Rydberg Fingerprint Spectroscopy of Hot Molecules: Structural Dispersion in Flexible Hydrocarbons

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We explore how structural dispersion in flexible hydrocarbon chain molecules at very high temperatures is reflected in the photoionization spectra of Rydberg levels. The spectra of *N*,*N*-dimethylisopropanamine, *N*,*N*-dimethyl-1-butanamine, *N*,*N*-dimethyl-2-butanamine, *N*,*N*-dimethyl-3-hexanamine, and 1,4-dimethylpiperazine, taken at effective vibrational temperatures of 700−1000 K, show well-resolved features stemming from the 3p and 3s Rydberg states. The line shapes observed in molecules with internal rotation degrees of freedom show that multiple structures are populated. Following up on the discovery that low-lying Rydberg states provide sensitive fingerprints of molecular structures, this work supports Rydberg fingerprint spectroscopy as a tool to probe structural details of molecules in the presence of complex energy landscapes and at high vibrational temperatures. A simple model accounts for the sensitivity of Rydberg fingerprint spectroscopy to the molecular shape, as well as the relative insensitivity of the spectra toward vibrational excitation.

Introduction

The characterization of molecular structures has provided profound insights into the physicochemical properties of molecules and has greatly aided scientific disciplines ranging from chemistry to material science and biology. Building on well-established methods such as diffraction or absorption spectroscopy, different disciplines have benefited from the specialization of common techniques: for example, the coupling of mass spectrometry with the chromatographic separation of analytes allows for cleaner sample analysis,[1,2] and the ability of time-resolved two-dimensional spectroscopy to selectively probe specific structural components of highly complex species is of tremendous help in the study of biopolymers.[3−5]

Despite this impressive progress, many fundamental problems involving the characterization of molecular structures remain challenging. Of particular note are the difficulties of observing molecular structures of even medium-sized molecules during chemical reactions. The problems stem from two specific sources: first, the molecules that undergo chemical transformations are often able to move about multiple internal degrees of freedom. And, second, the very ability to undergo a chemical reaction implies that the internal energy of the molecule is high, and at least comparable to the energy barriers that separate the reactants from the products.

Large molecules with many flexible bonds often feature a complex, multidimensional energy landscape with multiple minima. One approach to study such systems is to freeze out the thermal motion of the molecules, effectively condensing them in a structure associated with an energy minimum.[6,7] This approach sheds light on the ground state molecular structures and can even be used to analyze the intricate and shallow van der Waals potential energy surfaces that exist between molecules. With very few exceptions,[8] however, the freezing of molecular motions runs counter to the study of molecular transformations, which invariably require the excitation of molecules to energies that are significant in comparison with the hills in the energy landscape.

The observation of molecules during chemical reactions has been achieved by ultrafast time-resolved spectroscopy: by employing linear and nonlinear spectroscopic techniques in combination with ultrashort laser pulses, one can probe the motions of molecules during the breakage of chemical bonds in exquisite detail.[9−12] However, many of those investigations focus on small molecules with relatively straightforward potential energy surfaces of low dimensionality. The study of reaction dynamics of large, polyatomic molecules is much more complicated, because the reactions occur on multidimensional energy landscapes. This results in complex motions of atoms and functional groups and in complicated spectra that can often not be interpreted. Yet from a chemist's point of view the interesting reactions are just those that involve polyatomic molecules with significant internal energy and a multitude of isomeric or conformeric molecular structures, or in other words, a dispersion of molecular structures. Those reactions are always in what has been termed the statistical limit, where the spectra of the molecular eigenstates are intrinsically unresolvable.[13] It is this combination of spectra that are often intrinsically unresolvable with the desire to observe the dispersion of molecular structures that makes the time-resolved investigation of chemical dynamics so difficult. The challenge is out to develop a method that is capable of probing molecular structures associated with complex energy landscapes in the presence of chemically significant energies.

The binding energies of Rydberg electrons are inherently sensitive to the structure of the molecular ion cores,[14−19] a discovery that we have used to characterize the shapes of molecules in a technique that we call Rydberg Fingerprint Spectroscopy (RFS).[20−22] The binding energy, E_B, associated with an electron in a Rydberg orbital can be analyzed and assigned in terms of its principal quantum number, n, and the quantum defect, δ_l,[23−25] where n is an integer and δ_l is a number

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typically between 0 and 1 that depends on the angular momentum, l, of the electron:

$$E_B = \frac{R_{Ry}}{(n - \delta_l)^2}$$

Here, R_{Ry} is the Rydberg constant, 13.606 eV. Because the potential energy surface of the Rydberg state is nearly identical to that of the ion,[26] the ionization from the Rydberg state leaves the vibrational energy content of the molecule largely untouched, so that the binding energy is directly calculated by subtracting the kinetic energy of the ejected electron, E_{e-}, from the energy of the photon, $E_{h\nu}$. The quantum defects so obtained have been found to be sensitive to the size, shape and charge distributions of molecules. This can be rationalized by considering the electron as passing the ion core during its round trip, and allowing for a structure-sensitive phase shift arising from each passage. Because the electron wave function has to be constructively interfering after each round trip, the phase shifts incurred during the elastic scattering from the ion core must be reflected in the binding energy of the electron.

