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Showcasing ion spectroscopy from the group of
**Prof. Jos Oomens and Dr Giel Berden at the FELIX
 Laboratory at Radboud University in the Netherlands**

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

Strong charge delocalization causes the computed structural parameters of triphenylamine (TPA) to remain virtually unchanged upon removal of an electron. Nonetheless, the IR spectra of TPA and its radical cation are clearly distinct, as analyzed on the basis of experimental IR spectra of the isolated, ionized forms of TPA recorded using the FELIX free electron laser. Infrared ion spectroscopy, combining tandem mass spectrometry and IR laser spectroscopy, is applied in fundamental as well as applied analytical challenges of molecular structure.

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

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The effect of ionization by oxidation and protonation on the structure and IR spectrum of isolated, gas-phase triphenylamine (TPA) has been investigated by infrared multiple photon dissociation (IRMPD) spectroscopy in the fingerprint range from 600 cm⁻¹ to 1800 cm⁻¹ using an infrared free electron laser. IR spectra calculated using density functional theory (DFT) convincingly reproduce the experimental data. Spectral and structural differences are identified among neutral TPA, TPA^{•+} and protonated TPA and qualitatively related to effects of resonance delocalization. As a consequence of electron delocalization, computed structural parameters for TPA remain virtually unchanged upon removal of an electron. Nonetheless, CC and CN stretching vibrations in the IR spectra of TPA^{•+} undergo a red shift of up to 52 cm⁻¹ as compared to those in TPA. Since ionization also strongly influences the relative band intensities, a vibrational projection analysis was used to correlate vibrational modes of TPA with those of TPA^{•+}. The experimental IR spectrum of gas-phase protonated TPA indicates that protonation occurs on the nitrogen atom, despite delocalization of the lone electron pair. Upon protonation, the structure changes from the nearly planar geometry to a near-tetrahedral configuration.

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1 Introduction

Triphenylamine (TPA) is an organic nitrogen-containing compound that can be considered as a derivative of ammonia in which all three hydrogen atoms are substituted by phenyl groups to form a tertiary amine. TPA-based compounds are used in organic light emitting diodes (OLEDs),^{1–5} organic field-effect transistors (OFETs),⁶ photovoltaics,⁷ as semiconductors,⁸ as photoconductors,^{9–11} as laser dyes¹² and in mechanoluminescent materials¹³ because of their high hole-transport properties.^{14,15} In recent years, TPA derivatives have been used in dye-sensitized solar cells (DSSCs) for the photovoltaic conversion of sunlight into electricity.^{16–24} TPA moieties (one or multiple units) are used as electron donors and as an additional chromophore when attached to a dye molecule, increasing the electron donating ability and enhancing charge separation, in order to increase the photo-energy conversion.^{21–26}

The structure and properties of neutral TPA have been thoroughly studied. Contrary to aliphatic amines, TPA has a very low basicity²⁷ because of resonance delocalization of its lone pair of electrons throughout the entire structure.²⁸ Unlike ammonia, the three N–C bonds lie in the same plane due to resonance delocalization as depicted in Fig. 1b. Such a structure is not necessarily obvious because of the resulting steric hindrance between the phenyl groups. This causes the molecule to adopt a propeller-like structure with the phenyl groups being tilted by more than 40° reducing the overlap between the nitrogen lone-pair p-orbital and the phenyl π -orbitals. The propeller-like geometry avoids molecular aggregation and allows solvent molecules to penetrate effectively. The spectroscopic properties of neutral TPA have been extensively investigated by both theory and experiment in the gas phase using a variety of techniques including (rotationally resolved) laser induced fluorescence (LIF)²⁹ and gas-phase electron diffraction,^{30,31} as well as in condensed phases using crystallography³² and FTIR absorption spectroscopy in an argon matrix.³³ Experimental UV-VIS absorption spectra of TPA in EtOH were also reported along with theoretical calculations.³⁴ An experimental gas-phase IR absorption spectrum of neutral TPA is available from the NIST WebBook.³⁵

The TPA radical cation has received far less attention. In 1979, Duke *et al.* reported on ultraviolet photoelectron spectroscopy (UPS) of the radical cation both in condensed phases and

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† Electronic supplementary information (ESI) available: Experimental constants of TPA, schematic representation of the torsional angle of TPA, calculated vibrational IR frequencies of TPA and TPA^{•+} at the B3LYP/6-31++G(d,p) level of theory, and calculated proton affinity of TPA protomers. Vibrational projection analysis (ViPA) of TPA^{•+} on TPA. See DOI: 10.1039/c7cp02638b

