

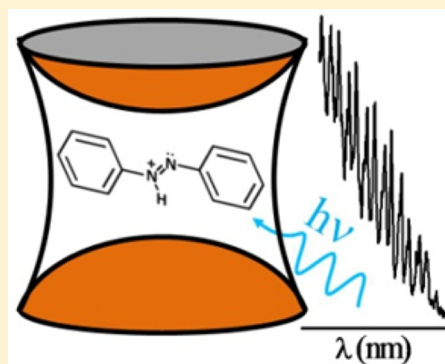
Photodissociation UV–Vis Spectra of Cold Protonated Azobenzene and 4-(Dimethylamino)azobenzene and Their Benzenediazonium Cation Fragment

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ABSTRACT: Gas phase photodissociation electronic spectra of protonated azobenzene (ABH^+) and 4-(dimethylamino)azobenzene (dmaABH^+) were measured in a cryogenically cooled ion trap at temperatures of a few tens of Kelvin. Experimental results were complemented with electronic structure calculations in the ground state at the MP2/cc-pVDZ level of theory, and in the low lying excited states using the RI-CC2 method. Calculated energies revealed that only the *trans* isomers of the azonium molecular ions (protonation site on the azo group) will likely exist in the trap at the temperatures achieved in the experiment. The first transition of *trans*- ABH^+ is $\pi^* \leftarrow \pi$, and the absorption band in the spectrum appears strongly red-shifted from that of the neutral molecule. The calculations showed that upon excitation the quasi-planar ground state (S_0) transforms into a chairlike excited state (S_1) by twisting the CNNC dihedral angle about 96° . A 41 cm^{-1} active vibrational progression found in the ABH^+ spectrum may be associated with the twisting of the azo bond. Conversely, the electronic spectrum of dmaABH^+ exhibits a steep and unstructured $S_1 \leftarrow S_0$ absorption corresponding to a less distorted S_1 state. The next two quasi-degenerate bands in the ABH^+ spectrum evidence sharper onsets and a charge transfer character. Using a second fragmentation laser and an additional He cooling pulse in the trap, it was possible to measure the UV spectrum of cold benzenediazonium fragments.



1. INTRODUCTION

In the electronic ground state, azobenzene ($\text{C}_6\text{H}_5\text{—N=N—C}_6\text{H}_5$, hereafter denoted AB) can adopt *cis* and *trans* configurations defined by the relative orientation of the two phenyl rings attached to the azo group, the *trans* isomer being approximately 0.6 eV^1 more stable than the *cis* one, and the *trans* \rightarrow *cis* isomerization barrier in the gas phase being about 1.1 eV^2 . It is well-known^{3,4} that *trans* \rightarrow *cis* isomerization of AB takes place in the electronic excited state when the molecule is excited at 365 nm , whereas the reverse reaction can be thermally activated in the ground state (in the dark, the half-life of *cis*-AB in solution is several hours, at room temperature) or induced photochemically by irradiation at 420 nm (lifetime on the picosecond scale).⁵ The photoisomerization mechanism of AB remains a matter of debate despite many years of experimental^{6–9} and theoretical^{10–13} studies. These results have been interpreted in terms of the contribution of two basic pathways that can in principle take place depending on the excitation scheme used: an inversion mechanism involving an in-plane bending of the azo-ring bonds and an out-of-plane rotation of the NN double bond. The advantageous photochromic properties of AB and its derivative compounds, as well as the ease of attaining optical control of the switching process between two photostable states, motivated research concerning the use of these molecules as molecular devices. A wide variety of complex molecular systems functionalized with ABs that

exhibit phototriggerable optical, mechanical and functional changes have been reviewed in the last years.^{14–17}

When dissolved in strong acidic aqueous solutions, ABs can attach a hydrogen ion to a free electron pair in the azo group forming azonium ions (see Scheme 1a for the particular case of protonated *trans*-azobenzene, denoted *trans*- ABH^+). In azonium ions the positive charge is delocalized by resonance in the aromatic system, lowering the energy of the π^* level. As a result, the $\pi\pi^*$ absorption band of *trans*- ABH^+ is shifted $\sim 100\text{ nm}$ (7900 cm^{-1}) to the red with respect to the same transition of AB.¹⁸

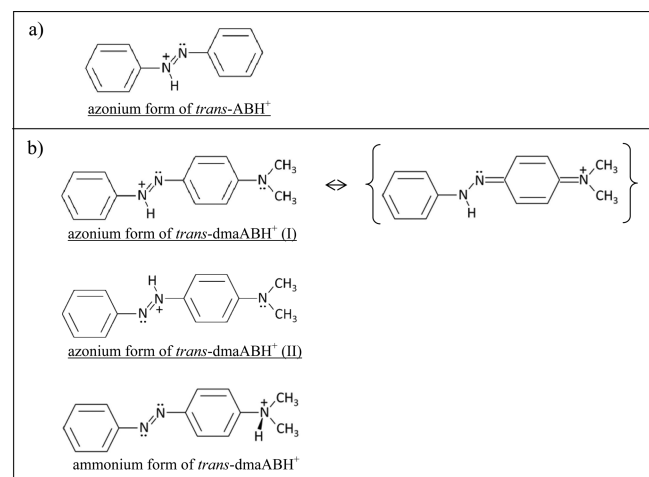
The introduction of additional functional groups on the phenyl rings of AB can dramatically alter the absorption spectra and the photochemical properties. Aminoazobenzenes are of particular interest because these molecules are known to experience tautomeric equilibria in solution, as a result of their multiple protonation sites, and therefore significant pH dependence in their optical absorption spectra. In acidic solutions, protonated aminoazobenzenes (denoted aABH^+ s) may form azonium or ammonium ions depending, respectively, on whether the hydrogen ion is attached to the azo or the amino group. See Scheme 1b for the particular case of

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Scheme 1. (a) Azonium Form of Protonated *trans*-Azobenzene (*trans*-ABH⁺); (b) Azonium Forms (I) and (II), and Ammonium Form of Protonated *trans*-4-(Dimethylamino)azobenzene (*trans*-dmaABH⁺)^a



^aMolecular ions studied in the present paper are underlined.

protonated *trans*-4-(dimethylamino)azobenzene (denoted *trans*-dmaABH⁺). There are two possible structures for the azonium tautomer, depending on the protonation site, indicated in Scheme 1b as (I) when the H atom is next to the unsubstituted ring and (II) when it is attached to the other nitrogen atom. The positive charge in the azonium form (I) is easily delocalized on the aminosubstituted aromatic ring by formation of a quinoid structure and, consequently, the NN bond adopts a hydrazone character. On the contrary, the ammonium tautomer localizes the positive charge on the sp³ nitrogen atom, preserving the azo character of the NN bond. The equilibrium between aABH⁺'s azonium and ammonium ions in liquid solution has been extensively studied^{19,20} on account of the distinct UV–vis absorption spectrum of the different tautomers: (i) the visible absorption at $\lambda_{\text{max}} \sim 500$ nm (20000 cm⁻¹) is assigned to the $\pi\pi^*$ transition of azonium ions, which is supported by the high π electronic delocalization in the molecule, and (ii) the UV band appearing at $\lambda_{\text{max}} \sim 320$ nm (31250 cm⁻¹) is attributed to the ammonium ions, because this type of tautomer is expected to have a spectrum similar to that of the neutral AB molecule ($\lambda_{\text{max}} \sim 321$ nm, $\nu_{\text{max}} \sim 31153$ cm⁻¹).¹⁸

Protonated azo compounds show faster *cis* → *trans* thermal isomerization rates, which have been explained in terms of a weaker double bond character of the azo bond due to the strong electron withdrawing effect of the positive charge introduced in the molecule upon protonation.^{20,21} The possibility of modulating the activation barrier for the *cis* → *trans* reaction of azo compounds by triggering the local pH has been proposed in the literature^{19,20} as an additional means of controlling a photodevice.

