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This paper extends recent work on the excited states of methyl amine to some other simple amines. Jet-cooled mass-resolved multiphoton ionization spectroscopy is reported for methyl amine, dimethyl amine, trimethyl amine, ethyl amine, diethyl amine, and triethyl amine. A set of high-level calculations for methyl amine supports the assignment of S_1 as a $3s$ Rydberg state by predicting the experimental transition energy to within about 1000 cm^{-1} after including vibrational zero-point energies for each potential energy surface. Perturbations observed in the experimental $S_1 \leftarrow S_0$ spectrum prompt a series of calculations which implicate a dissociative $3s$ Rydberg state in both the perturbation in the spectrum and in the photodissociation of methyl amine at these energies. A series of excited state calculations performed at the ground state geometry for methyl amine, dimethyl amine and trimethyl amine indicates the relative energies of the bound $3s$ and $3p$ Rydberg states as well as the first dissociative $3s$ Rydberg state. Taken together, this work presents a picture of the S_1 and S_2 excited states in which dissociative low-lying Rydberg states play a significant role in both the spectroscopy and photochemistry of the simple amines. [S0021-9606(97)00209-2]

INTRODUCTION

Study of the excited electronic states and photochemistry of simple alkyl amines has a number of motivations. First, these states are not well characterized, even to the point of distinguishing Rydberg and valence electronic states. Second, the lack of firmly assigned spectroscopic data for any of the simple alkyl amines has been an impediment to progress in the theoretical and experimental studies of the photochemical properties and dynamics of their excited states. Third, a number of important systems, such as energetic materials (RDX, HMX, etc.), biologically active molecules (neurotransmitters, and others), and natural products, contain the alkyl amino unit and their properties and behavior depend on alkyl amino excited states and dynamics. Fourth, simple alkyl amines can appear as impurities and decomposition products of energetic materials and can be useful in their detection and identification through spectroscopic means.

Our interest in these systems has grown out of a program to study the ignition and chemistry of energetic materials. One class of these materials can explode only by shock ignition in condensed phase. The shearing of crystal planes can cause large electric fields (10^8 V/cm) that can generate excited electronic states, ions and radicals, all of which can be highly chemically reactive. In many instances one has no compelling reason to prefer a ground state reaction path over a dissociative excited electronic state mechanism.

The explosive RDX is a cyclic, saturated sym-triazine with NO_2 groups bonded to the three ring nitrogen atoms. Piperidine and substituted piperidine compounds (2,2,6,6,-tetramethyl-, nitro-, N-oxy-) can be chosen to model the spectra and behavior of RDX but their spectra, at least initially, are too broad to be diagnostically useful. The absence of sharp spectra for these model systems mandates the search for progressively more simple amines that can be explored and understood. Methyl amine[1] is the first compound in this series of model systems: it yields analyzable spectra and reasonable theoretical predictions. The combined experimental and theoretical work on methyl amine provides a number of insights into the series of alkyl substituted amines that can be employed to interpret the unresolved experimental spectra of other simple amines.

In the 1930's, Herzberg[2] grouped ammonia with the simple amines in an effort to explain the broad, semiperiodic UV absorption spectra of these compounds in terms of an excitation to $3s$ Rydberg states. Mulliken[3] suggested that a $3s$ Rydberg state, largely isolated on the nitrogen atom, would lead to a planar geometry for the excited Rydberg state, which in turn would have poor Franck–Condon overlap with the ground state. These assumptions rationalize the general appearance of the spectra obtained for this group of molecules.

Over the intervening 60 years since this early work, the excited states and photochemistry of ammonia have become much better understood.[4–18] Multiphoton ionization[13–18] experiments on ammonia have made clear that the higher n Rydberg states are observed. The $\tilde{A}$ state of ammonia is a $3s$ Rydberg state of A_2' symmetry which is predissociative and has been the subject of a large body of work.[19–21] Regardless of the mechanism of predissociation from the $\tilde{A}$ state of ammonia, both the photofragments arising from this process and predissociating excited states of NH_3 and ND_3 are observed.[22,23]

The simple amines have been traditionally treated by extending the work done on ammonia. Even as the knowledge of the excited state electronic structure of ammonia has improved, the older arguments of Herzberg and Mulliken have been sufficient to explain the other simple amines: the broad UV and multiphoton spectra of these molecules have not allowed a very detailed analysis. Spectroscopic studies of the amines without mass resolution are problematic because

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of clustering. Even when mass-resolved spectroscopy has been performed on the alkyl amines, the molecules have generally not been cold enough to present an assignable spectrum. For the larger members of this series, the mixing of more than one excited state high up in a shallow vibrational potential energy surface has made interpreting the broad spectra a daunting task. One usually has assumed that amine photodissociation, which produces hydrogen, proceeds as it does in ammonia by exciting the nitrogen atom and breaking an N–H bond.[24–29]