Our research on RFS has already established that the large size of Rydberg orbitals makes the technique sensitive toward the global structure of the molecule: changes of the chemical structure far from the ion core have been found to affect the term value of the Rydberg states. Similarly, we have shown that the Rydberg fingerprint spectra are not particularly sensitive toward thermal excitation.[15] Thus, the ingredients are in place to explore if RFS can be applied to observe the structural dispersion of molecules that are vibrationally excited to a chemically significant energy.

The subjects of our studies are a set of saturated hydrocarbon chain molecules connected to a tertiary amine group: *N*,*N*-dimethylisopropanamine (DMIPA), *N*,*N*-dimethyl-1-butanamine (DM1BA), *N*,*N*-dimethyl-2-butanamine (DM2BA) and *N*,*N*-dimethyl-3-hexanamine (DM3HA). For comparison we also measured the spectrum of the cyclic 1,4-dimethylpiperazine (DMPZ). In these molecules, the tertiary amine group lends itself to facile excitation to the $n = 3$ Rydberg states and, therefore, serves as a "Rydberg chromophore". The aliphatic chains allow for rotation about carbon−carbon single bonds and thereby provide a complex energy landscape that is only weakly coupled to the Rydberg chromophore. Conceptually, we visualize the Rydberg excited systems as consisting of a positive ion core at the amine site, with a Rydberg electron wave function that is delocalized over a large volume with a characteristic dimension of 1−2 nm. This wave function encompasses the aliphatic tail and can therefore spy on the structural features of the molecule.

Our experiments are conducted by exciting the sample molecules to the 3p Rydberg state using a 5.96 eV photon, and observing the photoelectron spectrum obtained upon ionization with a 2.98 eV photon (Figure 1). The straightforward analysis of the spectrum in terms of the binding energy of the Rydberg electron provides the desired Rydberg fingerprint spectrum. From previous work on the relaxation dynamics of tertiary amines,[27,28] we know that the excitation from the ground state, where the amine group has a pyramidal geometry, to the planar 3p Rydberg excited state, deposits about 1 eV of energy into vibrations. Separately, the internal conversion from 3p to 3s proceeds on a subpicosecond time scale, and deposits another 0.5 eV of energy into the vibrational modes. Intramolecular vibrational relaxation quickly distributes this energy among the degrees of freedom available in the Rydberg chromophore and the aliphatic chains. In molecules with short hydrocarbon chains this implies that the typical assortment of stretching and bending vibrations are excited. In the larger molecules, there are additionally the rotations about the carbon−nitrogen and carbon−carbon single bonds, which allow the molecules to assume multiple global structures. In the limit of very large chain molecules this type of motion is observed as the folding of macromolecules such as proteins. The question we ask here is how the dispersion of molecular structures in highly energetic aliphatic amines manifests itself in the Rydberg fingerprint spectra.

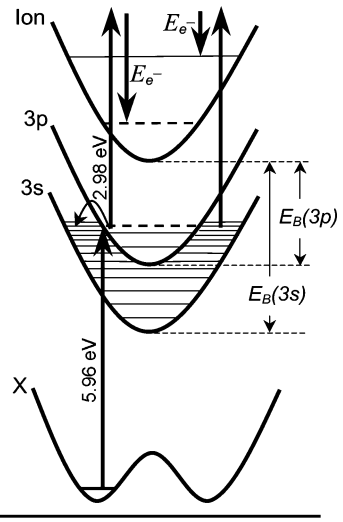


Figure 1. 1 + 1′ REMPI excitation and ionization scheme used in our investigations: Excitation by a 5.96 eV photon excites the tertiary amine to the 3p Rydberg state, which rapidly decays to the lower 3s state. Subsequent ionization by a time-delayed 2.98 eV photon produces either fast electrons if ionized from the 3p level or slow electrons if ionized out of 3s. E_B denotes the binding energy of the electron in the representative state.