In spite of the abundant research available in the literature on the structural and photophysical properties of protonated azo compounds, no experimental studies have been performed in the gas phase for these molecular ions. Spectroscopic information about isolated ABH⁺ and aABH⁺s will contribute to clarify the assignments of the bands observed in solution by working in a solvent-free environment, allowing a more reliable comparison of the experimental data with the calculations.

Moreover, an additional advantage of probing isolated ions at very low temperatures in the gas phase is the very low possibility that intramolecular proton transfer reactions take place. Therefore, structural details as the protonation site²² in the molecule and the flexibility of the molecular structure upon excitation will also be attainable from the gas phase spectra of the cold ions complemented with ab initio calculations.

In this work we have measured the UV–vis spectra of isolated cold ABH⁺ and dmaABH⁺ ions via photofragmentation spectroscopy. The ions were prepared and cooled to a few tens of Kelvin into a cryogenic ion trap. Under these conditions and according to ab initio calculations, both molecules are protonated on the azo group (azonium tautomer) and the ions adopt a nonplanar configuration (see text). We have also recorded the UV–vis spectrum of the benzenediazonium cation (C₆H₅N₂⁺, denoted BD⁺) one the most abundant photofragments generated from the studied protonated azo compounds. This cation is a fundamental reaction intermediate with well-known applications to the dye industry, and for which UV–vis spectroscopic characterization is scarce.

2. METHODS

The experimental setup has been described in detail in earlier work.^{23,24} Here, we will present a brief summary of the main components of the apparatus and give a short explanation of the technique used to prepare the ions and record the photofragmentation electronic spectra. The protonated parent ion (ABH⁺ or dmaABH⁺) is produced in an electrospray source from a solution of water/methanol (1:1 in volume) at a concentration of 0.1 mM, containing a trace of acetic acid. We tried to observe the formation of dimers by increasing the concentration of the solution but no cluster signals were found in the mass spectrum. The ions formed in the source are injected into a cryogenically cooled Paul trap through a mass gate. It takes several tens of milliseconds to cool the ions to a temperature of about 40 K by collisions with cold He atoms pulsed into the trap. After this time, a first laser pulse is triggered and photodissociation of the cold parent ions takes place. Ionic fragments as well as the remaining parent ions can be extracted from the trap and mass-analyzed in a time-of-flight (TOF) mass spectrometer and their intensities quantified as a function of the laser wavelength. In addition, the ion fragments can be cooled by introducing a second He pulse in the trap 1 ms after the fragmentation laser pulse and probed by a second laser pulse triggered after a delay of some tens of milliseconds. Well-resolved electronic spectra of cold daughter ions can be obtained in this way. To ensure proper cooling conditions in the trap (product ion temperatures as low as those of parent ions, namely $T < 40$ K), a solution of benzylamine was occasionally electrosprayed in the source and the absence of vibrational hot bands in the benzylium ion ($m/q = 91$) spectrum (produced by photofragmentation of protonated benzylamine) was verified. One or more specific photofragments can be removed from the ion trap by exciting their axial micromotion applying specific auxiliary dipolar radiofrequencies, according to a procedure recently implemented in the setup.²⁵

Two optical parametric oscillator (OPO) lasers (EKSPLA model-NT342B) were used in the experiments, operating at a 10 Hz repetition rate and having 8 cm⁻¹ of spectral resolution and a scanning step of 0.02 nm. The lasers were focused to a 2 mm² spot in the trap and the OPO pulse energy was roughly 0.5 mJ.

Ab initio calculations were carried out with the TURBO-MOLE program package,²⁶ making use of the resolution-of-identity (RI) approximation to evaluate the electron-repulsion integrals. Ground state (S_0) equilibrium geometries of protonated species were optimized at the MP2 (second order Møller–Plesset perturbation) level of theory using the cc-pVDZ (correlation-consistent polarized valence double-zeta) basis set. Vertical excitation energies, oscillator strengths, and equilibrium geometries of the lowest excited singlet states were computed at the CC2²⁷ (second-order approximate coupled cluster) level, because standard time-dependent DFT (density functional theory) is well-known to produce substantial errors in representing charge transfer (CT) excited states.²⁸ Moreover, we have chosen the RI-CC2 method because it proved useful in describing the electronic transitions of similar aromatic ions with nitrogen functional groups.^{29,30} In all the calculations the starting geometries had C_s symmetry and were constrained to distinguish between π or σ orbitals and A' or A'' excited states. In the case of the benzenediazonium ion fragment, adiabatic excitation energies were calculated in addition to the vertical excitation values. For doing this, the energies of the ground and the first two excited states were computed for the optimized $S_1(A')$ and $S_2(A')$ excited state geometries, in C_s symmetry. Additional excited state optimizations were performed for this system and protonated azobenzene, relaxing the condition of maintaining C_s symmetry and allowing nonplanar geometries.

3. RESULTS

3.1. Electronic Spectra of ABH^+ and $dmaABH^+$ Parent Ions. Figure 1a shows the difference mass spectrum (in the presence and in the absence of the fragmentation laser) obtained upon photodissociation of the parent ion ABH^+ ($m/q = 183$, negative peak) at 384.0 nm ($\nu = 26042 \text{ cm}^{-1}$). The two most abundant ion fragments (positive peaks) correspond to the phenyl cation ($m/q = 77$), formed by heterolytic cleavage of