A recent study of the spectra of methyl amine[1] presents a somewhat different view of its excited states than that discussed above for ammonia. This work is based on supersonic expansion cooled, vibrationally resolved, mass detected multiphoton spectroscopy supported by Hartree–Fock calculations of the ground and excited electronic state vibrations. Nearly all the major low-lying vibronic features can be assigned for methyl amine in the first excited electronic state (S_1). Perturbations observed in the high energy region of the long vibrational progressions in this spectrum prompted a series of high level *ab initio* calculations. The first excited state of methyl amine can be assigned as a ''planar'' 3*s* Rydberg state with major contribution coming from the nitrogen 3*s* atomic orbital and some contribution from the carbon 3*s* atomic orbital. Spectral perturbations can arise from either a bound valence state, which also has a planar geometry, or a ''nonplanar'' dissociative 3*s* Rydberg state, with majority contribution (~75%) from the carbon 3*s* atomic orbital.

Photodissociation of methyl amine at these energies ($\sim 4.5\times 10^4$ cm^{-1}) has been observed by a number of groups.[26–29] Since the only valence state that is calculated to fall in this region is bound, the second 3*s* Rydberg state is apparently the one involved in the dissociation of methyl amine by hydrogen elimination. Thus, the gross features of the methyl amine spectrum in the vicinity of 44 000 cm^{-1} and the photodissociation data can be explained by the interaction of two 3*s* Rydberg states with very different geometries: a bound 3*s* Rydberg state, with majority contribution from the 3*s* nitrogen atomic orbital; and a dissociative 3*s* Rydberg state with majority contribution from the 3*s* carbon atomic orbital. Another result of these calculations is that, no matter what the final product structure, (i.e., $CH_2{=}NH$, $CH_2NH_2^*$, CH_3N, or something else) the hydrogen elimination process in methyl amine at these energies is associated with an excitation on the carbon atom rather than the nitrogen atom.

Some multiphoton ionization experimental spectra for simple amines (di- and tri-methyl, mono-, di-, tri-ethyl amine) are reported in this work. These spectra are generally broad and unresolved, but the limited experimental data—particularly including the ethyl amine and dimethyl amine spectra—can be explained using the insights gleaned from methyl amine studies.[1] If this view is correct, the first few absorption bands in the ultraviolet of these simple amines in the vicinity of 40 000 cm^{-1} arise from interaction of bound and dissociative 3*s* Rydberg states. As larger members of this series are considered, the dissociative 3*s* Rydberg states fall in the same region as the appearance of the 3*p* Rydberg states. These results are relevant to the study of larger simple amines for which the nature and possible interconversion of S_1 and S_2 have been the subject of controversy (see Ref. 30). The possible mixing of these states is further complicated by the fact that the bound and dissociative states differ in geometry from each other, as well as the ground state. More importantly perhaps, these studies emphasize the general importance of bound and dissociative low *n* Rydberg states for excited state properties and behavior of simple molecular systems.

EXPERIMENTAL PROCEDURES

The experimental approach and conditions employed in this work are basically the same as previously reported.[1] Either a Quanta-Ray DRC-II or a DCR-III Nd/YAG laser is used to pump a PDL II tunable dye laser employing C500, C480, C460, or C440 Exciton dye solutions as the active medium. The fundamental of the dye laser output is focused with a lens (25–50 cm focal length) onto a molecular beam produced by expanding ~0.5% of the sample (3% for dimethyl amine) in a carrier gas of 70% neon in helium. A Wiley–McLaren time of flight mass spectrometer is used to detect multiphoton mass-resolved excitation spectra. As previously noted for methyl amine, a family of peaks separated by 1 amu is observed in the vicinity of the mass channel of interest and additional peaks are observed for higher masses associated with methyl amine clusters. The propensity of these molecules to cluster necessitates low concentrations of alkyl amines in the expansion.

These molecules undergo internal rotational and large amplitude translational motion and are thus hard to cool. The ground states have an ammonialike ''inversion'' mode. Each additional internal rotor increases the difficulty experienced in cooling the species in the molecular beam due to the increase in low energy internal modes. Franck–Condon factors are important in understanding methyl amine's spectrum and as the molecules to be studied become larger, their geometry becomes less well defined and more nonrigid.

Large ionization cross sections are observed for all the molecules studied with the exception of dimethyl amine. The first ionization thresholds decrease for the higher members of the amine series and the intensities of the spectra change significantly as the number of photons required for ionization drops from 4 to 3. Large differences are observed between the ion distributions in the (1+1) and (2+2) methyl amine experiments. Clusters of these simple amines can photodissociate and produce fragments with the same mass as the monomer. The expansion conditions have to be adjusted to compromise between minimum clustering and maximum cooling of the monomer.