Fig. 1 Resonance structures for (a) $\text{TPA}^{\bullet+}$, (b) neutral TPA. No analogous resonance structures are possible for protonated TPA (c). The resonance hybrid of $\text{TPA}/\text{TPA}^{\bullet+}$ is a combination of the all possible resonance structures.

in the gas phase.³⁶ They concluded that while the condensed-phase structure of the radical is very similar to that of the neutral species, the gas-phase structure of the radical is almost planar. More recently, theoretical investigations of its vibronic coupling constants have been reported in order to explain the favorable hole-transport properties of triphenyl-based molecules.³⁷

Here, we report gas-phase infrared spectra for the TPA radical cation ($\text{TPA}^{\bullet+}$) and protonated TPA (TPA-H^+). These spectra are compared to the IR spectrum of the neutral species and to density functional theory (DFT) calculated spectra, which provides detailed information on the structural changes upon oxidation in the gas phase.

2 Methods

2.1 Experimental

The ions are generated and analyzed in both a home-built Fourier transform ion cyclotron resonance mass spectrometer (FTICR MS)^{38,39} and in a modified commercial quadrupole ion trap (QIT) mass spectrometer.^{40,41} Fingerprint infrared multiphoton dissociation (IRMPD) spectra were recorded for the mass-selected ions by monitoring the wavelength-dependent photo-fragmentation yield induced by the infrared irradiation from the Free Electron Laser for Infrared eXperiments (FELIX).^{42,43}

In the FTICR MS, $\text{TPA}^{\bullet+}$ ions were generated from an approximately 1 mM solution of TPA in methanol using an electrospray ionization source (Z-Spray, Micromass, UK). Ions were accumulated for 7–8 seconds in a linear hexapole before being injected into the ICR cell through an electrostatic quadrupole deflector and an rf octopole ion guide. The TPA ion of

interest was isolated using a stored waveform inverse Fourier transform (SWIFT) excitation pulse⁴⁴ and subsequently irradiated for 5–6 seconds by the infrared FEL radiation from FELIX operating at a repetition rate of 10 Hz, producing 6 μs long macropulses with energies of 30 to 60 mJ having a bandwidth of approximately 0.4% of the centre frequency. When the frequency of the laser is resonant with a vibrational band of the ion, absorption of multiple photons occurs and results in an increase in internal energy, finally leading to unimolecular dissociation.^{39,45} $\text{TPA}^{\bullet+}$ ions studied here are comparatively difficult to dissociate with the infrared FEL radiation alone. To enhance the IR-induced dissociation, the ions were post-excited using 5 ms of irradiation from a continuous wave CO_2 -laser (10.6 μm , 30 W) directly after each FEL pulse.⁴⁶ After the interaction of the ions with the IR light, a mass spectrum of the ion population in the ICR cell is obtained from an excite-detect procedure described in detail elsewhere.⁴⁴ The frequency dependent fragmentation yield, defined as $\sum(\text{fragment ions})/\sum(\text{precursor} + \text{fragment ions})$, obtained from 2 summed mass spectra, is plotted as a function of laser frequency in order to provide the infrared spectrum of the ion. The yield was corrected linearly for frequency dependent variations in laser pulse energy. Spectra were recorded from 600 to 1800 cm^{-1} (fingerprint region) with a 5 cm^{-1} step size. The wavelength of the FEL was calibrated using a grating spectrometer.

In the QIT (Bruker, AmaZon Speed ETD, Bremen, Germany), $\text{TPA}^{\bullet+}$ and TPA-H^+ ions were generated *via* electrospray ionization of $\sim 1 \mu\text{M}$ solutions of TPA in acetonitrile/water (1 : 1 ratio). If required, 0.1% of formic acid was added to enhance protonation. At every IR frequency step, the ions were irradiated with the FEL for 0.2–1 s and 3/5-fold averaged mass spectra were stored. No CO_2 laser was used to enhance the dissociation induced by the IR FEL, however the helium pressure in the QIT was reduced in order to reduce collisional de-excitation and hence enhance IR-induced dissociation.⁴⁰

