Bull. Chem. Soc. Jpn., **55**, 3422—3423 (1982) [Vol. 55, No. 11

Multiphoton Ionization Spectrum of *p*-Terphenyl in a Supersonic Free Jet

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(Received May 24, 1982)

The one-photon absorption spectrum of *p*-terphenyl vapor was observed in a supersonic free jet by using multiphoton ionization spectroscopy. In the spectrum were observed the progressions of the in-phase and out-of-phase torsional vibrations of the benzene rings. It was concluded that *p*-terphenyl has a planar structure in the first excited singlet state, whereas it is twisted in the ground state.

It has long been predicted that there exist low-lying hidden electronic excited states in polyphenyls[1,2] and their identifications have been of continuing interest for the spectroscopists. However, the electronic absorption spectra of polyphenyls in vapor are completely diffuse at room temperature due to excitation of low-frequency vibrations, which prevents conclusive assignment of the excited states. It was recently demonstrated for biphenyl, however, that the diffuseness can be removed in a supersonic free jet.[3] In the jet spectrum the well-resolved vibrational structure was observed and its analysis led us definite assignment of the S_1 and S_2 states and revealed the planar structure in the excited states. The success for biphenyl seems to promise that the systematic study of the electronic spectra of polyphenyls is possible by using a supersonic free jet. In this paper we report the one-photon electronic absorption spectrum of *p*-terphenyl in a supersonic free jet. In the case of *p*-terphenyl, the molecule has two torsional vibrations of the in-phase and the out-of-phase mode and the conjugation between the benzene rings is expected to be stronger than in biphenyl. It seems interesting to study how these effects are reflected in the electronic spectrum.

Experimental

The spectrum was observed by multiphoton ionization spectroscopy. Because of the high sensitivity, this method is quite suitable for observing the spectrum of a molecule with very low vapor pressure such as *p*-terphenyl. The ionization potential of *p*-terphenyl is 7.8 eV and the lowest excited state lies at about 4 eV. Hence in the excitation with the second harmonic of the visible dye laser ($\approx$300 nm), one can obtain the one-photon resonant two-photon ionization spectrum of the molecule. *p*-Terphenyl vapor obtained by heating the sample at 400 K was seeded in 3 atm He gas and the mixed gas was expanded from a pulsed nozzle (400 μm diameter) which is synchronized with a N_2 laser pumped scanning dye laser (Rhodamine B). The experimental setup is the same as reported in our previous works.[4,5] *p*-Terphenyl was zone-refined and was free from impurities, which was confirmed by their layer chromatography and gas chromatography with several developing solvents.

Results and Discussion

In Fig. 1 is shown a part of the observed one-photon resonant two-photon ionization spectrum of *p*-terphenyl in a supersonic free jet. The frequencies of the observed bands and their assignments are listed in Table 1. As is seen from the figure and table, the simple vibrational structure appears in the cold spectrum in contrast to the broad spectrum at room temperature. The observed spectrum consists of the two progressions A and B (see Fig. 1) and their combinations (see Table 1). Since both A and B progressions start from the same band at 32460 cm^{-1} and no prominent vibrational structure was observed to the red of the band, we assign it to be the 0-0 band of the first singlet excited state (S_1).

The frequency intervals of the A and B progressions are 62 and 89 cm^{-1}, respectively, and the spacings are almost constant for the two progressions (see Table 1). In the case of biphenyl,[3] the observed low-frequency vibration ($\approx$60 cm^{-1}) was assigned to the torsional mode of the benzene rings from the isotopic

Table 1. Vibronic bands of *p*-terphenyl in the MPI spectrum in a supersonic free jet

$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}$/cm^{-1}	Analysis	Assignment[a)]
32460	0		0-0
32522	62	0+62	A_0^1
32549	89	0+89	B_0^1
32583	123	0+2×62	A_0^2
32612	152	0+62+89	$A_0^1B_0^1$
32639	179	0+2×89	B_0^2
32645	185	0+3×62	A_0^3
32673	213	0+2×62+89	$A_0^2B_0^1$
32699	239	0+62+2×89	$A_0^1B_0^2$
32705	245	0+4×62	A_0^4
32725	265	0+3×89	B_0^3
32733	273	0+3×62+89	$A_0^3B_0^1$
32760	300	0+2×62+2×89	$A_0^2B_0^2$
32768	308	0+5×62	A_0^5
32790	330	0+62+3×89	$A_0^1B_0^3$
32798	338	0+4×62+89	$A_0^4B_0^1$
32824	364	0+3×62+2×89	$A_0^3B_0^2$
32830	370	0+6×62	A_0^6
32850	390	0+2×62+3×89	$A_0^2B_0^3$
32853	392		
32864	404	0+5×62+89	$A_0^5B_0^1$
32870	410		
32887	426	0+4×62+2×89	$A_0^4B_0^2$
32891	431	0+7×62	A_0^7
32913	453	0+3×62+3×89	$A_0^3B_0^3$
32921	461	0+6×62+89	$A_0^6B_0^1$
32947	487	0+5×62+2×89	$A_0^5B_0^2$
32950	490	0+8×62	A_0^8

a) A and B represent the out-of-phase and in-phase torsional vibrations, respectively.