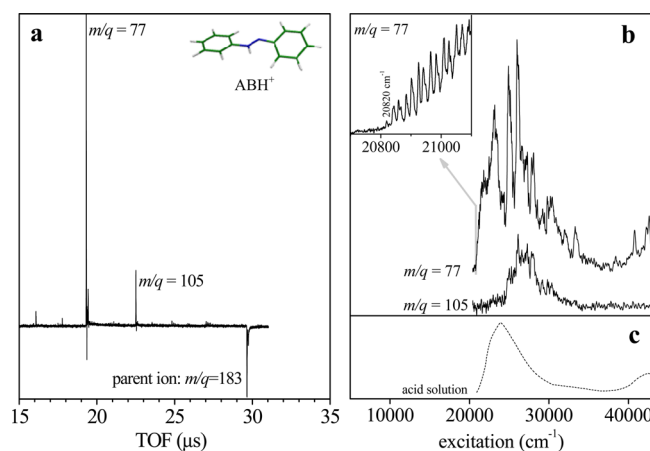


Figure 1. (a) Difference mass spectrum (fragmentation laser on–laser off) of ABH^+ ($m/q = 183$, negative peak) at $\lambda = 384.0 \text{ nm}$ ($\nu = 26042 \text{ cm}^{-1}$). Ion fragment signals (positive peaks) at $m/q = 77$ and 105 correspond respectively to phenyl and BD^+ cations. (b) Photodissociation electronic spectra of ABH^+ obtained from $m/q = 77$ and 105 mass channels. The absorption starts at $\nu = 20820 \text{ cm}^{-1}$ ($m/q = 77$ spectrum) and exhibits a vibrational progression, zoomed in the inset at a higher spectral resolution. Loss of benzene from ABH^+ to yield BD^+ ($m/q = 105$ spectrum) is restricted to the range 24390–33330 cm^{-1} . (c) Electronic spectrum of the conjugated acid of AB in strong acid solution (bulk).¹⁸

the C–N bond between one of the aromatic rings and the azo group, and BD^+ ($m/q = 105$), formed by loss of benzene (B). The CID mass spectrum³¹ at low fragmentation energy also yields the phenyl cation as the main fragment, followed by BD^+ which is about 5 times less intense.

Photodissociation electronic spectra of ABH^+ are given in Figure 1b for the mass channels $m/q = 77$ and 105. The absorption starts at $\nu = 20820 \text{ cm}^{-1}$ for the spectrum recorded on $m/q = 77$ evidencing three additional electronic transitions: two sharp bands starting at $\nu = 24534 \text{ cm}^{-1}$ and $\nu = 25648 \text{ cm}^{-1}$, and an UV band starting at $\nu = 37979 \text{ cm}^{-1}$. Both visible and UV absorptions are also present in the spectrum of the conjugated acid of AB measured in an ethanol–water solution having 65% sulfuric acid¹⁸ (Figure 1c).

The first excited state exhibits a low frequency vibrational progression in the vicinity of the band origin that can be analyzed in terms of a 41 cm^{-1} active mode starting most likely at $\nu = 20820 \text{ cm}^{-1}$ and $\nu = 20842 \text{ cm}^{-1}$ (FWHM of peaks = 12 cm^{-1}). In the inset of Figure 1b there is a zoomed view of this spectral region where the laser was scanned in 0.02 nm steps to achieve the maximal spectral resolution. The transition starting at $\nu = 20820 \text{ cm}^{-1}$ is very weak and cannot be straightforwardly assigned to the 0–0 transition. The absence of a strong 0–0 transition implies a large change in geometry in the excited state, as will be discussed later. The second spectrum in Figure 1b reveals that at $\nu = 24390 \text{ cm}^{-1}$ a new fragmentation channel opens with the production of BD^+ and then closes at about $\nu = 33330 \text{ cm}^{-1}$. In Scheme 3 we propose a mechanism for this fragmentation channel in the excited state, which involves a charge transfer in the molecule followed by an H atom migration.

Photodissociation difference mass spectrum of $dmaABH^+$ ($m/q = 226$) at 275.0 nm ($\nu = 36364 \text{ cm}^{-1}$) is given in Figure 2a. As in the case of ABH^+ , phenyl ($m/q = 77$) and benzenediazonium ($m/q = 105$) cations are the main photofragments, followed by the (dimethylamino)phenyl

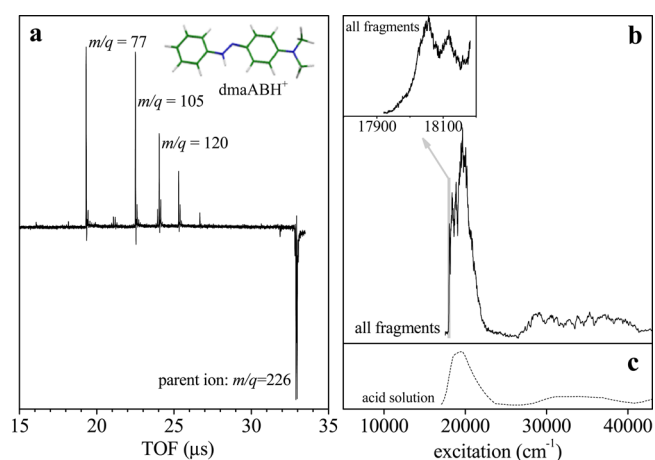


Figure 2. (a) Difference mass spectrum (fragmentation laser on–laser off) of $dmaABH^+$ ($m/q = 226$, negative peak) at $\lambda = 275.0 \text{ nm}$ ($\nu = 36364 \text{ cm}^{-1}$). Ion fragment signals (positive peaks) at $m/q = 77$, 105, and 120 correspond respectively to phenyl, BD^+ , and (dimethylamino)phenyl cations. (b) The photodissociation electronic spectra of $dmaABH^+$ is the same for all fragment mass channels ($m/q = 77$, 105, and 120), and therefore, we present the sum of all of them. The absorption starts at $\nu = 17912 \text{ cm}^{-1}$, and the band rising is zoomed in the inset. (c) Electronic spectrum of the conjugated acid of $dmaAB$ in acid solution (bulk).¹⁹

cation ($m/q = 120$) and other minor fragments. Phenyl and (dimethylamino)phenyl cations likely originate from heterolytic cleavage of the C–N bond at both sides of the azo group, whereas BD^+ forms by loss of benzene. In contrast to what is observed for ABH^+ , the photoproduct branching ratio of dmaABH^+ is invariant as a function of the excitation frequency and, therefore, the photodissociation electronic spectra in the Figure 2b results from adding up the signal from all mass channels.

The electronic spectrum of dmaABH^+ exhibits a two-band system, one in the visible and the other in a spectral range given by $\nu = 27800\text{--}41700\text{ cm}^{-1}$. Considering the width of the bands it remains uncertain how many electronic states are involved in the absorption spectrum. The visible absorption of this ion is shifted about $\nu = 2900\text{ cm}^{-1}$ to the red in comparison to ABH^+ (the band starts at $\nu = 17912\text{ cm}^{-1}$), which is a direct consequence of the extended conjugation caused by the presence of the electron-donating dma group. The absorption spectrum of a solution of dmaABH^+ in acidulated acetonitrile¹⁹ is shown in Figure 2c for comparison.

The absorption bands of dmaABH^+ are found broad and do not exhibit a sharp vibrational structure, in contrast to the ABH^+ spectrum. This is shown in the inset of Figure 2b where the onset of the visible band origin was scanned with a higher resolution. Although the onset of the band at $\nu = 17912\text{ cm}^{-1}$ does not appear to be a well-defined 0–0 transition, the absorption rises more steeply (within $\sim 50\text{ cm}^{-1}$) than in the case of ABH^+ , as evidenced by comparing the low-energy parts of ABH^+ and dmaABH^+ spectra plotted in Figure 3. It is not

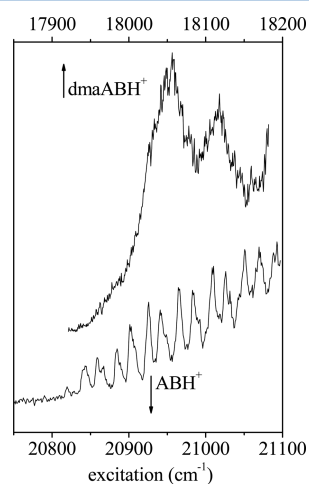


Figure 3. Low-energy part (350 wavenumbers) of ABH^+ and dmaABH^+ spectra normalized by the corresponding absorption band maxima.

clear whether the broadened spectrum of dmaABH^+ is originating from very low vibrations or from lifetime broadening, which would reveal that the excited state is relatively short-lived as it was found in protonated DNA bases.³² With a multi-Lorentzian fit, a FWHM of $\sim 70\text{ cm}^{-1}$ can be determined for the two bands in the inset of Figure 2b, which accounts for an excited state lifetime of about 50 fs, if the broadening is exclusively limited by the lifetime.