EXPERIMENTAL RESULTS

The spectrum of methyl amine is presented in Fig. 1. The full width at half maximum (FWHM) of the observed features is as narrow as 20 cm^{-1}. These are as sharp and resolved as any reported alkyl amine vibronic features, and

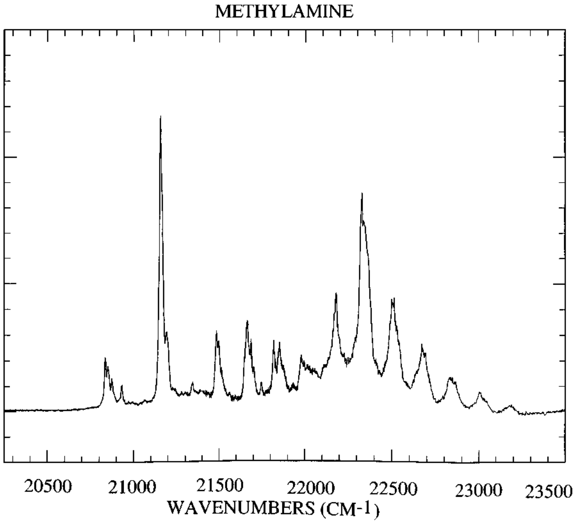

FIG. 1. The (2+2) mass resolved excitation spectrum (MRES) of methyl amine. The laser wave numbers are plotted on the x axis. The spectrum covers several dye regions. A significant geometry change between an ''ethanelike'' ground state and a ''planar'' excited state leads to vibrational progression involving combinations of the ''amine wagging'' and ''amine scissors'' modes. The transition origin is not observed. Significant perturbations become important above 22 000 cm^{-1}.

this width suggests that methyl amine is quite well cooled in the expansion. The small features in the vicinity of the first vibronic peak near 41 620 cm^{-1} are consistent with internal rotor structure. The transition origin is assigned to lie at 39 770 cm^{-1} and is not directly observed due to the small Franck–Condon factors associated with the first 2000 cm^{-1} of spectrum. An ''ethanelike'' ground state geometry changes upon electronic excitation to a ''planar'' excited state for the H_2NC atoms. All major features in the region below 45 000 cm^{-1} can be assigned to combinations of two vibrations: ν_4 (amino scissors) and ν_9 (amino wag). These modes bring the excited state geometry into coincidence with that of the ground state.

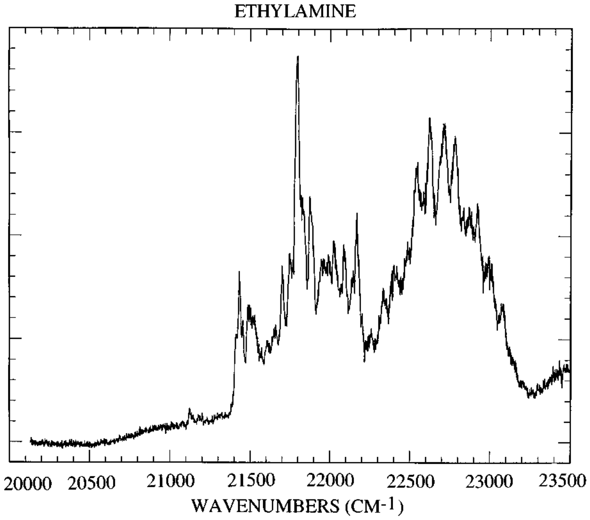

FIG. 2. The (2+2) mass resolved excitation spectrum (MRES) of ethyl amine. The spectrum is more congested than that of methyl amine, but the overall appearance is very similar.

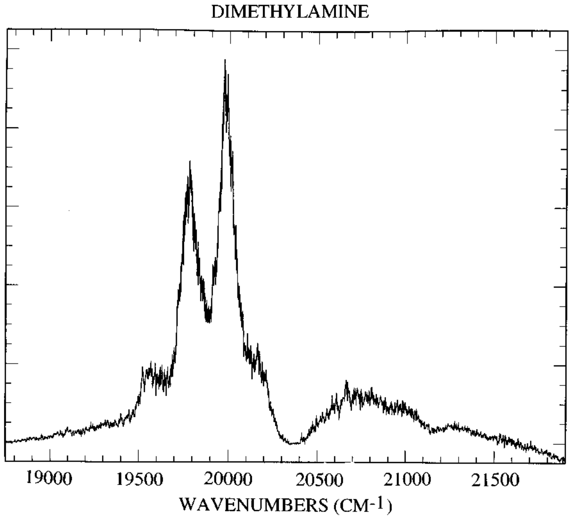

FIG. 3. The (2+2) mass resolved excitation spectrum (MRES) of dimethyl amine. This spectrum is unlike any of the others in this study. The spectrum is shifted to the red and the signal intensity is much lower than the other amines in this investigation.

The spectrum of ethyl amine is presented in Fig. 2. The spectrum is generally quite similar in appearance to that of methyl amine although it is more congested and less well resolved. Considering the increased difficulty of cooling a molecule with additional internal low energy modes and the possibility that more than one geometry exists for this species, the similarities between the spectrum of methyl amine and ethyl amine are quite striking.