Experimental Details

The sample molecules are seeded in a helium carrier gas and entrained in a molecular beam where they undergo photoexcitation and ionization by sequential absorption of two photons. The experiments were performed using a molecular beam apparatus outfitted with a time-of-flight photoelectron spectrometer as previously described.[29,30] The apparatus was interfaced with a commercial, variable pulse duration regenerative amplifier laser system (Positive Light, Spitfire) operating at a repetition rate of 5 kHz. To create the ultrashort seed pulses, a 6 W Nd:YVO_4 CW diode laser (Spectra Physics, Millenia) pumped a titanium:sapphire oscillator laser (Spectra Physics, Tsunami) running at 80 MHz, having a near-IR tuning range between 760 and 840 nm. For seeding the regenerative amplifier, the bandwidth of the oscillator output was reduced, generating amplified pulses of picosecond duration. At the wavelength of the experiment, 836 nm, we obtained approximately 400 μJ pulses with a duration no shorter than 15 ps as measured by autocorrelation. The 836 nm output was upconverted to the second (415.8 nm) and fourth (207.9 nm) harmonics using BBO crystals. These harmonics, with bandwidths of 12 and 23 meV, respectively, served as the probe and pump pulses, respectively.

The molecular beam and the laser beams crossed at the laser focus, where the intensity was approximately 1.7×10^{12} W/cm^2 for the second harmonic, and 5.1×10^{10} W/cm^2 for the fourth harmonic. Nascent photoelectrons were allowed to traverse a 14.6 cm field-free drift tube before being detected by a

microchannel plate detector. The energy resolution of the photoelectron spectrometer approaches 10 meV for slow electrons, but can be somewhat larger for faster electrons. In the present experiments, the spectral resolution was limited by the bandwidth of the fourth harmonic laser pulse.

The tertiary amines DMIPA, DM1BA and DMPZ were purchased from Aldrich and used without further purification. DM2BA was synthesized from 2-butylamine in an Eschweiler−Clarke reaction,[31] whereas DM3HA was synthesized via an S_N2-type reaction using the cyanoamine adduct of propanal, dimethylamine and cyanide, reacted with the Grignard reagent propylmagnesium-bromide. To reduce clustering of the amines in the molecular beam,[32] the samples were placed in temperature-controlled baths ranging from 0 to −60 °C with seeding in the helium carrier gas.

Results

Rydberg fingerprint spectra were taken for DMPZ, DMIPA, DM2BA, DM1BA, and DM3HA. Ignoring the internal rotation of the methyl rotors, these molecules have 0−4 internal rotations about C−C or C−N skeleton bonds, respectively (insets in Figure 2). Spectra were taken at two delay times between the 207.9 nm pump pulse and the 415.8 nm probe pulse. The first (Figure 2) corresponds to approximately zero delay time, where both pulses are roughly coincident in time. Spectra taken at a nominal delay time of 30 ps are displayed in Figure 3. Given the long pulse duration, determination of the precise temporal overlap was difficult, and in the 30 ps case, there may well be a residual overlap between the wings of the laser pulses.

The spectra show that the Rydberg level structure of the molecules under consideration is quite analogous. The 3p states have binding energies of about 2.2−2.3 eV, respectively. In spectra taken with a femtosecond laser pulse, all three of the 3p peaks are apparent.[28] In the spectra presented here only one of them is seen, suggesting that the others decay on a somewhat faster time scale. The 3s Rydberg levels are at binding energies of 2.7−2.9 eV, and feature peak shapes that will be discussed in some detail later.

From the spectra, it is again immediately apparent that RFS is sensitive to the outer fringes of the molecular structure. The center of the positive charge is, at least for the noncyclic amines, localized at the nitrogen atom. The immediate vicinity of the nitrogen consists of two methyl groups, and the carbon atom of the aliphatic chain. Even so, the RFS of the molecules reveal distinct binding energies of the Rydberg states, supporting again our earlier observation that the Rydberg spectra provide sensitive structural fingerprints. Even the isomeric DM1BA and DM2BA molecules have very distinct 3s Rydberg peaks, although the energies (but not the intensities!) of the 3p peaks appear to be closely matched. Table 1 lists the quantum defects δ of the observed Rydberg peaks. For the 3s peaks, the positions corresponding to the greatest intensity are listed.

The RFS of DMPZ is slightly different from that of the other amines. In particular, the binding energy of the 3s state is the lowest of the group. We do not observe the 3p Rydberg peak, suggesting that the excitation photon energy is not sufficient to reach that state. That would imply that the binding energy of 3p is also lower than in the other molecules. It is conceivable that the reason for this distinct behavior is a delocalization of the positive charge between the two nitrogen atoms on the piperazine frame. There is, however, no independent support for this conjecture.