3.2. Electronic Spectrum of the Benzenediazonium (DB^+) Fragment. Photolysis of benzenediazonium salts in solution is known³³ to occur principally via dissociative loss of molecular nitrogen, giving the corresponding phenyl cation as

the primary product. Likewise, the photofragmentation mass spectrum of isolated BD^+ ions provides clear evidence for the formation of phenyl cations upon absorption of UV light. BD^+ ions produced in the trap by photodissociation of ABH^+ at $\lambda = 384\text{ nm}$ ($\nu = 26042\text{ cm}^{-1}$) were cooled to $T < 40\text{ K}$ before making use of a second laser to record the electronic spectrum. As an example, we present in Figure 4 two mass spectra of BD^+

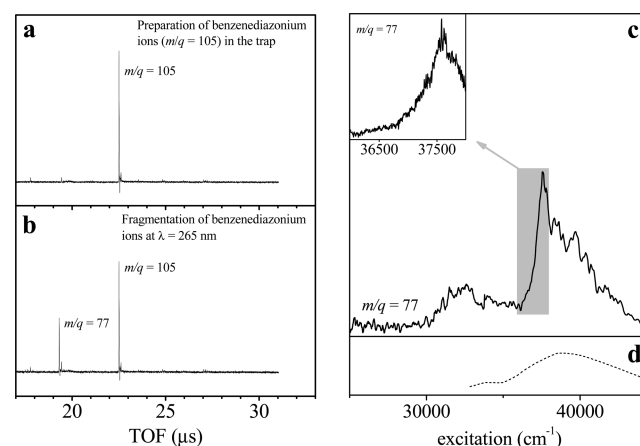


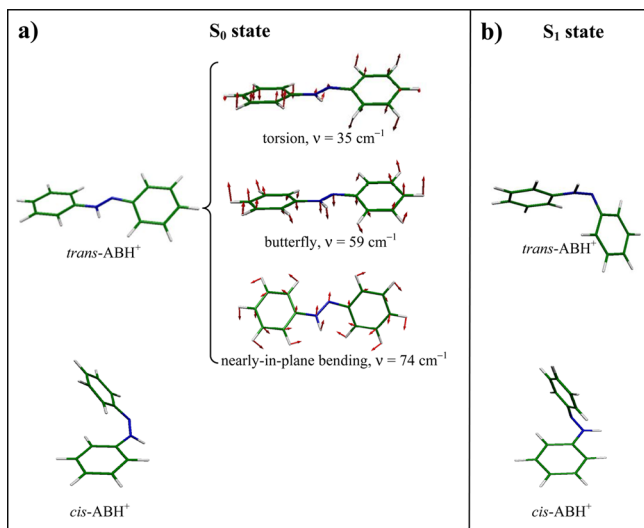
Figure 4. (a) Mass spectrum of ABH^+ photofragments at $\lambda = 384\text{ nm}$ ($\nu = 26042\text{ cm}^{-1}$) after removal of phenyl and residual parent ions from the trap by applying an auxiliary radiofrequency. Under these conditions, BD^+ ($m/q = 105$) is the most abundant ion in the trap. (b) Photodissociation mass spectrum of BD^+ ions at 265 nm ($\nu = 37736\text{ cm}^{-1}$). The main resulting fragment is the phenyl cation ($m/q = 77$). (c) Photofragmentation spectrum of BD^+ ions obtained from the $m/q = 77$ mass channel. The band starting at $\nu = 36232\text{ cm}^{-1}$ is zoomed in the inset. (d) Electronic spectrum of benzenediazonium fluoroborate in ethanolic solution (bulk).³⁴

ions recorded before (a) and after (b) excitation at $\lambda = 265\text{ nm}$ ($\nu = 37736\text{ cm}^{-1}$), where it becomes clear that the phenyl cation is the main photoproduct. The absence of ABH^+ parent ions and phenyl fragments before excitation was ensured by the use of auxiliary dipolar radiofrequencies²⁵ that removed these ions from the trap.

In view of the high efficiency of production of BD^+ fragments from ABH^+ ions, we were able to perform a photodissociation experiment as a function of the wavelength of a second laser. The absorption spectrum of cold BD^+ ions recorded in this way on the phenyl cation ($m/q = 77$) mass channel is shown in Figure 4c. The spectrum consists of two band systems, one in the $\nu = 30500\text{--}35700\text{ cm}^{-1}$ spectral region starting at $\nu = 30572\text{ cm}^{-1}$ and the other one starting at $\nu = 36232\text{ cm}^{-1}$. In the inset of Figure 4c the onset of the stronger band is zoomed at higher resolution (0.02 nm scanning step) with no evidence of sharp vibrational structures, despite the low temperature achieved. For comparison, the spectrum of benzenediazonium fluoroborate in ethanolic solution is given in Figure 4d.³⁴

3.3. Calculations. Calculations done on ABH^+ were restricted to ions protonated on one of the two equivalent nitrogen atoms of the azo group (Scheme 1a), which is the most plausible situation. We found that the *trans* isomer of ABH^+ is the most stable structure, about 0.35 eV (MP2 level of theory, cc-pVDZ basis set) lower in energy than the *cis* homologue, which adopts a twisted conformation upon geometry optimization (Scheme 2a). The same result was obtained using DFT B3LYP/cc-pVDZ level calculations, where the *trans*–*cis* energy difference results 0.48 eV. Consequently,

Scheme 2. (a) MP2-Optimized Structures of *trans*-ABH⁺ and *cis*-ABH⁺ in the S₀ State, and Lower Frequency Vibrations of *trans*-ABH⁺; (b) CC2-Optimized Structures of *trans*-ABH⁺ and *cis*-ABH⁺ in the S₁ State



we focused our attention to the *trans*-ABH⁺ ion, because the population of the *cis* isomer is expected to be negligible in the trap. Compared to the neutral *trans*-AB molecule, for which a planar structure is well established, the *trans*-ABH⁺ ion is slightly twisted out of the plane in the ground state due to steric hindrance between the acidic H atom and the adjacent aromatic ring. A small angle of 18° comes out from our S₀ calculation (Scheme 2a), which is enough to break the C_s symmetry. The lowest frequency vibrational modes calculated for *trans*-ABH⁺ in the ground state are also depicted in Scheme 2a; they can be associated with a torsional movement around the azo bond, an out-of-plane butterfly motion and a nearly in-plane collective molecular bending. In panel b of Scheme 2 we show the optimized twisted structure of the S₁ state of *trans*-ABH⁺ formed by torsion of the CNNC dihedral angle (96° in S₁), as well as the structure of *cis*-ABH⁺, which maintains its chairlike form in S₁. We have observed in the optimization process that the S₁ state of *trans*-ABH⁺ crosses the ground state through a conical intersection, as will be discussed later.