This is not true of the spectrum for dimethyl amine presented in Fig. 3. This spectrum is quite different from those obtained for any of the other amines in this study. As mentioned before, the ionization signal is of much lower intensity for dimethyl amine than the other amines. The dimethyl amine spectrum is shifted to the red and appears over a narrower range of energies in comparison to the other amines. The dimethyl amine molecule is known to cluster very efficiently, but this is also true of several of the other amines in this study which exhibit more similar spectra.

The remaining higher amines produce very broad spectra which are positioned over roughly the same energy region as methyl amine. While some individual features may be present in the diethyl amine spectrum, in general the spectra of the higher amines are unresolved in this set of experiments. One is tempted to blame most of the broadening on poor cooling for molecules with so many possible internal motions, but decreased excited state lifetime can also contribute to the broadening of these spectra. The spectra of diethyl amine, trimethyl amine and triethyl amine appear in Figs. 4(a), 4(b), and 4(c), respectively.

CALCULATIONS, PROCEDURES, AND RESULTS

The calculations reported here are performed with the HONDO 8.5[31] set of programs. All of the calculations use a

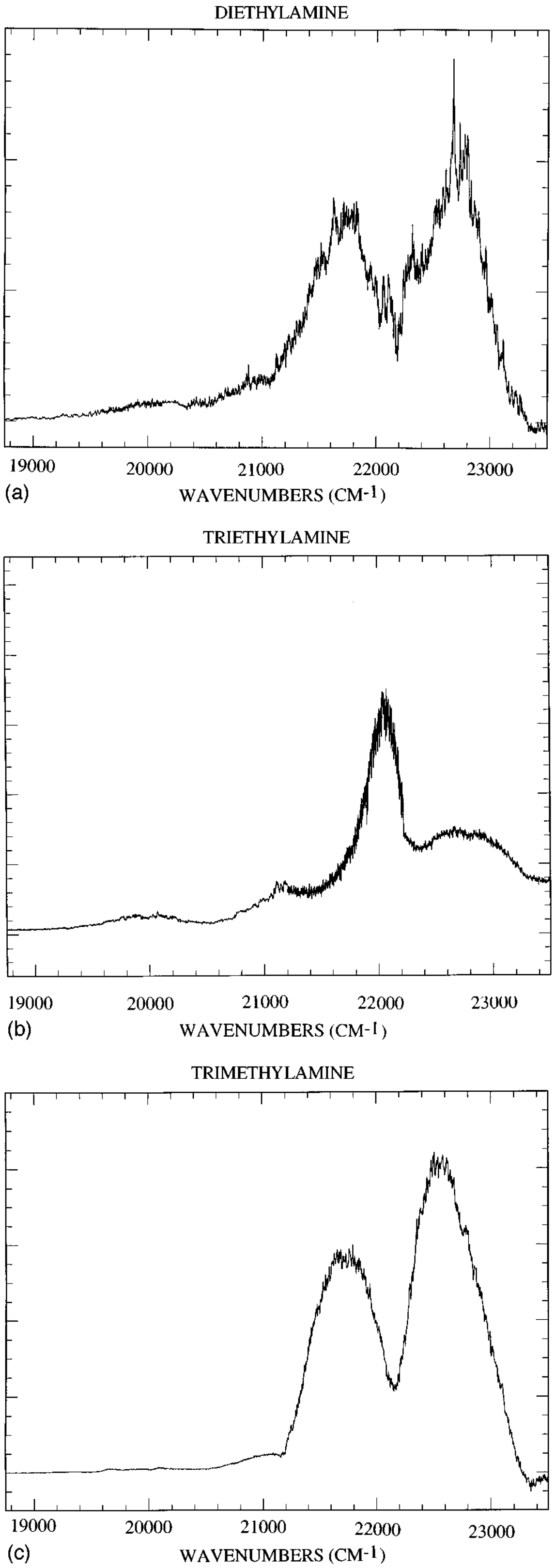

FIG. 4. (a) The (2+2) mass resolved excitation spectrum (MRES) of diethyl amine. (b) The (2+2) mass resolved excitation spectrum (MRES) of trimethyl amine. (c) The (2+2) mass resolved excitation spectrum (MRES) of triethyl amine.