With the exception of the piperazine, the spectra at zero time delay show the 3p peaks prominently. After 30 ps the 3p signals

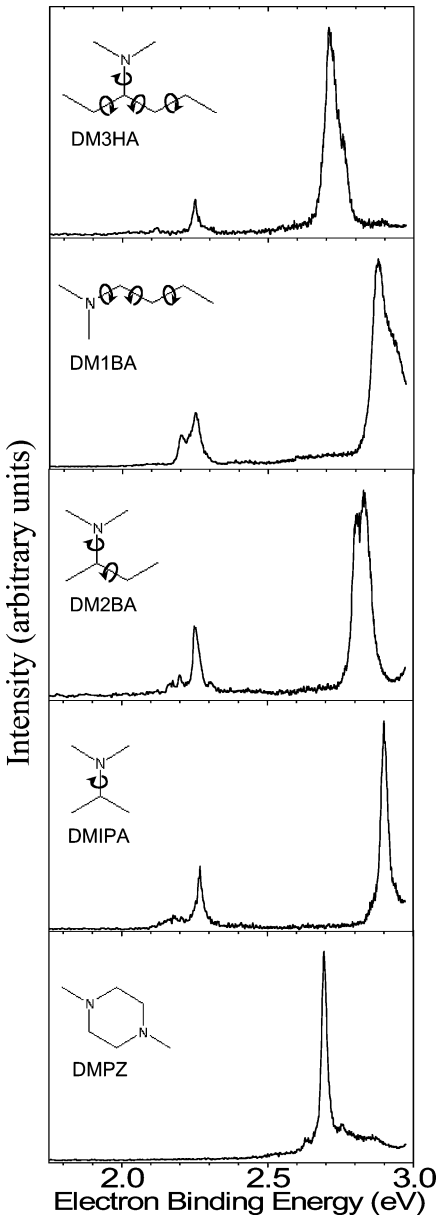


Figure 2. Rydberg fingerprint spectra of the depicted molecules taken with a pump − probe delay time near zero. The circular arrows denote the various C−C and C−N internal rotations discussed in the results section.

are almost completely gone, suggesting that the 3p state decays into the 3s state. In the case of DMIPA we have carefully mapped out this internal conversion, and found that this internal conversion occurs with a decay constant of 700 fs.[28] DMIPA remains stable in the 3s state for many picoseconds. Fragments that are observed in the mass spectrum are generated on the ion surface after the ionization by the probe pulse. From the spectra presented here, in particular from the observation that the 3s peaks in the spectra with 30 ps are not shifted compared to those with zero time delay, we conclude that the other amines exhibit similar behaviors.

One important question to consider is which electronic state is prepared by the initial excitation. From the time-resolved experiments on DMIPA we know that with femtosecond excitation, the direct excitation to 3s is negligibly small, and the molecule is exclusively prepared in 3p.[28] The amine group has a pyramidal geometry in the ground electronic state, but becomes planar upon excitation. This leads to good Franck−

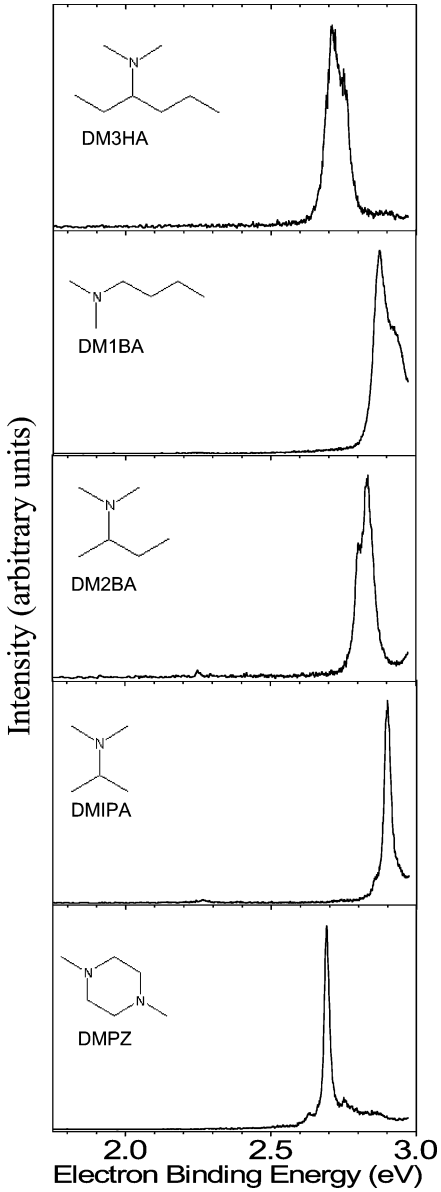


Figure 3. RFS spectra of the investigated molecules taken with a nominal pump − probe delay time of 30 ps.