2.2 Computational modelling

Quantum-chemical calculations at the DFT level were performed to aid in structural and vibrational assignments, using the Gaussian 09 revision D 01⁴⁷ software package. Although TPA is known to possess C_3 symmetry,²⁹ no symmetry constraints were imposed in the calculations. Hybrid⁴⁸ B3LYP/6-31++G(d,p) and gradient-corrected^{49,50} BLYP/cc-pVTZ levels of theories were employed (for consistency purposes only). Harmonic frequencies were computed for the optimized geometry of the molecules. Computed harmonic frequencies were scaled by a factor of 0.975 for the B3LYP/6-31++G(d,p) level (which was found to give the best match for many experimental IRMPD spectra, see *e.g.* ref. 41 and 51) and 0.997⁵² for the BLYP/cc-pVTZ level to account for anharmonicity and basis set incompleteness. All calculated linear IR spectra were convoluted using a 20 cm^{-1} FWHM Gaussian line shape function for comparison with experimental IR spectra. Additionally, single point energy calculations were performed at the MP2(full)/6-311+G(2d,2p) level of theory for all tautomers of protonated TPA (including *ortho*, *meta* and *para*-protonated) to assess their relative stability. Their relative Gibbs free energies and gas-phase proton affinities (PA) at 298.15 K are computed at

the MP2(full)/6-311+G(2d,2p)//B3LYP/6-31++G(d,p) level of theory. Charge and bonding properties in the molecule were computationally investigated by natural population analysis (NPA) and natural bond orbital (NBO) analysis as implemented in Gaussian09. Finally, B3LYP/6-31++G(d,p) harmonic frequencies of TPA^{•+} and TPA were employed in a vibrational projection analysis (ViPA)^{53,54} in order to quantitatively identify the similarities of the normal mode characters between TPA^{•+} and TPA.

3 Results and discussion

The gas-phase IR spectrum of neutral TPA is taken from the NIST WebBook³⁵ and is shown in Fig. 2a. The experimental IRMPD spectrum of TPA^{•+} (m/z 245) was measured in both the FTICR MS and the QIT MS (see Fig. 3a–c). Upon IRMPD, the main fragmentation product was found at m/z 244, corresponding to the loss of atomic hydrogen. Additionally, a minor fragment with m/z 166 was observed and is attributed to the subsequent loss of a benzene ring from the m/z 244 ion. The IRMPD spectra of TPA^{•+} taken in the FTICR and QIT agree well, where the spectrum taken without helium gas in QIT more

Fig. 2 Experimental IR absorption spectra of neutral TPA³⁵ (a), along with the calculated IR spectra at the B3LYP/6-31++G(d,p) (b) and BLYP/cc-pVTZ (c) levels of theory. The optimised structure is shown in panel (b). Experimental IR bands are labelled from A to H for assignments given in Table 1.

Fig. 3 IRMPD spectrum of TPA^{•+} (red) taken in the FTICR MS (a), in the QIT MS with (b) and without (c) helium buffer gas. The computed IR spectra at the B3LYP/6-31++G(d,p) and BLYP/cc-pVTZ levels of theories are shown in panels (d) and (e). Both computed spectra show a close match in terms of line positions, while the BLYP/cc-pVTZ spectrum matches better in terms of relative intensities near 1200 cm⁻¹. Experimental IR bands are labelled from I to P for assignments in Table 1 and the optimised structure is shown in panel (d). The horizontal dotted line indicates an apparent cut-off; excitation at bands having an intensity below this line does not energise the molecule sufficiently for the dissociation threshold to be reached in our experiments. Note that in order to recover bands P and O, band L in panel (c) is saturated.

closely mimics the IR spectrum measured in the FTICR (Fig. 3). At higher (standard) helium gas pressures in the QIT, collisional deactivation competes with dissociation, reducing the observed fragmentation yield.⁴⁰

In the FTICR, no IR photodissociation of TPA-H⁺ could be observed. The infrared spectrum of TPA-H⁺ shown in Fig. 4a was measured in the QIT. Photodissociation yields under 'regular' experimental conditions were very low due to the high stability of protonated TPA for IR photodissociation. In order to be able to record the IRMPD spectrum shown in Fig. 4, TPA-H⁺ ions had to be irradiated with 10 macro pulses of the FEL without helium gas in the ion trap. IRMPD fragments of TPA-H⁺ (m/z 246) were found at m/z 169 and 92, representing the loss of one and two phenyl groups respectively.