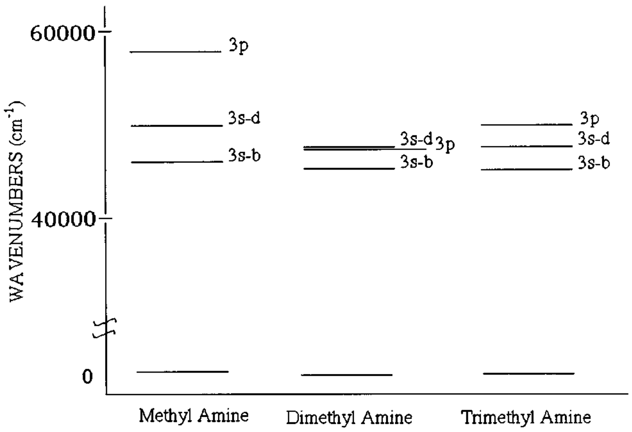

FIG. 5. Relative energy levels calculated for the excited states of methyl amine, dimethyl amine, trimethyl amine. The Hartree–Fock optimized ground state geometry is used as a reference in all cases to indicate relative vertical transition energies. Methyl amine has only one dissociative $3s$ Rydberg state and this is well separated from the $3p$ Rydberg state. Substituted amines have a higher density of $3s$ Rydberg states which overlap the energy region occupied by the $3p$ Rydberg orbitals. In the figure the dissociative $3s$ Rydberg states are labeled as $3s-d$, and the bond $3s$ Rydberg states are labeled $3s-b$.

double zeta valence plus polarization (DZP) basis set augmented with $3s$ Rydberg (or $3p$ Rydberg) orbitals on both the nitrogen and carbon atoms. Results of Hartree–Fock calculations are used as inputs for CAS-MP2[32,33] calculations. All calculations are performed at the Hartree–Fock ground state optimized geometries.

One of the results of the methyl amine study is that, while one heavy atom makes the majority contribution to a particular Rydberg orbital, the $3s$ Rydberg states of the molecule are not completely isolated on either heavy atom. In the Parsons and Weisskopf[34] model of the quantum defect for atoms, the Rydberg electron is Pauli excluded from only a relatively small region near the atomic core. If the Parsons and Weisskopf view is applied to a molecular system with multiple centers, the excited electron is still only excluded from relatively small regions within the two heavy atoms that contribute atomic orbitals to the Rydberg state. Thus, in the case of molecular systems, the low-lying Rydberg states of a molecule can participate almost fully in the photophysics and photochemistry of the valence region. As a consequence, it is appropriate to consider the $3s$ Rydberg states of the amines in terms of an MO model.

Another result of the methyl amine study is that an additional $3s$ Rydberg state with majority contribution from the carbon atom $3s$ orbital, and located somewhat higher in energy than the first excited $3s$ Rydberg state, is apparently involved in the photodissociation of the molecule. Evidence for the existence of this state can be found in perturbations of the methyl amine spectrum and in the recent photodissociation study of Waschewsky *et al.*[27]

CAS-MP2 calculations for methyl amine, ethyl amine, and dimethyl amine $3s$ Rydberg states appear in Fig. 5 and Table I. These calculations are performed at the Hartree–Fock optimized ground state geometry (refer to Table II) in order to generate vertical transition energies. This approach

TABLE I. CAS-MP2 calculated energies of several Rydberg states for the simple amines reported as vertical transitions from the ground state.

Species	Ground state	1st 3*s* Rydberg state	2nd 3*s* Rydberg state	1st 3*p* Rydberg state
	(A') (a.u.)	(A') (a.u.)	(A') (a.u.)	(A'') (a.u.)
Methyl amine	−95.566 425 8	−95.356 535 6	−95.347 857 5	−95.331 563 6
Dimethyl amine	−134.746 078 3	−134.541 962 8	−134.530 752 4	−134.531 613 4
Trimethyl amine	−173.936 741 1	−173.733 306 8	−173.721 657 3	−173.710 749 2

is less accurate at calculating transition energies than that of Ref. 1 in which the geometries are optimized at the CAS (or MCSD) level for all the bound states, but it has the considerable advantage of being able to treat the lowest dissociative states.

DISCUSSION

The mass resolved excitation spectra reported here are a significant improvement over the excited state data previously available in the literature for the smaller members of this series of molecules. This is largely due to mass resolution and improved cooling in the supersonic expansion. Our detailed study of methyl amine provides a physical picture of the excited states in which the lowest energy 3*s* Rydberg bound state is perturbed by a dissociative 3*s* Rydberg state. An extension of this model can help to explain the experimental data for this group of simple amines.

The view of the excited states of methyl amine taken in our earlier study[1] is a little unusual. Spectroscopists working in the UV are typically presented with sharp lines and diffuse bands. If the sharp lines can be fit to the characteristic n^{-2} pattern, they are assigned as Rydberg states. All other states are presumed to be valence states. Broad absorption bands are presumed to be associated with dissociative valence

TABLE II. Hartree–Fock optimized ground-state geometries (in Å) for the energy calculations in Table I. Hartree–Fock optimized geometries of the ground states of methyl amine, dimethyl amine, and trimethyl amine. (All calculations reported in Table I are performed at these geometries.)