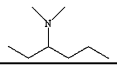
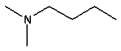
Condon factors for excitation to vibrations in the umbrella coordinate with high quantum numbers. Given the short lifetime of the 3p state, and the close spacing of vibrational energy levels, no wavelength tuning is required to resonantly excite DMIPA to 3p. It is likely that the situation is quite analogous in the other amines.

This provokes the question as to why the spectra show the 3p Rydberg levels at all, even though those states have decay times as short as 700 fs and the ionization occurs with a 15 ps pulse. The situation is entirely analogous to one that we have investigated some time ago:[33,34] the coherence bandwidth of the excitation pulse couples some fraction of the molecular eigenstates that, together, make up the oscillator-strength carrying resonance. As a result, the observed spectrum displays the admixtures of the contributing electronic states. This leads to the appearance of the 3p resonances in the spectra, even though their intensity may be greatly reduced.

Discussion

An evaluation of the approximate effective temperature of the subject molecules in the respective electronic states requires knowledge of the adiabatic ionization potentials (IP) of the respective ions, as well as the excitation energies of the 3p and 3s Rydberg states. Theoretical values for the adiabatic ionization energies of the noncyclic molecules have been published by Sølling et al.[35] For 1,4-dimethylpiperazine we estimate the adiabatic ionization energy by subtracting the average value of the difference between vertical and adiabatic IP's for a selection of amines (0.79 eV), from its published vertical IP value of 8.41 eV,[36] thus resulting in an estimated adiabatic IP of 7.62 eV. With the adiabatic IP's on hand, we can calculate the adiabatic electronic energies of the Rydberg states by subtracting our measured binding energies from the adiabatic IP's. The energy deposited in the vibrational manifold upon excitation to 3p, and after internal conversion to 3s, is obtained by subtracting these electronic energies from the photon energy. All those values are listed in Table 2.

TABLE 1: Structure, Binding Energies (BE), and Quantum Defects (δ) for the Molecules Used in This Investigation[a]

Sample	Structure	3*p*		3*s*	
		BE[b]	δ[c]	BE[b]	δ[c]
N,N-Dimethyl-3-hexanamine (DM3HA)		2.250 (0.013)	0.541 (0.007)	2.713 (0.040)	0.761 (0.020)
N,N-Dimethyl-1-butanamine (DM1BA)		2.253 (0.024)	0.543 (0.013)	2.876 (0.049)	0.825 (0.024)
N,N-Dimethyl-2-butanamine (DM2BA)		2.253 (0.014)	0.543 (0.007)	2.834 (0.032)	0.809 (0.016)
N,N-Dimethyl-isopropanamine (DMIPA)		2.272 (0.010)	0.553 (0.005)	2.900 (0.014)	0.834 (0.008)
1,4-Dimethyl-piperazine (DMPZ)		-	-	2.693 (0.011)	0.752 (0.006)

[a] BE is in units of eV and the δ values are unitless. [b] The reported uncertainties in the BE are assumed to be the half-width at half-maximum of the respective Rydberg peaks. [c] The uncertainties in the quantum defects are calculated using the quoted uncertainties in the binding energies for the respective Rydberg peaks.

To estimate the effective vibrational temperature, we used a set of vibrational frequencies obtained by density functional theory calculations at the B3LYP/6-31G(d) level for the molecules in their respective ground electronic states. Even though this disregards the structure change in the amine group upon electronic excitation, it is a reasonably good approximation for a qualitative discussion. We also assume that before the laser excitation the molecules in the molecular beam are at 0 K. Though some molecules may well retain residual vibrational energy after cooling in the molecular beam expansion, any error made in this approximation is quite small. Table 2 includes the effective vibrational temperatures in the 3p and the 3s Rydberg states obtained in this way.

Several important points are immediately apparent from Table 2. Most importantly, the amine molecules excited to their Rydberg states are very hot, with vibrational temperatures ranging from about 700 K to almost 1000 K. The 3p Rydberg states obtain their vibrational energy from the Franck−Condon overlap to the sloped part of the amine umbrella potential. This alone serves to heat the molecules to some 700 K. The internal conversion from 3p to 3s deposits additional energy in the vibrational manifold, which raises the temperature further.