The calculated vertical transition energies of the S_{i=1–3} excited states and the corresponding oscillator strengths are given in Table 1 for *trans*-ABH⁺, as well as the resultant frontier orbitals. The energies of the band onsets measured in the experiment are also included in the table for comparison. The first excited state (S₁) exhibits a marked $\pi\pi^*$ character (bonding π -HOMO to antibonding π^* -LUMO transition) and an oscillator strength close to 1 (Table 1). We have assigned the first band of the ABH⁺ spectrum starting at $\nu = 20820 \text{ cm}^{-1}$ to the S₁ ← S₀ transition, which represents a strong red shift in comparison to the analogous $\pi^* \leftarrow \pi$ excitation in neutral AB. The next two transitions are close in energy, showing an important CT character as suggested by the shape of the molecular orbitals involved in the S₂ ← S₀ (LUMO ← HOMO–1) and S₃ ← S₀ (LUMO ← HOMO–2) transitions. Upon excitation, electron density is transferred from the π orbitals of rings 1 or 2 toward the protonated azo group. We have assigned the sharp bands observed at $\nu = 24534 \text{ cm}^{-1}$ and $\nu = 25648 \text{ cm}^{-1}$ to the S₂ ← S₀ and S₃ ← S₀ CT transitions, in that order. The CC2 vertical transition energies reported in

Table 1. (Left Panel) CC2 Vertical Excitation Energies (E₀) for *trans*-ABH⁺ in the S₀ Geometry, Transition Wavenumbers (ν_0), and Oscillator Strengths (f);^a (Right Panel) Isodensity of the Involved Frontier Orbitals^b

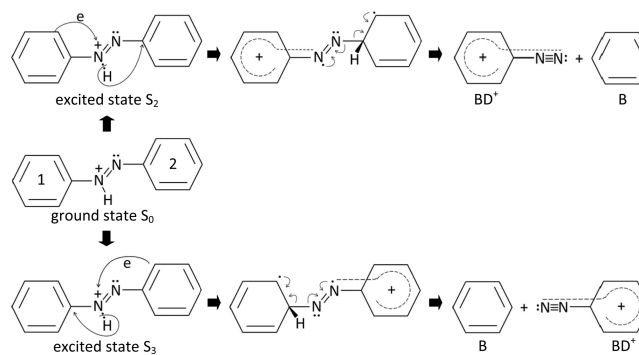
	E ₀ /eV (ν ₀ /cm ⁻¹)	E _{exp} /eV (ν _{exp} /cm ⁻¹)	f	transition	
S ₁	2.94 (23714)	2.58* (20820)	0.91	LUMO←HOMO	LUMO HOMO
S ₂	3.33 (26860)	3.08 (24534)	0.03	LUMO←HOMO-1	HOMO-1
S ₃	3.34 (26940)	3.21 (25648)	0.01	LUMO←HOMO-2	HOMO-2

^aExperimental wavenumbers (ν_{exp}) are taken from band origins. (*) weak band, the onset may not correspond to the 0–0 transition. The ground state geometry was optimized, in the C_s symmetry, at the MP2 level of theory, using the cc-pVDZ basis set. ^bThe ring closer to the protonation site is indicated as 1.

Table 1 are always larger³² than the corresponding experimental energies because the excited state potential is not optimized.

The band assignment presented in Table 1 allowed us to propose a plausible photofragmentation mechanism for the (ABH⁺ → BD⁺ + B) reaction which, as shown in Figure 1b, only takes place when the excitation is restricted to the 24390–33330 cm⁻¹ spectral range. Under these conditions, both S₂ ← S₀ and S₃ ← S₀ excitations are able to neutralize the positive charge in the protonated azo group by CT from one of the rings, and this triggers the concurrent homolytic cleavage of the NH bond and an H radical migration to the other ring (see fragmentation pathways in S₂ and S₃ excited states in Scheme 3).

Scheme 3. Plausible Fragmentation Pathways of *trans*-ABH⁺ in S₂ and S₃ Excited States for the (ABH⁺ → BD⁺ + B) Reaction^a



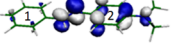
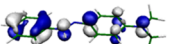
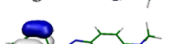
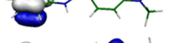
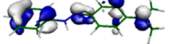
^aExcitation is restricted to the 24390–33330 cm⁻¹ spectral range.

Unlike what happens with AB, where the molecule has two equivalent protonation sites in the azo group, dmaAB can be protonated in three different positions corresponding to each one of the lone electron pairs on the nitrogen atoms (Scheme 1b). Due to the asymmetry of the molecule, the two nitrogen atoms of the azo group are slightly dissimilar, leading to the azonium structures indicated as I and II. The S₀ geometry optimization of both azonium ions of *trans*-dmaABH⁺ evidenced that structure I is 0.06 eV lower in energy than II

at the MP2 level, and 0.20 eV lower when the DFT method is used. The small computed energy difference between isomers I and II points out that both azonium ions might in principle coexist in the trap under our experimental conditions. However, recent Raman studies¹⁹ performed on dmaAB/ acetonitrile acidic solutions excited on the band maximum of Figure 2c evidenced selective enhancement of quinoid modes, implying that the preferred protonation site corresponds to structure I (Scheme 1). The third conceivable protonation site on the amino group leads to a significantly less stable tautomeric structure in the ground state, being 0.29 eV higher in energy than the azonium structure I at the MP2 level, and 0.75 eV higher from DFT calculations. The preference of structure I is consistent with previous ¹³C and ¹⁵N NMR measurements combined with MINDO calculations³⁵ done on 4-aminoazobenzene and is in accordance with the higher proton affinity computed for the dmaAB azo nitrogen using semiempirical AM1 and ab initio STO-3G studies.³⁶ By considering the low temperatures achieved in our experiment and taking into account the larger stability of the azonium structures derived from the calculations, it is possible to assume that the ammonium tautomer will likely not be present in the trap. Consequently, we have assigned the entire spectrum shown in Figure 2b to the azonium form of *trans*-dmaABH⁺, without the possibility to distinguish between isomers I and II.