Molecule	Atom	*X*	*Y*	*Z*
Methyl amine	C	0.005 049 654 9	0.000 177 685	0.000 000 000 0
	N	2.746 444 978 6	0.043 126 416 4	0.000 000 000 0
	H	−0.666 480 196 8	−1.017 346 888 9	1.651 133 478 2
	H	−0.666 480 196 8	−1.017 346 888 9	−1.651 133 478 2
	H	−0.891 480 068 1	1.861 240 674 4	0.000 000 000 0
	H	3.409 767 069 0	0.941 938 001 2	1.524 611 925 0
	H	3.409 767 069 0	0.941 938 001 2	−1.524 611 925 0
Dimethyl amine				
	N	0.215 412 559 2	−0.125 457 667 4	0.000 000 155 1
	C	1.407 736 848 0	0.801 612 879 7	2.285 841 130 5
	C	1.407 735 212 4	0.801 613 167 1	−2.285 841 936 1
	H	−1.613 696 383 4	0.344 714 128 7	−0.000 000 066 3
	H	3.300 644 891 4	0.026 345 865 8	2.438 083 699 5
	H	0.344 744 457 2	0.176 294 665 8	3.921 260 410 1
	H	1.558 430 853 8	2.860 978 524 7	2.359 239 516 7
	H	3.300 645 715 2	0.026 345 666 1	−2.438 083 664 9
	H	0.344 744 925 8	0.176 294 787 0	−3.921 259 841 0
	H	1.558 431 071 4	2.860 978 451 5	−2.359 239 454 5
Trimethyl amine				
	C	−2.189 110 519 0	0.097 167 331 8	−0.001 331 065 2
	N	0.524 604 246 5	−0.262 338 583 7	0.028 740 211 3
	C	1.672 863 547 8	0.822 957 696 7	2.264 209 265 3
	C	1.690 594 563 6	0.692 706 736 7	−2.255 976 372 7
	H	−3.006 789 298 5	−0.634 418 385 4	1.728 399 037 8
	H	−3.009 061 015 2	−0.935 404 653 8	−1.570 324 837 1
	H	−2.737 330 020 0	2.085 568 253 4	−0.181 743 199 8
	H	3.674 334 522 7	0.384 139 231 5	2.299 730 474 1
	H	0.822 298 125 6	0.019 529 280 0	3.946 536 556 6
	H	1.463 760 843 6	2.880 772 804 0	2.356 198 998 4
	H	3.681 824 259 5	0.210 255 190 9	−2.280 479 360 0
	H	0.812 986 975 0	−0.160 948 542 1	−3.898 382 504 3
	H	1.523 853 919 4	2.749 734 109 8	−2.435 577 255 3

states. While Rydberg photochemistry, dissociative states, state mixing, and the importance of correlation between Rydberg states and their dissociation products is theoretically appreciated,[24,35–38] such an overall approach is not typically part of an experimental investigation of the excited state properties of most systems.

Nonetheless, the methyl amine study does indeed, of necessity, involve *ab initio* calculations to interpret the experimental data. At low energies, the observed spectrum can be assigned to a transition involving a bound 3s Rydberg state. At higher energies, significant perturbations are observed in the methyl amine spectrum, which are coincident with observed photofragmentation.

If the Rydberg states of ethyl amine are similar to those of methyl amine, one would expect a similar spectrum with a larger degree of vibrational ''congestion''. This is what is observed in Fig. 2. As expected, methyl amine and ethyl amine almost certainly have similar electronic structure and the S_1 state is a 3s Rydberg state with majority occupation of the 3s orbital on the nitrogen atom.

The spectrum of dimethyl amine is somewhat of a surprise with regard to its low energy, small signal intensity, width of its resolved features, and overall appearance. These features can be understood, nonetheless, in terms of the above ''molecular orbital'' picture of 3s Rydberg states arising from one nitrogen and two carbon atom 3s atomic orbitals. The molecular 3s Rydberg states arising from these orbitals on similar carbon atoms will interact and lower the energy of the first excited (bound) 3s Rydberg state. Additionally, more of the molecular Rydberg states will be dissociative. Between the poor Franck–Condon factors for the low-lying vibronic transitions and the encroachment of dissociative states which reduce the overall intensity and lifetimes of the bound states, the spectrum of dimethyl amine can at least be qualitatively modeled.

As the number of carbon atoms increases, the number of dissociative 3s Rydberg states also increases. The spectra of the larger amines become more congested and contain less detail. The calculations reported here suggest that this is not only due to reduced cooling of internal motions for the higher mass simple amines, but also because the bound 3s and 3p Rydberg states are no longer well separated from each other or the dissociative 3s Rydberg states.

A more traditional view of the first excited state of methyl amine can be presented in terms of hyperconjugation. This lower energy 3s Rydberg state (with majority occupation on the nitrogen atom) leaves the nitrogen atom with a single electron in the orbital which had a pair of electrons in the ground electronic configuration. This singly occupied orbital on nitrogen will interact with an adjacent C–H bond and help to stabilize the molecule by adding some π character to the C–N bond. The carbon atom participates in the increased π bond character at the cost of contributing less electron density to a C–H bond. This more weakly bonded hydrogen atom interacts with the large singly occupied orbital on the nitrogen atom as well as the diffuse 3s Rydberg orbitals. This ''back interaction'' between the weakened C–H bonded hydrogen atom and electron density on the nitrogen atom is typically referenced to in this instance as ''hyperconjugation.''