Referring to the spectra of Figures 2 and 3, we note that the Rydberg fingerprint spectra of the flexible hydrocarbon chain molecules are well resolved even in the presence of the very significant amounts of vibrational energy. This is in dramatic

TABLE 2: Adiabatic Ionization and Excitation Energies, Vibrational Energy Content, Estimated Effective Vibrational Temperatures and Full Widths at Half-Maxima of the Observed RFS Peaks, for the 3p and 3s Rydberg States

	backbone internal rotations	adiabatic ionization energy[a] (eV)	adiabatic electronic energy of 3p (eV)	vibrational energy in 3p (eV)	vibrational temp in 3p (K)	fwhm of 3p peak (meV)	adiabatic electronic energy of 3s (eV)	vibrational energy in 3s (eV)	vibrational temp in 3s (K)	fwhm of 3s peak (meV)
N,*N*-dimethyl-3-hexanamine (DM3HA)	4	6.90	4.65	1.31	691	26	4.19	1.78	812	81
N,*N*-dimethyl-1-butanamine (DM1BA)	3	7.19	4.94	1.03	714	47	4.31	1.65	917	98
N,*N*-dimethyl-2-butanamine (DM2BA)	2	7.01	4.76	1.21	771	28	4.18	1.79	952	64
N,*N*-dimethyl-isopropanamine (DMIPA)	1	7.25	4.98	0.99	765	19	4.35	1.61	994	27
1,4-dimethyl-piperazine (DMPZ)	0	7.62[b]					4.93	1.04	726	22

[a] Adiabatic IE from ref 29, calculated at 0 K, using B3LYP/6-31G(d). [b] Estimated adiabatic IE using the vertical value from ref 30 less the average difference between the vertical and adiabatic IE values for the group of aliphatic amines investigated in ref 29.

contrast to photoionization experiments on electronic relaxation phenomena involving valence-excited states. There, photoionization leads to changes in vibrational frequencies as well as transitions between modes with different quantum numbers, leading to a very broad and unresolved photoelectron spectrum.[37] However, this is not the case in the current investigation. Because the ion and Rydberg state potential energy surfaces are nearly identical,[26] all the vibrational peaks are clustered within the small width of the Rydberg peaks. As a result, the photoelectron spectra are well resolved despite the large amount of energy deposited into the vibrational degrees of freedom. Clearly, the information content of RFS is preserved in molecules at temperatures where chemical reactions are rapid. This establishes the first main point of this paper.

The second important point relates to the way that the structural dispersion of the molecular systems is reflected in the Rydberg spectra. Table 2 includes a listing of the full widths at half-maximum of the Rydberg peaks observed in the RFS. To understand the line widths, we first recognize that underneath even the apparently sharp peaks, there are numerous unresolved peaks representing different vibrational states. The initial excitation to 3p prepares the molecule in a superposition of many vibrational states, as the density of states, even counting only those with decent Franck−Condon overlap with the ground state, is very high. In addition, the internal conversion from 3p to 3s is likely a statistical limit decay, implying that a very large number of almost isoenergetic vibrational modes are excited. The spectra obtained by ionization from the Rydberg states are, in first approximation, not sensitive to this vibrational energy content of the molecule.

The 3s peaks observed in 1,4-dimethylpiperazine and *N*,*N*-dimethylisopropanamine have fairly narrow line widths. This is so even though about 1.04 and 1.61 eV of energy is distributed among the vibrational coordinates in the two molecules, respectively. The effective temperature of the molecules is very high, approaching 1000 K in the case of DMIPA. The cyclic piperazine has fewer possibilities for different molecular structures. DMIPA has available a rotation about the N−C bond. However, given that the methyl groups of the amine and the propyl are at staggered positions,[35] there are only two symmetry equivalent minima on that coordinate. In the absence of any possible structural rearrangement involving the carbon skeleton, the only mechanism for line broadening is from the dependence of the Rydberg binding energy on the vibrational excitation and the excitation of the methyl group rotations. From the spectra it is apparent that those contributions alone, even at the high temperatures of this experiment, do not cause any significant broadening of the line width.

From the data in Table 2 we note that DM2BA, DM1BA, and DM3HA have decreasing effective vibrational temperatures in their 3s states, and all of them have temperatures that are lower than that of DMIPA. Nevertheless, the line widths for the 3s Rydberg peaks that these larger molecules exhibit are all much larger than those of DMIPA or DMPZ. Clearly, the reason for the increased line widths is something other than mere vibrational excitation. Structural dispersion is more prominent in the molecules with longer hydrocarbon chains. Counting only the rotations about skeleton bonds, DM2BA has two such internal rotations, DM1BA has three, whereas DM3HA has four. In general, the number of available internal rotations about the hydrocarbon skeleton bonds correlates quite well with the large observed line widths. This suggests that the large line widths observed are due to the dispersion of molecular structures present in these hot molecules. The one exception to this trend, the slightly narrower line width of DM3HA compared to that for DM1BA, could be due to accidental spectral overlaps or small populations in some of the structures.