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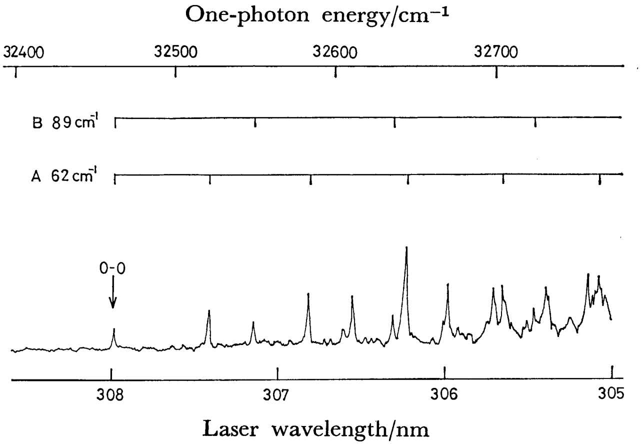

Fig. 1. The one-photon resonant two-photon ionization spectrum of *p*-terphenyl in a supersonic free jet.

ratio of the vibrational frequency. The low-frequency vibrations of *p*-terphenyl are also considered to be the torsional ones. In the case of *p*-terphenyl, however, there exist two torsional vibrations of the in-phase and the out-of-phase mode. Hence it seems quite reasonable to assign 62 and 89 cm^{-1} of the A and B progressions to the in-phase and out-of-phase torsional vibrations. In order to establish the assignment, the **GF** matrix calculation was made with the simplified force field of $V=(1/2)K\{(\Delta\tau_1)^2+(\Delta\tau_2)^2\}+K_{12}(\Delta\tau_1)(\Delta\tau_2)$, where $\Delta\tau$ is internal coordinate of the torsion of the interphenyl bond. It was found that a reasonable set of the force constants is obtained only when 62 and 89 cm^{-1} are assigned to the out-of-phase and in-phase modes, respectively. The force constants obtained are $K=1.7\times10^{-12}$ dyn cm/rad† and $K_{12}=-0.3\times10^{-12}$ dyn cm/rad. It is interesting to note that the value of K is $\approx$1.4 times larger than the corresponding force constant of biphenyl ($K=1.2\times10^{-12}$ dyn cm/rad). This is consistent with the expectation that conjugation between the benzene rings is stronger in *p*-terphenyl than in biphenyl.

Another interesting information obtained from the observed spectrum is the molecular geometry of *p*-terphenyl in the S_1 state. The harmonic torsional progressions of A and B suggest that *p*-terphenyl has a planar or a perpendicular form in the S_1 state. The fact that the S_1 state of *p*-terphenyl (33000 cm^{-1}) lies much lower in energy than that of biphenyl4) implies the more extensive conjugation between the benzene rings in the former molecule than in the latter. The biphenyl molecule in the S_1 state has the planar structure owing to the predominance of the conjugation over the repulsion between the ortho-hydrogens.4) We therefore can conclude that *p*-terphenyl also has a planar structure in the S_1 state.

Although the geometry of *p*-terphenyl vapor in the electronic ground state is not known yet, the molecule is considered to have a twisted structure as in the solution.6) The twisted structure of the S_0 state is also consistent with the observed progression of torsional vibrations in the S_0-S_1 absorption spectrum, since the final state S_1 is planar as discussed above. The facts that only several members of the torsional progression were observed and that the 0-0 band appeared strongly are in contrast with the case of biphenyl where the torsional progressions with more than 20 quanta were observed and the 0-0 band was too weak to be observed. This strongly indicates from the Franck-Condon principle that although both biphenyl and *p*-terphenyl in vapor have a planar structure in the excited states, the dihedral angle of the latter is smaller than that of the former ($\approx$42°) in the ground states. The smaller dihedral angle for *p*-terphenyl is consistent with the result that in solution the angle is 10° compared with 20° in biphenyl.6)

The authors wish to thank Prof. N. Mikami for his valuable discussions.

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† 1 dyn$=10^{-5}$ N.