Continuing with a hyperconjugation model, the second 3s Rydberg state of methyl amine will have majority occupation on the carbon atom. The orbital associated with the lone pair of electrons on the nitrogen atom in the ground state is singly occupied in both 3s Rydberg states, but when the 3s Rydberg state on the carbon atom is populated, the contribution of the carbon atom to one of the C–H bonds is greatly diminished. The second 3s Rydberg state of methyl amine begins to dissociate by hydrogen elimination at the CH_3 moiety.

The first excited Rydberg states of both methyl amine and ethyl amine are expected to be stabilized by hyperconjugation. This is not true for the first 3s Rydberg state of dimethyl amine (or any of the other simple amines considered here), because the expected planar excited state geometry will be so unfavorable for π character in the C–N bonds that the molecule will be destabilized instead of stabilized.

Larger alkyl amines have also been studied[25] and interaction between the S_1 and S_2 Rydberg states has been suggested to be important. In these systems, the S_2 state is expected to have mostly 3p character. In this previous work the model alkyl amine has been taken as triethylamine. Below we view this series from the methyl amine, etc. calculations reported above (see Table I).

In the case of methyl amine, the 3p Rydberg state is calculated to fall well above the dissociative 3s Rydberg state. The possible role of an excited valence state is not completely certain, but the best calculations performed here have found only a bound valence state at energies well above these Rydberg states. The significant geometry difference between the ground state and the first excited state of methyl amine means that a vertical transition accesses the vibrational potential energy surface 1850 cm^{-1} above the excited state zero-point level. Perturbations appear in the mass resolved excitation spectrum of methyl amine about another 2000 cm^{-1} above the appearance of the first vibrational peak. This is close to the calculated difference in vertical transition energy between the first (bound) and the second (dissociative) 3s Rydberg states.

The difference between the highest 3s Rydberg states and the lowest 3p Rydberg states could be calculated only for methyl amine since the two lowest 3s Rydberg states converged in this calculation; however, with the exception of methyl amine and ethyl amine, the vertical transition energy of the highest (dissociative) 3s Rydberg state will fall near or above that of the 3p Rydberg state for the remaining simple amines. The mixture of several bound and many dissociative Rydberg states is made enormously more complicated by the large geometry differences between excited and ground states.

While the assignment of the first excited state of methyl and ethyl amines as a bound 3s Rydberg state is quite certain, the identification of comparable states in higher alkyl amines is a more open issue. For dimethyl amine, the bound 3p Rydberg states move to lower energy and can interact with the dissociative 3s states. For higher members of the amine series, the $3p$ states could even move below the bound $3s$ states.[30] Since vertical transitions from the ground state access a mixture of bound and dissociative Rydberg states far from equilibrium geometry, even the distinction between $3s$ and $3p$ states would be difficult to draw.

A number of model ring (e.g., piperidine, piperazine, etc.) compounds produce the same sort of broad, unresolved multiphoton ionization spectra reported here for trimethyl amine and triethyl amine. Dissociative low-lying Rydberg states and $3s/3p$ Rydberg state mixing seem to be important for these molecular systems as well.

CONCLUSIONS

Trends in the excited states of a series of simple amines are reconsidered following the collection of mass-resolved excitation spectra for these species cooled in a molecular beam and a set of CASMP2 Rydberg state calculations. This work is possible because a recent study has significantly improved the understanding of the excited states of methyl amine.

The physical picture which emerges from the methyl amine study is that the spectroscopy of this molecule is dominated by low-lying Rydberg excited states which are both bound and dissociative in character. A ''molecular orbital'' scheme is necessary to describe the $3s$ Rydberg states of methyl amine as not simply localized on a single heavy atom. In methyl amine, a significant gap between the lowest $3p$ Rydberg state and the highest dissociative $3s$ Rydberg state exists.

This picture is extended to other simple amines, and experimental spectra appear to indicate that dissociative Rydberg states are very important to the understanding of the excited states of these molecules as well. For the higher simple amines, dissociative $3s$ Rydberg states overlap in energy with $3p$ Rydberg states and the concomitant mixing of states may be significant in an interconversion between S_1 and S_2.

Dissociative Rydberg states are apparently more important and pervasive than has previously been appreciated. At least one class of ''energetic materials'' are compounds for which dissociative Rydberg states might be important for chemistry, as well as spectroscopy.

