ROYAL SOCIETY
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Journal Name

ARTICLE

Supplementary Information (SI)

Gas-phase vibrational spectroscopy of triphenylamine: the effect of charge on structure and spectra

Musleh Uddin Munshi,[a] Giel Berden[a], Jonathan Martens[a] and Jos Oomens[a, b,]*

[a]Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, The Netherlands.

[b]University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands.

*E-mail: joso@science.ru.nl

Torsion angles

$$\angle C_{13}NC_1C_2 = \phi_1$$

$$\angle C_1NC_7C_8 = \phi_2$$
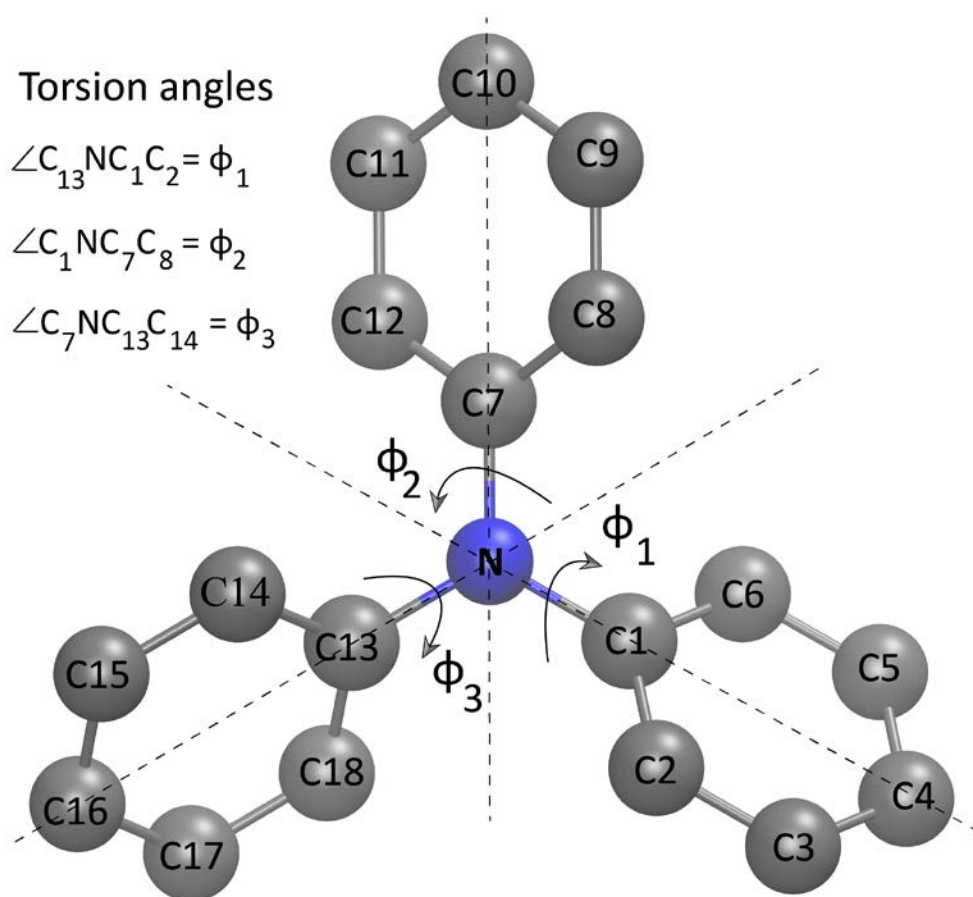
$$\angle C_7NC_{13}C_{14} = \phi_3$$

Figure S1 Schematic representation of TPA (or a radical cation of TPA) geometry, all atoms are numbered except the nitrogen atom at the centre; hydrogen atoms are omitted for clarity. The nitrogen atom is considered in the plane of the paper with carbon atoms C1, C4, C7, C10, C13 and C16. The plane of each of the phenyl moieties makes an angle around the C-N bonds with the plane of the paper; these angles are referred to as torsion angle and are labelled as ϕ_1, ϕ_2, ϕ_3, where 0° corresponds to all the atoms being in the plane of the paper. All the torsion angles rotate in the same direction around each of the dotted lines.