The vertical transition energies (ground state geometry) calculated for the first three excited states of isomers I and II of *trans*-dmaABH⁺ are given in Table 2. The resulting energy

Table 2. (Left Panel) CC2 Vertical Excitation Energies (E_0) of the Azonium Tautomer of *trans*-dmaABH⁺ in the S_0 Geometry, Transition Wavenumbers (ν_0), and Oscillator Strengths (f);^a (Right Panel) Isodensity of the Involved Frontier Orbitals^b

iso-mer	E_0 /eV (ν_0 /cm ⁻¹)	E_{exp} /eV (ν_{exp} /cm ⁻¹)	f	transition	
S_1	(I) 2.62 (21133)	2.22 (17912)	1.35	LUMO←HOMO	LUMO 
	(II) 2.38 (19198)				HOMO 
S_2	(I) 3.76 (30331)		0.01	LUMO←HOMO-1	HOMO-1 
	(II) 3.60 (29036)				HOMO-2 
S_3	(I) 4.00 (32258)		0.01	LUMO←HOMO-2	HOMO-2 
	(II) 3.77 (30414)				

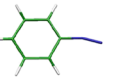
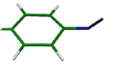
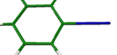
^aThe experimental wavenumber (ν_{exp}) is taken from the band origin. The ground state geometry was optimized, in the C_s symmetry, at the MP2 level of theory, using the cc-pVDZ basis set. ^bThe ring closer to the protonation site is indicated as 1.

values are close to those calculated previously¹⁹ for the azonium ion of 4-aminoazobenzene. The excitation to the S_1 state (LUMO ← HOMO) can be characterized as a $\pi^* \leftarrow \pi$ transition with a significant oscillator strength, which can be associated with the first band of the dmaABH⁺ spectrum starting at $\nu = 17912$ cm⁻¹.

According to our calculations, the second band system observed in the experiment starting at $\nu = 26546$ cm⁻¹ (3.29 eV) could originate from the $S_2 \leftarrow S_0$ or $S_3 \leftarrow S_0$ transitions although, unlike what happens in unsubstituted ABH⁺, these two transitions cannot be easily assigned in the spectrum of dmaABH⁺. The excited state energies of isomers I and II in Table 2 are very close and, because the experimental bands are very broad, it is not possible to exclude the contribution of isomer II to the spectrum.

Finally, both vertical (E_0 , S_0 geometry) and adiabatic (E_1 , S_1 geometry; E_2 , S_2 geometry) low-lying excitation energies were computed for the benzenediazonium fragment and summarized in Table 3, relative to the ground state energy. The two band

Table 3. (Left Panel) CC2 vertical (E_0 , S_0 Geometry) and Adiabatic (E_1 , S_1 Optimized C_s Geometry; E_2 , S_2 Optimized C_s Geometry) Excitation Energies of BD⁺, Transition Wavenumbers ($\nu_{i=0,2}$), and Oscillator Strengths (f);^a (Right Panel) BD⁺ Geometries Corresponding to the Ground State (S_0) and the Conical Intersections ($S_0 = S_1$) and ($S_1 = S_2$), Determined by Performing out-of-Plane Optimizations of the First and Second Excited States

	E_0 /eV (ν_0 /cm ⁻¹)	E_1 /eV (ν_1 /cm ⁻¹)	E_2 /eV (ν_2 /cm ⁻¹)	E_{exp} /eV (ν_{exp} /cm ⁻¹)	f	
S_1	4.40 (35486)	3.98 (32092)		3.79* (30572)	0.04	$S_1=S_2$ 
S_2	4.97 (40080)		4.82 (38865)	4.49* (36232)	0.36	$S_0=S_1$ 
						S_0 

^aExperimental wavenumbers (ν_{exp}) are taken from band origins. (*) weak band, the onset may not correspond to the 0–0 transition. Ground and excited state geometries were optimized, in the C_s symmetry, respectively, at MP2 and CC2 levels of theory, using the cc-pVDZ basis set.

systems observed in the spectrum of BD⁺ were assigned to the first two $\pi^* \leftarrow \pi$ transitions ($S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$) shown in the table. As usual, calculated vertical excitations E_0 are about 0.5 eV higher than the experimental values, and the adiabatic transition energies E_1 (S_1 geometry) and E_2 (S_2 geometry) become closer to the experimental values. The experimental band onsets included in the table may not correspond to 0–0 transitions, considering the absence of sharp absorption peaks in the spectrum.

4. DISCUSSION

If one compares the slow rising of the first *trans*-ABH⁺ band system (Figure 1b) with typical well-defined vibrational structures measured in our setup for other cold aromatic molecules protonated on nitrogen atoms,^{37,38} it is possible to postulate that in addition to thermal broadening a substantial change in the potential upon photoexcitation and hence a low Franck–Condon factor exists for this transition. The large geometrical change adopted by the molecule upon excitation can be visualized by comparing the optimized structures of *trans*-ABH⁺ in the S_0 and S_1 states that are displayed in Scheme 2. Half of the molecule flips to a perpendicular position leading to a chairlike structure, with a CNNC dihedral angle of about 96°. This implies that in the S_1 excited state the observed planar-to-chair isomerization reaction of *trans*-ABH⁺ proceeds via a mechanism that resembles the rotation pathway described for the *trans* → *cis* isomerization in neutral ABs. However, the yield of *cis*-isomers might be very low in the case of protonated ABs, because the chair-to-planar back reaction is expected to be very fast. Rotation around the NN bond will be certainly favored by protonation on one of the N atoms because it decreases the double bond character.

The loss of planarity of ABH⁺ in S_1 could also be responsible of the absence of BD⁺ fragments ($m/q = 105$) in the

photodissociation spectrum for $\nu < 24390 \text{ cm}^{-1}$. According to the fragmentation mechanism proposed in Scheme 3, the ($\text{ABH}^+ \rightarrow \text{BD}^+ + \text{B}$) reaction would be favored by an in-plane ring \rightarrow azo electron transfer, in which one π electron of the ring migrates to the empty p orbital on the positively charged N atom to extend the conjugation. In addition, the twisting process occurring in the S_1 state would convert very quickly the electronic energy into S_0 vibrational energy through the S_1 – S_0 conical intersection found in the calculations, and this will favor the release of $m/q = 77$ fragments like in the case of CID fragmentation in the ground state. The 41 cm^{-1} active vibrational progression observed in the ABH^+ spectrum (inset of Figure 1b) may also be associated with the twisting of the azo bond if one considers that the calculated NN torsional mode in the ground state is very close in energy ($\nu = 35 \text{ cm}^{-1}$, in Scheme 2).

The next two quasi-degenerate bands in the spectrum of ABH^+ exhibit sharper onsets than that of the first band. This observation is compatible with having sufficiently large Franck–Condon factors to compensate the low oscillator strength values calculated for $S_2 \leftarrow S_0$ and $S_3 \leftarrow S_0$ excitations. As a result, it can be assumed that the geometry of S_2 and S_3 states will be akin to that of the S_0 state.

As shown in Figure 3, the first band in the spectrum of dmaABH^+ exhibits a different behavior than that of ABH^+ . The onset is markedly steeper in the case of dmaABH^+ , evidencing a smaller distortion of the S_1 equilibrium geometry. One can tentatively assign this difference to the resonance donating effect of the terminal dimethylamino group, which contributes to preserve a quasi-planar geometry in the excited state. The similar geometries of the ground and first excited states of dmaABH^+ may also account for the production of $m/q = 105$ fragment ions.