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[1] D. P. Taylor and E. R. Bernstein, J. Chem. Phys. **103**, 10453 (1995).
[2] G. Herzberg and R. Kölsch, Electrochem. **39**, 572 (1933).
[3] R. S. Mulliken, J. Chem. Phys. **3**, 506 (1935).
[4] (a) M. N. R. Ashfold, D. W. Chandler, and A. J. R. Heck, Chem. Phys. **201**, 237 (1995); (b) D. H. Mordaunt, R. N. Dixon, and M. N. R. Ashfold, J. Chem. Phys. **104**, 6472 (1996); (c) *ibid.* **104**, 6460 (1996); (d) J. H. Glownia, S. J. Riley, S. D. Colson, and G. C. Nieman, *ibid.* **73**, 4296 (1980).
[5] S. W. Liefson, Astrophys. J. **63**, 73 (1936).
[6] A. B. F. Duncan and G. R. Harrison, Phys. Rev. **49**, 211 (1936).
[7] A. E. Douglas and J. M. Hollas, Can. J. Phys. **39**, 479 (1961).
[8] R. Rianda, R. P. Frueholz, and W. A. Goddard III, Chem. Phys. **19**, 131 (1977).
[9] M. N. R. Ashfold, R. N. Dixon, K. N. Rosser, R. J. Stickland, and C. M. Western, J. Chem. Phys. **101**, 467 (1986).
[10] M. N. R. Ashfold, R. N. Dixon, R. J. Stickland, and C. M. Western, Chem. Phys. Lett. **138**, 201 (1987).
[11] M. N. R. Ashfold, R. N. Dixon, N. Little, R. J. Strickland, and C. M. Western, J. Chem. Phys. **89**, 1754 (1988).
[12] X. L. Li, X. Xie, L. Li, X. Wang, and C. Zhang, J. Chem. Phys. **97**, 128 (1992).
[13] J. H. Glownia, S. J. Riley, S. D. Colson, and G. C. Nieman, J. Chem. Phys. **73**, 4296 (1980).
[14] J. H. Glownia, S. J. Riley, S. D. Colson, J. C. Miller, and R. N. Compton, J. Chem. Phys. **77**, 68 (1982).
[15] J. M. Allen, M. N. R. Ashfold, R. J. Strickland, and C. M. Western, Mol. Phys. **74**, 49 (1991).
[16] W. E. Conaway, R. J. S. Morrison, and R. N. Zare, Chem. Phys. Lett. **113**, 429 (1985).
[17] R. S. Morrison, W. E. Conaway, and R. N. Zare, Chem. Phys. Lett. **113**, 435 (1985).
[18] (a) T. Nishiya, J. Phys. Chem. **96**, 4276 (1992); (b) X. Li, B. Jiang, and X. Xie, J. Optical Soc. Am. B **7**, 1884 (1990).
[19] V. M. Donnelly, A. P. Baronavski, and J. R. McDonald, Chem. Phys. **43**, 271 (1979).
[20] A. E. Douglas, Discuss. Faraday Soc. **35**, 158 (1963).
[21] R. Runu, S. D. Peyerimhoff, and R. J. Buenker, J. Mol. Spectrosc. **68**, 253 (1977).
[22] J. B. Pallix and S. D. Colson, J. Phys. Chem. **90**, 1499 (1986).
[23] T. Seideman, J. Chem. Phys. **103**, 10556 (1995), and references therein.
[24] E. Kassab, J. T. Gleghorn, and E. M. Evleth, J. Am. Chem. Soc. **105**, 1746 (1983), and references therein.
[25] M. R. Robin, *Higher Excited States of Polyatomic Molecules* (Academic, New York, 1974).
[26] E. P. Gardner and J. R. McMesby, J. Phys. Chem. **86**, 2646 (1982).
[27] G. C. G. Waschewsky, D. C. Keichen, P. W. Browning, and L. J. Butler, J. Phys. Chem. **99**, 2635 (1995).
[28] N. Tanaka, J. Oike, Y. Kajii, K. Shibuya, and M. Nakata, Chem. Phys. Lett. **232**, 109 (1995); N. Nishi and H. Shinonara, Ann. Rev. Instit. Mol. Sci. Myodaiji. Okazaki, Japan, 76 (1981).
[29] J. V. Michael and W. A. Noyes, J. Am. Chem. Soc. **85**, 1228 (1963).
[30] J. E. Mathis and R. N. Compton, J. Chem. Phys. **104**, 8341 (1996).
[31] M. Dupuis, F. Johnson, and A. Marquez, *Hondo 8.5 from CHEM-Station* (IBM Corporation, Kingston, NY, 1994).
[32] C. W. Murray and E. R. Davidson, Chem. Phys. Lett. **198**, 451 (1991).
[33] P. M. Kozlowski and E. R. Davidson, J. Chem. Phys. **100**, 3672 (1994).
[34] R. G. Parsons and V. F. Weisskopf, Z. Phys. **202**, 492 (1967).
[35] R. S. Mulliken, Acc. Chem. Res. **9**, 7 (1976).
[36] R. S. Mulliken, Chem. Phys. Lett. **46**, 197 (1977).
[37] G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 3 (Van Nostrand, New York, 1996), and references therein.
[38] E. M. Evleth, J. T. Gleghorn, and E. Kassab, Chem. Phys. Lett. **70**, 151 (1980).