<sup>8</sup> photosensitized reactions of ethylene is probably the removal of a hydrogen atom with the formation of a vinyl radical, although the simultaneous occurrence of reactions analogous to those with mercury ( $^3P_1$ ) is not excluded.

Such differences were not unexpected in view of the energies involved. The latest estimates of the C—H bond strength in ethane<sup>9-11</sup> are in the neighborhood of 96 to 98 kcal. while that of propane<sup>9</sup> is 95.5 or 91 kcal. depending on whether the H is removed from a primary or a secondary carbon atom. This makes it possible for a  $\text{Hg}(^3P_1)$  atom (112.2 kcal.) to remove a hydrogen atom even if the hydride ( $\Delta H = 8.5$  kcal.) is not formed and for a  $\text{Cd}(^3P_1)$  atom (87.3 kcal.) to remove one provided the hydride ( $\Delta H = 15.5$  kcal.) is formed. On the other hand, while the C—H bond strength in ethylene is not known

<sup>7</sup> E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.* **10**, 22 (1942).

<sup>8</sup> H. Habeeb, D. J. LeRoy, and E. W. R. Steacie, *J. Chem. Phys.* **10**, 261 (1942).

<sup>9</sup> E. C. Baughan, M. G. Evans, and M. Polanyi, *Trans. Faraday Soc.* **37**, 377 (1941).

<sup>10</sup> D. P. Stevenson, *J. Chem. Phys.* **10**, 291 (1942).

<sup>11</sup> H. G. Andersen, G. B. Kistiakowsky, and E. R. Van Artsdalen, *J. Chem. Phys.* **10**, 305 (1942).