As already pointed out, in the conditions of the trap, protonation of AB or dmaAB leads to the azonium form of the molecular ions. We have neglected the presence of the ammonium mesomer of dmaABH^+ because of the large energy difference found in the S_0 states. Moreover, supplementary excited state calculations carried out for the ammonium tautomer of dmaABH^+ have shown that the first transition having a non-negligible oscillator strength value appears at 3.79 eV ($\nu = 30581 \text{ cm}^{-1}$), and this does not match with the observed spectrum or in any case the ammonium band would be obscured by the $S_2 \leftarrow S_0$ transition of the azonium form.

The spectrum of cold BD^+ given in Figure 4c does not present well-resolved vibrational structures as those observed for similar systems in comparable conditions.^{30,39} This is an indication that a substantial change in geometry occurs in the excited state or that its lifetime is very short. To study this possibility, we have optimized S_1 and S_2 excited states of BD^+ by releasing the constraint of maintaining the ground state C_s geometry at cc-pVDZ/CC2 level. The computed S_1 and S_2 geometries show that the diazonium group ($-\text{N}^+\equiv\text{N}$) abandons the plane defined by the aromatic ring and bends. Two conical intersections associated with the crossings $S_1 = S_0$ and $S_2 = S_1$ emerge from the calculations at the geometries depicted in the right panel of Table 3, and no barrier was found in these optimization processes. A fast internal conversion through the two aforementioned conical intersections could account for the absence of a well-defined vibrational progression in the BD^+ absorption bands. Accordingly, a fast deactivation of BD^+ is expected to take place by relaxation processes linked to the torsion of the diazonium group.

5. CONCLUSIONS

UV–vis electronic spectra of ABH^+ , dmaABH^+ , and BD^+ ions confined in a cryogenically cooled trap were measured by photodissociation spectroscopy and the results were interpreted with the aid of ab initio calculations that include vertical excitation energies, normal modes in the S_0 state, and geometry optimizations in the ground and low lying excited states.

According to our ab initio computations, *cis* isomers do not exist at the temperature of the trap, and the protonated forms of *trans*-AB and *trans*-dmaAB in the trap correspond to azonium structures, with no preference between isomers I and II in the case of dmaABH^+ . We have shown that the $S_1 \leftarrow S_0$ transition of ABH^+ and dmaABH^+ mainly corresponds to a LUMO \leftarrow HOMO ($\pi^* \leftarrow \pi$) excitation, the band of the substituted azobenzene being strongly red-shifted due to the donating effect of the dma lone electron pair into the π system. At slightly higher energies, two intense CT transitions ($S_2 \leftarrow S_0$ and $S_3 \leftarrow S_0$) are clearly distinguished in the ABH^+ spectrum. In contrast to S_1 , S_2 and S_3 states preserve a quasi-planar structure in which an electron transfer takes place via the π orbitals system, along with the production of BD^+ photofragments. Despite the size of the molecular ions involved in this study, we conclude that fragmentation is not exclusively due to internal conversion but some electronic properties of the excited states are revealed in the measured fragmentation patterns.

An efficient photoisomerization process connected to the torsion of the azo bond was shown in this study for ABH^+ ions. It consists of a planar-to-chair dynamics that is related to the *trans* \rightarrow *cis* rotation mechanism described in photoexcited neutral ABs. Photoisomerization was found very sensitive to substitution by dma groups. The more pronounced rising of the first absorption band measured in the dmaABH^+ electronic spectrum, and the good yield of BD^+ fragments upon S_1 excitation, allowed us to speculate that the planar-to-chair dynamics is hindered in this case. A reason for that is the larger resonance delocalization induced by the dma terminal group, which may contribute to preserve a quasi-planar geometry in the S_1 excited state.