The well-known propeller-like structure of TPA is reproduced by our calculations (see rotational constants in ESI,[†] Table S1);

Fig. 4 IRMPD spectrum (red trace) recorded in the QIT MS for TPA-H⁺ without helium buffer gas (a). Experimental IR bands are labelled from Q to V for assignments (see Table 3). Calculated IR spectra for the possible protomers of protonated TPA are shown in (b–e) with their relative Gibbs free energies. Geometries and corresponding frequencies (scaled 0.975) are computed at the B3LYP/6-31++G(d,p) level of theory while relative Gibbs free energies are calculated at the MP2(full)/6-311+G(2d,2p)//B3LYP/6-31++G(d,p) level. Protonation site is indicated with an arrow. The IRMPD spectrum (a) closely matches with the N-protonated isomer (b) which is also the minimum energy structure.

bond lengths and bond angles are given in Table 2, and agree well with experiment.^{29,31} Note that the B3LYP CC and CN bond lengths match the experimental values better than BLYP values, which typically provides larger values for these bonds compared to B3LYP (see *e.g.* ref. 55). The torsional angle denoted as ϕ (for definition see ESI,[†] Fig. S1) of TPA is well estimated by both levels of theory (within $\sim 3^\circ$).

Inspection of the highest occupied molecular orbital (HOMO) (Fig. 5) suggests that the lone pair electrons on the nitrogen atom are highly delocalized throughout the structure due to conjugation as also suggested by the resonant Lewis structures in Fig. 1b.⁵⁶ In addition to the N-atom, the HOMO has high amplitudes at the phenyl carbon atoms in *ortho* and *para* positions, while much less on the *meta* positions, indeed as suggested by the Lewis structures in Fig. 1b. On the other hand, the partial double bond character of the N–C bonds is not obvious since the phenyl rings are twisted by more than 40°

reducing the overlap between the nitrogen lone-pair orbital and the phenyl π -orbitals. Indeed, an NBO calculation does not recognize any π -bonds between the nitrogen and the adjacent C-atoms.

3.1 Spectroscopy and structural properties of TPA^{•+}

TPA^{•+} has a structure very similar to its neutral counterpart. Table 2 compares structural parameters calculated in the present study with values that have been reported in the literature. We note that values reported in ref. 36 (from 1979) used an empirical pseudopotential model (CNDO/S3 model)⁵⁷ to mimic gas-phase UPS data. Their reported value for the torsional angle is 29° lower than our B3LYP/6-31++G(d,p) and BLYP/cc-pVTZ values ($\phi = 39^\circ$). Average bond lengths for the CN and CC bonds appear not to change upon ionization by amounts that could be considered significant. The torsional angles of the phenyl rings appear to undergo the largest change, although the 2° – 3° change in the direction of a flattening of the ion is very marginal indeed. These computed structures thus suggest that the effects of the removal of an electron are smeared out over the entire molecule to an extent that they become unnoticeable.

The IRMPD spectrum of TPA^{•+} shown in Fig. 3 is closely reproduced by theory showing maximum deviations between theoretical and experimental vibrational frequencies of only 10 cm^{-1} . For instance, considering the phenyl ring and CN stretching modes experimentally found at 1548 cm^{-1} (band I) are computed exactly at 1548 cm^{-1} by the BLYP/cc-pVTZ method (Table 1). This suggests that the effects of resonance delocalization on the vibrational frequencies – and hence on the force constants – are well reproduced by theory. Some of the predicted bands with low intensities remain unobserved, even with the maximum laser power settings, likely because at these frequencies the ions cannot be energized to exceed the dissociation threshold.

The experimental IR bands have been labelled and assigned with an approximate mode description inferred from the computed normal modes (Table 1). In the case of TPA^{•+}, bands I through K show dominant phenyl ring and C–N stretching character, similar to neutral TPA. To determine the similarities of the normal modes between TPA^{•+} and TPA, we employed a vibrational projection analysis (ViPA),^{53,54} designed for quantitative comparisons between similar systems. ViPA treats the set of normal modes of the considered individual systems as simple vectors; taking the dot product of each of the modes of TPA^{•+} (object molecule) with each of the vectors of the basis molecule TPA then relates their normal modes. We use this relation to compare normal mode frequencies between the neutral and radical cationic system.

