Mode-dependent enhancement and intramolecular dynamics via vibrationally mediated photodissociation

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Abstract

Vibrationally mediated photodissociation has been shown to control bond cleavage in molecules and probe their dynamics on the ground and excited potential energy surfaces. The application of this method to two seven-atom molecules illustrates surprising vibrational energy localization in methylamine (CH₃NH₂), a molecule with a torsional degree of freedom and unique information regarding intramolecular vibrational energy redistribution for the C–H methyl stretches of propyne (CH₃C \equiv C–H).

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(Some figures in this article are in colour only in the electronic version.)

1. Introduction

Vibrationally mediated photodissociation (VMP) [1, 2] is a double resonance technique for the promotion of molecules by near infrared/visible (NIR/VIS) and ultraviolet (UV) photons, to vibrationally excited states and subsequently to electronic states, where they fall apart via direct dissociation or predissociation. Since vibrational energy is vital to reactivity, it may affect the photodissociation outcome and provide invaluable information regarding the dynamics. Particularly, vibrational energy might be a key player in driving molecular transformations, provided that two main requirements are accomplished: excitation of a specific mode or bond and localization and preservation of the excitation until the reaction occurs. However, using this simplistic presentation belies the enormous complexity since even if photons are absorbed by specific vibrations of large molecules they do not vibrate separately but rather couple to other vibrations. Therefore, although specific vibrational modes are excited, the energy is almost instantly distributed via intramolecular vibrational energy redistribution (IVR) [3-5], making it difficult to manipulate transformations via vibrational excitation.

When vibrational spectra are measured at room temperature, their broadness causes difficulties in obtaining insight of IVR. This difficulty can be overcome by monitoring spectra of cold molecules, obtained by supersonic jet expansions, where the population in high rotational states, and consequently the inhomogeneous structure and spectral congestion, are reduced. One of the approaches is that of VMP, exploiting improved Franck Condon (FC) factors, allowing tracing of vibrational spectra at the low concentration of the sample in the jet. At that instance vibrational spectra are obtained by action spectroscopy, which probes the photofragment yield against the vibrationally exciting laser wavelength.

The present work reviews the use of VMP and its crucial role in studying the dynamics of two seven-atom molecules, namely methylamine and propyne. Methylamine is an attractive candidate because of its two strongly coupled large amplitude motions, the torsion of the methyl top and the inversion of the amine group [6]. In VMP of methylamine, the effect of differing skeletal motions on the photodissociation outcome was examined in the region of the fundamental C–H stretches. Propyne (CH₃C \equiv C–H) is an interesting system since it includes two C–H stretch types, acetylenic and methyl C–H, which are relatively decoupled and therefore an appealing candidate for studying vibrational energy flow patterns. The first to the fourth C–H methyl stretch overtones

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of propyne were monitored and analysed, allowing retrieval of the temporal behaviour of the initially prepared and doorway bright states.

2. Experiment

Briefly, rovibrational excitation of the fundamental CH₃ stretch region of methylamine and of the CH₃ stretch overtone regions of propyne was induced by stimulated Raman excitation (SRE) and direct excitation, respectively. The VMP of methylamine [7, 8] and propyne [9–11] was performed with a two-laser system [12]. In methylamine the first laser provided the beams for rovibrational excitation, i.e. tunable VIS and NIR beams, used as pump and Stokes for SRE. In propyne a NIR/VIS beam of the first laser was applied for overtone excitation. The second, UV laser, provided the 243.135 nm beam for photolysis of the vibrationally excited parents and for detection of the released H photofragments via (2+1) resonantly enhanced multiphoton ionization (REMPI). The two counterpropagating beams were directed into a Wiley-McLaren time-of-flight mass spectrometer (TOFMS), propagating perpendicularly to both the TOFMS and the molecular beam axis and brought to a common focus in the ionization region to detect the H photofragments. The UV was 10 ns delayed with respect to the rovibrational excitation beams.

Methylamine or propyne mixtures in argon were prepared and expanded through a pulsed nozzle/skimmer configuration toward the TOFMS interaction region, where they were intersected by the lasers. Typical working pressure was $\sim 5 \times 10^{-6}$ Torr and the background pressure about two orders of magnitude lower. Ions formed via REMPI in the focal volume region were subject to continuously biased extraction, acceleration stages, deflectors and Einzel lens before entering the field-free drift region and detected by a microsphere or multichannel plate. The detector output was fed into a digital oscilloscope and a boxcar integrator. The H REMPI signal was passed to a personal computer via an analogue to digital converter and accumulated for further analysis.