Table S1 Computed rotational constants (in GHz) are shown for neutral TPA and radical cation (TPA$^{•+}$) along with the experimentally determined values for neutral TPA in the gas phase. Parenthesized value is the standard deviation

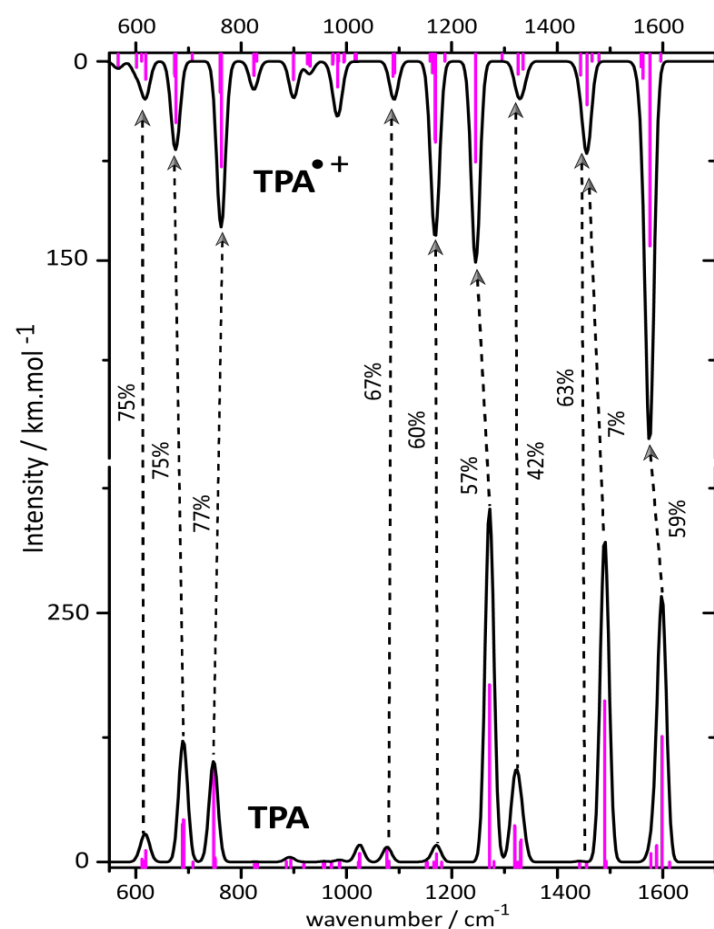| Methods	Rotational constants, (GHz)	
	Neutral TPA	Radical cation, (TPA$^{•+}$)
Exp (LIF) (for C3 symmetry, A=B)	A=B=0.4047(5) C=not known	(Not available)
B3LYP/6-31++G(d,p) BLYP/cc-pVTZ	A=0.3999, B=0.3987, C=0.2202 A=0.3961, B=0.3955, C=0.2185	A=0.3993, B=0.3992, C=0.2202 A=0.3993, B=0.3992, C=0.2202

Figure S2 This figure schematically shows the dominant vibrational projections (%) of the TPA$^{•+}$ (top) onto the TPA (bottom) normal modes employed ViPA. These results are taken from Table S2. Similar bands are connected with dotted lines and the percentages of the projections are also shown. For example, each of the IR bands of TPA$^{•+}$ from 600-800 cm^{-1} represent over 70% of the band character of TPA and are considered the most similar.

Table S2 Summary of the vibrational projection analysis (ViPA) of the TPA$^{\bullet+}$ normal modes onto the basis molecule TPA. In this ViPA analysis, optimized geometry and the corresponding force constants are required as input where hybrid B3LYP/6-31++G(d,p) level of theory was chosen. The calculated normal modes (cm^{-1}) are labelled (v_1-v_{39}) while their intensities (>0.5 k mol^{-1}) are shown in suffix for both TPA and TPA$^{\bullet+}$. The experimental frequencies (cm^{-1}) are also shown and the widths (FWHM in cm^{-1}) of the determined IR bands are given in parentheses. Differences in frequencies (Δcalc) are also presented between TPA and TPA$^{\bullet+}$ based on their correspondence calculated by ViPA—two theoretical IR bands are considered similar and compared only when any normal mode of the object molecule (TPA$^{\bullet+}$) has maximum projection (≤ 100%) onto a normal mode of another (TPA). According to this guideline, the experimental band shifts are calculated. Qualitatively, the theoretical predicted band shifts (Δv) are reproduced fairly well by the experiment