Substantial changes in band intensities are observed upon ionization, which makes the ViPA analysis essential to correlate bands in TPA and TPA^{•+}. For instance, the band of TPA^{•+} computed at 1456 cm^{-1} (band J in Fig. 3) possesses only 7% mode character of the dominant band of TPA at 1490 cm^{-1} (band B in Fig. 2). On the contrary, it has 63% similarity to the band at 1456 cm^{-1} which shows almost no intensity in TPA (see ESI,[†] Table S2 and Fig. S2).

The results of the ViPA analysis are presented in ESI,[†] Table S2 and Fig. S2. According to this ViPA analysis, the experimental IR

Table 1 Experimental vibrational frequencies (in cm^{-1}) of TPA and TPA^{*+} are compared with harmonic frequencies calculated at the B3LYP/6-31++G(d,p) (factored by 0.975) and BLYP/cc-pVTZ (factored by 0.997) levels of theory. Labels refer to Fig. 2 and 3. Experimental and theoretical band shifts ($\Delta\nu$ in cm^{-1}) of corresponding vibrational modes between TPA and TPA^{*+} are indicated for similar modes. Peak widths of the experimental bands (FWHM in cm^{-1}) are shown in parentheses. Assignments of the bands are based on the highest intensity (km mol^{-1}) contribution

Exp			B3LYP/6-31++G(d,p)			BLYP/cc-pVTZ			^a Assignments
TPA	TPA^{*+}	$\Delta\nu_{\text{exp}}$	TPA	TPA^{*+}	$\Delta\nu_{\text{B3LYP}}$	TPA	TPA^{*+}	$\Delta\nu_{\text{BLYP}}$	
1590 (28) A	1548 (23) I	42	1599	1575	24	1566	1548	18	R str (s), CN str (w)
1494 (22) B			1490			1474			R str, CN str (s), CH bend
	1446 (18) J			1456			1445		R str, CNC bend, CH bend
1327 (~30) C			1319			1326			CNC bend, R twist, CH bend
1278 (25) D	1226 (40) K	52	1271	1245	27	1236	1215	21	CN str (s), CH bend
	1160 (28) L			1169			1163		CN str (w), CH bend (s)
1074 (16) E ₁			1077			1072			CH bend
1030 (17) E ₂			1024			1018			R str
	988 (13) M			983			986		R deformation
750 (16) F	758 (15) N	−8	748	762	−14	742	761	−19	CH oop
696 (19) G	672 (12) O	24	691	677	14	688	677	11	CH oop
622 (18) H	618 (10) P	4	619	619	0	621	620	1	CCC bend

^a R str – phenyl ring stretch; str – stretch; CH bend – in plane CH bending modes; CH oop – CH out of plane bending movement; R deformation – phenyl ring deformation modes; s – strong; w – weak.

Table 2 Computed bond lengths (Å) and bond angles (°) are compared to experimental (electron diffraction^{30,31}) values for TPA and reported³⁶ values for TPA^{*+} in the gas phase. Parenthesized values are standard deviations

Parameter	B3LYP/6-31++G(d,p)		BLYP/cc-pVTZ		Experiment ^{30,31}	Reported ³⁶
	TPA	TPA^{*+}	TPA	TPA^{*+}	TPA	TPA^{*+}
C–N _{mean}	1.422 (0)	1.415 (0)	1.430 (0)	1.423 (0)	1.418 (4)/1.42 (0.04)	
C–C _{mean}	1.399 (4)	1.401 (9)	1.402 (5)	1.404 (10)	1.399 (4)/1.392 (0.006)	
C–H _{mean}	1.086 (1)	1.085 (1)	1.088 (1)	1.087 (1)	1.123 (2)	
Bond and torsion angles, (°)						
∠ CNC _{mean}	120 (0.02)	120 (0.05)	120 (0.04)	120 (0.02)	119.9 (1)/116 (2)	120 (2)
φ _{mean}	42.08 (0.07)	39.25 (0.18)	42 (0.27)	39.67 (0.05)	45.2 (2.0)/47 (5)	10 (3)

band of TPA^{*+} at 1548 cm^{-1} (band I in Fig. 3) shows 59% similarity with the experimental IR band at 1590 cm^{-1} (band A in Fig. 2) in TPA. We thus infer a shift of 42 cm^{-1} as a consequence of oxidation of TPA. B3LYP/6-31++G(d,p) level of theory predicts a shift of 24 cm^{-1} for this band. Similarly, the band observed at 1278 cm^{-1} in TPA having predominant CN stretching character can be correlated according to the ViPA analysis to the 1226 cm^{-1} band in TPA^{*+} inferring an experimental redshift of 52 cm^{-1} upon oxidation. These red shifts are generally reproduced in the calculated IR spectra at both the BLYP/cc-pVTZ and B3LYP/6-31++G(d,p) (Table 1) levels of theory.