To understand the interplay of vibrational excitation and molecular structural dispersion with the photoionization from Rydberg states, it is instructive to consider a simple model.[15,38] According to the Born−Oppenheimer approximation, the nuclear vibrational motions proceed in a potential defined by the energy of all electrons at any particular geometry. For the Rydberg excited system, one assumes the Rydberg electron to be separated from all other electrons. This is justified by arguing that the spatial separation between the Rydberg electron and the valence electrons of the ion core is large, at least outside the volume of the ion core. For any given nuclear geometry, the wave function of the Rydberg electron, ψ_{Ry}, is separated from that of all the remaining electrons $\psi_{e'}$:

$$\psi = \psi_{e'}\psi_{Ry}$$

Here, the electron wave function of the ion core, $\psi_{e'}(R_i,r_{e'})$, is taken to depend only on the coordinates of the nuclei, R_i, and the coordinates of the electrons, e′, of the ion core, $r_{e'}$. The effect of the Rydberg electron on the ion core electrons is small because the electron density of the delocalized Rydberg wave function is small. Alternatively, one might recognize that the Rydberg electron moves much slower than the valence electrons and includes its effect parametrically, similar to the treatment of nuclear motions in the standard Born−Oppenheimer approximation.

The wave function of the Rydberg electron, $\psi_{Ry}(R_i,r_{e'},r_{Ry})$, is a function of the nuclear coordinates and all electron coordinates, i.e., those for both the ion core and the Rydberg

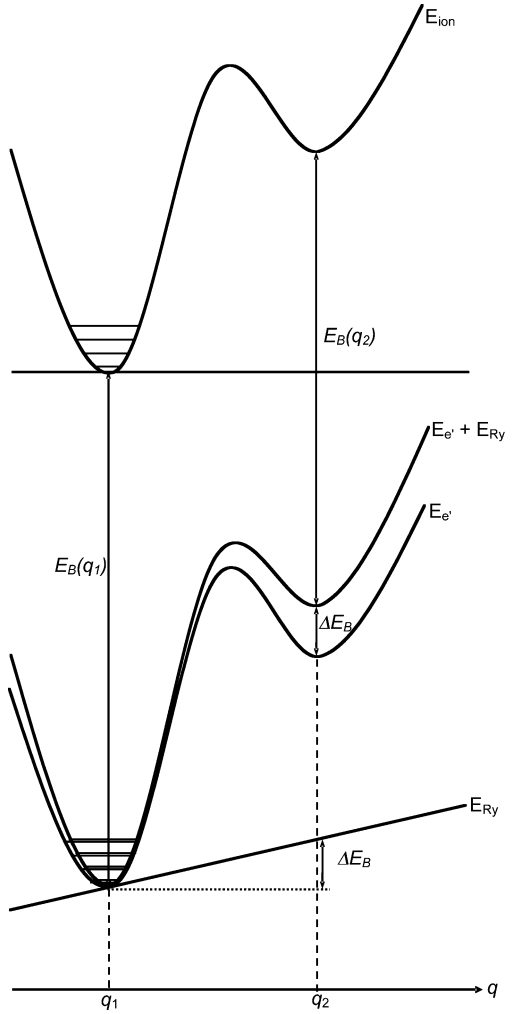


Figure 4. The potential energy surfaces for a molecule having two minima in its conformational energy landscape, identified by positions q_1 and q_2 along a displacement coordinate q. $E_{e'}$ represents the electronic energy of the ionic core and E_{Ry} is the energy of the Rydberg electron. The vibrational energy level structure of the Rydberg excited molecule, defined by the surface of $E_{e'} + E_{Ry}$, is close to that of the ion. The Rydberg states of the two conformers have binding energies $E_B(q_1)$ and $E_B(q_2)$, respectively, which differ by the amount ΔE_B.

electron. The Rydberg electron itself is therefore taken to move in the effective potential created by the electrons and the nuclear charges of the ion core. The total contribution of the electrons to the molecular potential energy surface is then given by

$$E = E_{e'} + E_{Ry}$$

where $E_{e'}$ is the electronic energy of the ion core and E_{Ry} is the energy of the Rydberg electron. The essence of this consideration is that the binding energy of the Rydberg electron, $E_B = -E_{Ry}$, and by implication the Rydberg fingerprint spectrum, is dependent on the molecular structure of the ion core.