Modes of TPA	TPA		TPA$^{\bullet+}$		Δcalc	Δexp	Decomposition of the TPA$^{\bullet+}$ modes into TPA modes (major contributions only)
	calc (cm^{-1})	exp	calc (cm^{-1})	exp			
v_1	1612		1596		16		62% v_1
v_2	1599$_{126}$	1590(28)A	1575$_{139}$	1548(23)I	24	42	59% v_2 + 8% v_3
v_3	1588$_{16}$		1563$_{13}$		25		71% v_3 + 9% v_2
v_4	1578$_8$		1559$_4$		19		73% v_4
v_5	1493		1479		14		65% v_5
v_6	1490$_{162}$	1494(22)B	1466		24		59% v_6 + 7% v_7
v_7	1456		1456$_{32}$	1446(18)J	0		63% v_7 + 7% v_6
v_8	1442$_1$		1444$_{10}$		-2		68% v_8
v_9	1331$_{21}$		1336$_3$		-5		39% v_9 + 6% v_{10} + 23% v_{11}
v_{10}	1325		1335$_6$		-10		57% v_{10} + 3% v_{11}
v_{11}	1319$_{36}$	1327(~30)C	1325$_{10}$		-6		42% v_{11}
v_{12}	1279$_{0.7}$		1294		-15		67% v_{12} + 3% v_{10}
v_{13}	1271$_{177}$	1278(25)D	1245$_{75}$	1226(40)K	26	52	57% v_{13} + 3% v_{15}
v_{14}	1181		1187		-6		58% v_{14} + 5% v_{16}
v_{15}	1171$_8$		1169$_{58}$	1160(28)L	2		60% v_{15} + 2% v_{13}
v_{16}	1166		1164		-13		69% v_{18}
v_{17}	1153		1163$_9$		-10		67% v_{17}
v_{18}	1151$_{0.7}$		1159		7		59% v_{16} + 7% v_{12} + 4% v_{14}
v_{19}	1080$_{0.9}$		1091$_8$		-11		67% v_{19} + 3% v_{21}
v_{20}	1076$_{13}$	1074(16)E$_1$	1088$_{11}$		-12		67% v_{20} + 5% v_{22}
v_{21}	1025$_8$	1030(17)E$_2$	1019		6		69% v_{21} + 6% v_{19}
v_{22}	1022		1016		6		69% v_{22} + 6% v_{20}
v_{23}	987$_1$		996		-25		78% v_{26} + 3% v_{25}
v_{24}	986$_1$		995$_{0.6}$		-23		80% v_{25} + 2% v_{26}
v_{25}	972		986		0		69% v_{24}
v_{26}	971		983$_{19}$	988(13)M	4		69% v_{23}
v_{27}	958		975		-17		78% v_{27}
v_{28}	956		974$_2$		-18		77% v_{28}
v_{29}	919		931$_3$		-12		52% v_{29} + 26% v_{31}
v_{30}	894$_4$		926$_2$		-32		80% v_{30}
v_{31}	886$_{0.6}$		900$_{13}$		-14		52% v_{31} + 20% v_{29}
v_{32}	831		830		1		80% v_{32}
v_{33}	826		825$_{10}$		1		81% v_{33}
v_{34}	751$_2$		762$_{79}$	758(15)N	-14	-8	77% v_{35} + 5% v_{34}
v_{35}	748$_{96}$	750(16)F	761$_{23}$		-10		77% v_{34}
v_{36}	709		707		2		69% v_{36}
v_{37}	691$_{42}$	696(19)G	677$_{46}$	672(12)O	11	24	76% v_{38} + 3% v_{37} + 2% v_{34}
v_{38}	688$_{37}$		674$_{11}$		17		81% v_{37} + 2% v_{38}
v_{39}	619$_{11}$	622(18)H	619$_{13}$	618(10)P	0	4	75% v_{39}

Table S3 Absolute Proton Affinity (in kJ mol^{-1}) obtained from the DFT calculations

	Absolute proton affinities of the protomers of TPA (kJ mol^{-1})			
DFT level of theory	N-protonated	para-protonated	ortho-protonated	meta-protonated
MP2(full)/6-311+G(2d,2p)//B3LYP/6-31++G(d,p)	913.5	891.1	872.2	769.4