Fig. 5 HOMO of TPA (a) and its radical cation (b) shown at an isosurface value of 0.03.

We interpret these downfield shifts of CC and CN stretching bands upon ionization as evidence for the resonance delocalisation in this molecule: removal of an electron from the HOMO reduces the electron density not only on the nitrogen centre but also in the CN and phenyl CC bonds causing a slight reduction in the corresponding force constants. As a consequence, these stretching bands in TPA^{*+} generally appear at lower frequencies relative to those of neutral TPA. The computed decrease of the torsional angles in TPA^{*+} , though small, is also a consequence of the reduced force constants in the CN bonds (Table 2).

For both neutral TPA and TPA^{*+} , the bands in the lower frequency range (800 to 600 cm^{-1}) are mainly related to C–H out of plane bending with the exception of the peak close to 620 cm^{-1} which results from a weak CCC bend. Ionization appears to have little effect on these low frequency bands.

The NBO analysis suggests that the occupancy of the nitrogen lone pair orbital in TPA is only 1.72, where the missing electron density is largely donated into π^* bonds on the phenyl rings, as reflected in the resonance picture in Fig. 1b. Upon ionization, the nitrogen lone pair occupancy drops only slightly to 1.46 (α and β spin orbitals added) and about $0.15e$ is removed from the π -bonds in each of the phenyl rings. Perhaps somewhat counter-intuitive, the NPA analysis places a $-0.480e$ partial charge on the N-atom in TPA, which changes only slightly to $-0.274e$ in

Table 3 Experimental vibrational frequencies (in cm^{-1}) of TPA-H^+ compared to theoretical frequencies (scaled) calculated at the B3LYP/6-31++G(d,p) and BLYP/cc-pVTZ levels of theories for the N-protonated isomer only. Values in parentheses are observed spectral bandwidths (FWHM in cm^{-1})

Label	Exp	Theory (DFT)		Assignments ^a
		B3LYP/6-31++G(d,p)	BLYP/cc-pVTZ	
Q ^b	1475 (38)	1488	1477	CC str (s), CN str (m), NH bend (s)
	1460	1468	1457	CHip(m), NH bend (s)
		1459	1450	CHip (s)
R	1345 (12)	1358	1353	NH bend (s), CNC bend (m)
S	1242 (12)	1252	1247	NH bend (s), CNC bend (s), CN bend
T	996 (13)	988	991	Ring deformation (s)
U ^b	738 (21)	746	741	CH oop (s), CNC bend (m)
	727	728	724	CH oop (s), CNC bend (m)
V	683 (14)	683	687	CH oop bend (m)

^a CC str – CC stretch of the phenyl rings; str – stretch; ip – in-plane bending mode; ring deformation – phenyl ring deformation; oop – out of plane; s – strong band; m – medium band. ^b Bands consist of two unresolved absorptions with almost equal intensity, which is confirmed by the computed spectra.

the cation. NPA charges on the carbon atoms (with H-atoms summed) in *para*, *meta* and *ortho* positions also change only slightly, from -0.016 , $+0.013$ and -0.003 in the neutral to $+0.094$, $+0.049$ and $+0.051$ in the cation. We conclude that these trends testify of strong charge delocalization resulting in the negligible structural changes upon ionization (Table 2). Nonetheless, the vibrational modes involving CC and CN stretching show small but significant red shifts revealing the general bond weakening upon loss of an electron.

3.2 Spectroscopy and protonation site of TPA-H^+

It is of interest to consider also the protonated form of TPA. Protonation on the nitrogen atom engages the lone-pair electrons into a σ -bond binding the proton, so that conjugation with the phenyl-ring π -electrons is disrupted. We investigate the effects on the IR spectrum, however, we shall first verify whether protonation indeed occurs on the nitrogen. Since the lone pair electrons are highly delocalised throughout the TPA structure, protonation on the phenyl ring carbon atoms either in the *para*- or *ortho*-positions may become competitive with protonation on the N-atom. A previous study suggests that for gas-phase aniline, ring protonation at the *ortho* or *para* position is energetically feasible along with N-protonation as confirmed by infrared photodissociation (IRPD) spectroscopy.⁵⁸ Our computations predict that despite the low proton affinity (PA) of TPA, the nitrogen atom remains the preferred protonation site, with protonation on the *para*- and *ortho* phenyl carbon atoms being disfavoured by 23 and 40 kJ mol^{-1} , respectively (Fig. 4). Our theoretical energy (enthalpy) of protonation on the N-atom ($913.5 \text{ kJ mol}^{-1}$) (see ESI,† Table S3) is close to the experimental PA ($903.7 \pm 8.4 \text{ kJ mol}^{-1}$), determined in the gas phase by mass-spectrometric methods.⁵⁹ Almost the same PA ($908.8 \text{ kJ mol}^{-1}$) is reported by Hunter and Lias.⁶⁰