In addition, we are presenting the photofragmentation UV spectrum of BD^+ , a very stable and fundamental ion that results from photofragmentation of ABH^+ . Although the ion is cooled in the trap, the observed spectrum is not well resolved, which is indicative of a strong change in the excited state geometry by torsion of the diazonium group or/and fast relaxation processes.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Schulze, F. W.; Petrick, H. J.; Cammenga, H. K.; Klinge, H. Thermodynamic Properties of the Structural Analogues Benzo[c]-cinnoline, trans-Azobenzene, and cis-Azobenzene. *Z. Phys. Chem.* **1977**, *107*, 1–19.
- (2) Andersson, J. A.; Petterson, R.; Tegnér, L. Flash Photolysis Experiments in the Vapour Phase at Elevated Temperatures I: Spectra of Azobenzene and the Kinetics of its Thermal cis-trans Isomerization. *J. Photochem.* **1982**, *20*, 17–32.
- (3) Ikeda, T.; Tsutsumi, O. Optical Switching and Image Storage by Means of Azobenzene Liquid-Crystal Films. *Science* **1995**, *268*, 1873–1875.
- (4) Tamai, N.; Miyasaka, H. Ultrafast Dynamics of Photochromic Systems. *Chem. Rev.* **2000**, *100*, 1875–1890.
- (5) Kobayashi, T.; Degenkolb, E. O.; Rentzepis, P. M. Picosecond Spectroscopy of 1-phenylazo-2-hydroxynaphthalene. *J. Phys. Chem.* **1979**, *83*, 2431–2434.
- (6) Rau, H.; Lueddecke, E. On the Rotation-Inversion Controversy on Photoisomerization of Azobenzenes. Experimental Proof of Inversion. *J. Am. Chem. Soc.* **1982**, *104*, 1616–1620.
- (7) Fujino, T.; Tahara, T. Picosecond Time-Resolved Raman Study of trans-Azobenzene. *J. Phys. Chem. A* **2000**, *104*, 4203–4210.
- (8) Chang, C.-W.; Lu, Y.-C.; Wang, T.-T.; Diau, E. W. -G. Photoisomerization Dynamics of Azobenzene in Solution with S₁ Excitation: A Femtosecond Fluorescence Anisotropy Study. *J. Am. Chem. Soc.* **2004**, *126*, 10109–10118.
- (9) Tan, E. M. M.; Amirjalayer, S.; Smolarek, S.; Vdovin, A.; Zerbetto, F.; Buma, W. J. Fast Photodynamics of Azobenzene Probed by Scanning Excited-State Potential Energy Surfaces Using Slow Spectroscopy. *Nat. Commun.* **2015**, *6*, 5860.
- (10) Monti, S.; Orlandi, G.; Palmieri, P. Features of the Photochemically Active State Surfaces of Azobenzene. *Chem. Phys.* **1982**, *71*, 87–99.
- (11) Crecca, C. R.; Roitberg, A. E. Theoretical Study of the Isomerization Mechanism of Azobenzene and Disubstituted Azobenzene Derivatives. *J. Phys. Chem. A* **2006**, *110*, 8188–8203.
- (12) Conti, L.; Garavelli, M.; Orlandi, G. The Different Photoisomerization Efficiency of Azobenzene in the Lowest nπ* and ππ* Singlets: The Role of a Phantom State. *J. Am. Chem. Soc.* **2008**, *130*, 5216–5230.
- (13) Cusati, T.; Granucci, G.; Persico, M. Photodynamics and Time-Resolved Fluorescence of Azobenzene in Solution: A Mixed Quantum-Classical Simulation. *J. Am. Chem. Soc.* **2011**, *133*, 5109–5123.
- (14) Bandara, H. M. D.; Burdette, S. C. Photoisomerization in Different Classes of Azobenzene. *Chem. Soc. Rev.* **2012**, *41*, 1809–1825.
- (15) Mahimwalla, Z.; Yager, K. G.; Mamiya, J.; Shishido, A.; Priimagi, A.; Barrett, C. J. Azobenzene Photomechanics: Prospects and Potential Applications. *Polym. Bull.* **2012**, *69*, 967–1006.
- (16) Beharry, A. A.; Woolley, G. A. Azobenzene Photoswitches for Biomolecules. *Chem. Soc. Rev.* **2011**, *40*, 4422–4437.
- (17) Shishido, A. Rewritable Holograms Based on Azobenzene-Containing Liquid-Crystalline Polymers. *Polym. J.* **2010**, *42*, 525–533.
- (18) Jaffé, H. H.; Yeh, S.-J.; Gardner, R. W. The Electronic Spectra of Azobenzene Derivatives and Their Conjugate Acids. *J. Mol. Spectrosc.* **1958**, *2*, 120–136.
- (19) Matazo, D. R. C.; Ando, R. A.; Borin, A. C.; Santos, P. S. Azo-Hydrazone Tautomerism in Protonated Aminoazobenzenes: Resonance Raman Spectroscopy and Quantum-Chemical Calculations. *J. Phys. Chem. A* **2008**, *112*, 4437–4443.
- (20) Dunn, N. J.; Humphries, W. H.; Offenbacher, A. R.; King, T. L.; Gray, J. A. pH-Dependent cis→trans Isomerization Rates for Azobenzene Dyes in Aqueous Solution. *J. Phys. Chem. A* **2009**, *113*, 13144–13151.
- (21) Sokalski, W. A.; Góra, R. W.; Bartkowiak, W.; Kobylinski, P.; Sworakowski, J.; Chyla, A.; Leszczynski, J. New Theoretical Insight into the Thermal cis–trans Isomerization of Azo Compounds: Protonation Lowers the Activation Barrier. *J. Chem. Phys.* **2001**, *114*, 5504–5508.
- (22) Féraud, G.; Esteves-López, N.; Dedonder-Lardeux, C.; Jouvét, C. UV Spectroscopy of Cold Ions as a Probe of the Protonation Site. *Phys. Chem. Chem. Phys.* **2015**, *17*, 25755–25760.
- (23) Alata, I.; Bert, J.; Broquier, M.; Dedonder-Lardeux, C.; Féraud, G.; Grégoire, G.; Soorkia, S.; Marceca, E.; Jouvét, C. Electronic Spectra of the Protonated Indole Chromophore in the Gas Phase. *J. Phys. Chem. A* **2013**, *117*, 4420–4427.
- (24) Féraud, G.; Dedonder-Lardeux, C.; Jouvét, C.; Inokuchi, Y.; Haino, T.; Sekiya, R.; Ebata, T. Development of Ultraviolet–Ultraviolet Hole-Burning Spectroscopy for Cold Gas-Phase Ions. *J. Phys. Chem. Lett.* **2014**, *5*, 1236–1240.
- (25) Kang, H.; Féraud, G.; Dedonder-Lardeux, C.; Jouvét, C. New Method for Double-Resonance Spectroscopy in a Cold Quadrupole Ion Trap and Its Application to UV–UV Hole-Burning Spectroscopy of Protonated Adenine Dimer. *J. Phys. Chem. Lett.* **2014**, *5*, 2760–2764.
- (26) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. Electronic Structure Calculations on Workstation Computers: The Program System Turbomole. *Chem. Phys. Lett.* **1989**, *162*, 165–169.
- (27) Hättig, C.; Weigend, F. CC2 Excitation Energy Calculations on Large Molecules Using the Resolution of the Identity Approximation. *J. Chem. Phys.* **2000**, *113*, 5154–5161.
- (28) Dreuw, A.; Head-Gordon, M. Failure of Time-Dependent Density Functional Theory for Long-Range Charge-Transfer Excited States: The Zincbacteriochlorin–Bacteriochlorin and Bacteriochlorophyll–Spheroidene Complexes. *J. Am. Chem. Soc.* **2004**, *126*, 4007–4016.
- (29) Féraud, G.; Broquier, M.; Dedonder-Lardeux, C.; Grégoire, G.; Soorkia, S.; Jouvét, C. Photofragmentation Spectroscopy of Cold Protonated Aromatic Amines in the Gas Phase. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5250–5259.
- (30) Féraud, G.; Dedonder-Lardeux, C.; Soorkia, S.; Jouvét, C. Photofragmentation Spectroscopy of Benzylum and 1-Phenylethyl Cations. *C. J. Chem. Phys.* **2014**, *140*, 024302.
- (31) Horai, H.; Arita, M.; Kanaya, S.; Nihei, Y.; Ikeda, T.; Suwa, K.; Ojima, Y.; Tanaka, K.; Tanaka, S.; Aoshima, K.; et al. MassBank: A Public Repository for Sharing Mass Spectral Data for Life Sciences. *J. Mass Spectrom.* **2010**, *45*, 703–714.
- (32) Berdakin, M.; Féraud, G.; Dedonder-Lardeux, C.; Jouvét, C.; Pino, G. A. Excited States of Protonated DNA/RNA Bases. *Phys. Chem. Chem. Phys.* **2014**, *16*, 10643–10650.
- (33) Gasper, S. M.; Devadoss, C.; Schuster, G. B. Photolysis of Substituted Benzenediazonium Salts: Spin-Selective Reactivity of Aryl Cations. *J. Am. Chem. Soc.* **1995**, *117*, 5206–5211.
- (34) Sukigara, M.; Kikuchi, S. Studies of the Photochemistry of Aromatic Diazo Compounds. I. Electronic Structure and Photodecomposition of Benzenediazonium Salt. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 461–466.
- (35) Kuroda, Y.; Lee, H.; Kuwae, A. Direct Evidence for the Site of Protonation of 4-Aminoazobenzene by Nitrogen-15 and Carbon-13 Nuclear Magnetic Resonance Spectroscopy. *J. Phys. Chem.* **1980**, *84*, 3417–3423.
- (36) Liwo, A.; Tempczyk, A.; Widernik, T.; Klentak, T.; Czermiński, J. A Theoretical Study of Protonation and Tautomerization of N-Substituted Aminoazobenzenes. *J. Chem. Soc., Perkin Trans. 2* **1994**, 71–75.
- (37) Féraud, G.; Broquier, M.; Dedonder-Lardeux, C.; Grégoire, G.; Soorkia, S.; Jouvét, C. Photofragmentation Spectroscopy of Cold Protonated Aromatic Amines in the Gas Phase. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5250–5259.

(38) Noble, J. A.; Dedonder, C.; Juvet, C. The Electronic Spectra of Protonated Nitrogen-Substituted Polycyclic Aromatic Hydrocarbon Molecules. *Astron. Astrophys.* **2015**, *577*, A79.

(39) Dedonder, C.; Féraud, G.; Juvet, C. Communication: Identification of Daughter Ions through Their Electronic Spectroscopy at Low Temperature. *J. Chem. Phys.* **2014**, *141*, 131101.