Armed with these insights we return to the discussion of our spectra and the question of structural dispersion versus vibrational motion. Figure 4 illustrates the situation for a case where a molecule has two minima in its energy landscape. The shape of the electronic energy, $E_{e'}$, is nearly identical for the ion and the Rydberg state. The energy of the Rydberg electron, E_{Ry}, is weakly dependent on the displacement along coordinate q that connects conformeric forms with different molecular structure;[39,40] to first order, we take its dependence to be linear. The total potential energy of the Rydberg excited molecule is given by the sum of the energies $E_{e'}$ and E_{Ry}. As a result, ionization of the molecule out of the Rydberg state at positions q_1 and q_2 gives binding energies that differ by the difference in the energies of the Rydberg electrons, ΔE_B. Those differences are observable as distinct peak positions in the RFS of conformeric molecular structures.

To assess the effect of the Rydberg electron on vibrational states, we first consider the influence of the linear term, E_{Ry}, near the minimum of the potential. The linear contribution of E_{Ry} simply shifts the potential energy curve for vibrational motion without changing the harmonic frequencies of the ion core. This results in a shift of the ionization energy of the Rydberg state that is independent of vibrational excitation, and which therefore would be included in the quantum defect of the Rydberg state. Even so, experiments by Bryant et al. on nitrogen oxide,[41] as well as Pratt's group on ammonia,[42] and aniline,[43] have revealed small shifts in the binding energies of Rydberg states arising from vibrational excitation. Those shifts clearly must arise from the curvature of the E_{Ry} curve with vibrational displacement and are, therefore, a second-order effect.

The conclusion of this discussion is that the dominant linear term of the E_{Ry} curve causes structural dispersion to be reflected in broad line widths, as we observe in our Rydberg fingerprint spectra. That effect is on the order of 60−100 meV, or 500−800 cm^{-1}. The vibrational excitation of the molecules leads, via the small nonlinearity of the E_{Ry} curve, to very small shifts of Rydberg peaks with vibrational excitation. Those shifts, which are on the order of 5 cm^{-1} for the vibrationally resolved spectra,[41−43] are manifest in our spectra, at most, as a slight broadening of the observed line widths.

Having established the main conclusions of this paper, a brief discussion of the peak widths of the 3p levels is required. In all spectra, the 3p levels feature a fairly narrow line width. This is so even though the temperatures are quite significant, although not as high as those in the 3s states. Several possible scenarios might explain these line widths. First, the 3p levels have a subpicosecond lifetime.[28] It is conceivable that the vibrational energy does not redistribute on this short time scale, implying that all of the vibrational excitation would be in the umbrella motion of the amine group. Yet as discussed above, the effect of that vibrational motion on the line width is expected to be small. Second, it is possible that even if the vibrational energy in 3p were distributed over the entire molecule, it would not suffice to surmount the barriers to rotation. This would prevent structural dispersion, and keep the line widths small. Finally, it is possible that the lifetime of 3p is too short for the accumulation of energy in the rotor coordinate that leads to the different molecular conformations, again preventing structural dispersion. Although we cannot determine which of those effects is at play, it does appear plausible that the 3p peaks can be relatively sharp.

Summary and Conclusions

Rydberg fingerprint spectroscopy has been shown to be a valuable tool to characterize the structures of molecules with many degrees of freedom in the presence of vibrational energies that are significant in comparison to the barriers in the energy landscape. The spectra provide a purely electronic spectrum that depends on the coordinates of all other electrons and all nuclei and, therefore, depends on the molecular structure. At the same time the spectra are, to first order, insensitive toward vibrational motions, so that all lines from vibrational modes are bunched up in narrow lines even when the effective vibrational temperatures are very high.

Although we cannot yet identify the conformeric molecular structures connected with a particular Rydberg peak, such an assignment may be possible by calculating the energy landscape of the ion and, with the aid of the observed Rydberg electron binding energy, infer the depths of the minima on the Rydberg surface. Using a Boltzmann distribution appropriate for the excited molecule, one may then compare the calculated peak area to the observed one. Work along this line is in progress.

The combination of the structural sensitivity with the insensitivity toward vibrations makes Rydberg fingerprint spectroscopy an ideal tool for studying chemical dynamics. In addition to its sensitivity toward local charge distributions, RFS is sensitive to the global molecular structure and can therefore probe folding phenomena that remain unobserved with other techniques. Moreover, it is straightforward to implement RFS with high time resolution, as is required for studying the dynamics of molecular reactions. Based on the foundation of the work presented here, it is now possible to probe the complicated multidimensional dynamics of molecules with many degrees of freedom.

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