Fig. 4a presents the fingerprint IRMPD spectrum of TPA-H^+ . The calculated IR spectrum for N-protonated TPA agrees well with all bands observed in the experimental IRMPD spectrum. Again, the lower-intensity IR bands remain unobserved in the experiment presumably because at these frequencies the ion cannot be energized to exceed the dissociation threshold. The IR bands are labelled, assigned and compared in Table 3.

The IR feature at the high-frequency end of the scan range, labelled as Q in Fig. 4, has two maxima centred at 1475 and 1460 cm^{-1} and the corresponding calculated values are within $\sim 10 \text{ cm}^{-1}$. The normal modes involve mainly the CC stretch (ring stretch) and NH bending, the latter being particularly characteristic for N-protonated TPA-H^+ .

Computed IR spectra of ring protonated TPA isomers do not match the experimental IRMPD spectrum (see Fig. 4). The predicted spectrum for the *ortho* protonated isomer exhibits basically only one strong band (near 1500 cm^{-1}), which happens to coincide with a strong band in the experimental spectrum, so that we cannot definitively exclude a partial contribution of this isomer to the ion population. However, based on the close match between the experimental and theoretical spectra of the N-protonated isomer and the computed thermodynamics, the presence of the *ortho*-protonated species is unlikely.

Table 4 lists computed structural parameters (bond lengths and angles) for N-protonated TPA. The CNC bond angle is found to be approximately 114° , confirming, as expected, the more tetrahedral arrangement of ligands around the nitrogen atom as compared to the neutral and radical cation forms of TPA. Moreover, the C–N bond lengths are significantly longer in TPA-H^+ , testifying of the disrupted conjugation between the N-atom and the phenyl ligands and their inherent purely single-bond character.

Table 4 Bond lengths ($\text{\AA}$) and bond angles ($^\circ$) of N-protonated TPA have been calculated at the B3LYP/6-31++G(d,p) and BLYP/cc-pVTZ level of theories. Parenthesized vales are standard deviations

Parameter	Theory (DFT)	
	B3LYP/6-31++G(d,p)	BLYP/cc-pVTZ
C–C	1.396 (2)	1.398 (3)
C–N	1.506 (0)	1.521 (0)
C–H	1.085 (1)	1.087 (3)
N–H	1.025 (0)	1.028 (0)
Bond angles ($^\circ$)		
$\angle \text{HNC}$	104.3 (0)	104.1 (0)
$\angle \text{CNC}$	114.1 (0)	114.2 (0.1)

4 Conclusions

Structural characterization and in particular the effects of resonance delocalization in TPA and its ionized forms (radical cation and protonated) have been investigated by IR spectroscopy in the gas phase and quantum-chemical (DFT) calculations. Due to the complete delocalization of the HOMO in the conjugated TPA system, one might expect all CC and CN bond lengths to increase upon ionization of the molecule. However, computed bond lengths are only marginally increased, within what can probably be considered the computational accuracy. Apparently, the strong delocalization causes the effect on each individual bond length to be minimal. On the other hand, vibrational frequencies of the normal modes having predominantly CN and CC stretching character are predicted to undergo a slight red shift upon ionization. The experimental IR spectrum of the gaseous TPA radical cation recorded here confirms these predictions. The experimental IRMPD spectrum and the calculated linear absorption spectrum are generally in excellent agreement.

The strong resonance delocalization also causes the proton affinity of TPA to be strongly reduced in comparison with non-conjugated tertiary amines. It is nonetheless possible to generate protonated TPA in our MS and its IR spectrum was also recorded. The spectrum confirms that despite the relatively low PA, protonation occurs on the nitrogen atom resulting in a near-tetrahedral geometry at the N-centre.

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