Simultaneously with the jet-cooled H action spectra, room temperature photoacoustic Raman (PAR) or PA spectra of methylamine and propyne, respectively, were monitored for obtaining the vibrational spectra and for calibrating the vibrational excitation laser wavelength. Also, the (1 + 1' + 1')REMPI spectrum of rovibrationally-excited methylamine was monitored by temporally overlapping SRE and UV beams and accessing the intermediate \tilde{A} potential energy surface. The acoustic signal or the REMPI signal were monitored by an additional boxcar channel and transferred to the computer.

3. Results and discussion

3.1. Methylamine

The effect of different skeletal motions on methylamine dissociation was determined by scanning the SRE laser beams across the $2770-3015 \text{ cm}^{-1}$ range. A representative room temperature PAR spectrum (figure 1(a)) shows two prominent features, and in between and nearby some additional

weak features related to overtones and combinations of CH₃ deformations [7, 8]. The main bands correspond to Q-branches of the degenerate CH₃ stretch (ν_2) at 2961 cm⁻¹ and the CH₃ symmetric stretch (ν_3) at 2820 cm⁻¹ and the weak bands to overtones or combinations of deformations, comprising CH₃ degenerate deformation ν_5 , CH₃ symmetric deformation ν_6 , CH₃ rock ν_7 , CH₃ degenerate deformation ν_{12} and CH₃ torsion ν_{15} .

The features corresponding to both the main and the weak bands are narrowed and enhanced in the action spectrum. In figure 1(b), monitored at significantly lower rotational temperature (15 K) than the PAR spectrum (figure 1(a)), the small features are surprisingly even more enhanced, with intensities of the order of those of stretches. This implies that the hardly observed bands in the PAR spectrum, becoming prominent in the action spectrum, acquire their intensity during the UV excitation or the photodissociation process. The vibrational mode-dependence of the H photofragment yield was suggested to be due to enhanced FC factors between the wavefunctions of the initially prepared states and those accessed during the UV excitation [7, 8].

The H atoms could be released from the methyl and the amine groups, but it was assumed [7, 8] that the photodissociation occurs through the major N–H dissociation channel [13–16]. To assess whether the improved FC factors are the reason for this mode-dependent photodissociation, the (1 + 1' + 1') REMPI spectrum of the parent was monitored, (figure 1(c)). Here the molecules were rovibrationally and then electronically excited to the \tilde{A} state followed by their ionization (inset of figure 1(c)). Immediately apparent is that the molecular REMPI spectrum shows a similar pattern to that of the H action of figure 1(b). Since the REMPI process probes directly the vibronic transition, it is rather likely that the initial, sustained vibrational excitation to selected overtones or combinations of CH₃ deformation enhances the FC factors.

Previous studies pointed out that IVR is accelerated in flexible molecules, when the prepared vibration is close to a centre of flexibility, and the IVR rates depend on the internal rotation barrier height [17]. Furthermore, it was shown that there is a systematic decrease in IVR lifetimes as the barrier is decreased from 1700 to $400 \,\mathrm{cm}^{-1}$ [17]. Based on this reasoning it is inferred that methylamine, which is characterized by a torsion barrier of $718 \,\mathrm{cm}^{-1}$ [6], should possess an IVR lifetime 200 ps. Since in VMP the delay between the SRE and UV beams is 10 ns, the results presented here clearly show that the initially prepared states live considerably longer, sustaining their nuclear motion and leading to favourable FC factors and successively to enhanced dissociation. Were IVR complete on the nanosecond (ns) timescale of the experiment, it would be expected that the FC factors from either type of initially prepared states would be identical. In contrast, the differing FC factors point to a persisting difference in the vibrational character of the initially prepared states. This mode-dependence provides evidence for a non-statistical behaviour and indicates localization of vibrational energy in a molecule with a torsional degree of freedom on a timescale significantly longer than anticipated.



Figure 1. Vibrational excitation of the C–H stretch region of methylamine: (a) room temperature photoacoustic Raman spectrum, (b) jet-cooled action spectrum monitoring the yield of H photofragments following 243.135 nm photodissociation of pre-excited methylamine and (c) resonantly enhanced multi-photon ionization spectrum. The insets display simple diagrams of the excitation scheme used to obtain each spectrum, where the potential energy surfaces for N–H dissociation are adopted from [16], the dashed line denotes C_s symmetry and the solid line C_1 symmetry.



Figure 2. Vibrational overtone excitation of the V = 2 (A), V = 3 (B), V = 4 (C) and V = 5 (D) manifolds of the C–H methyl stretch of propyne: (a) measured photoacoustic spectrum, (b) measured jet-cooled action spectrum and assignment, (c) symmetric rotor simulation of the action spectrum, and (d) stick spectrum reflecting the calculated positions derived from the vibrational Hamiltonian. The black and white sticks label the A_1 and E type bands, respectively. The dashed lines in the simulated spectrum, panel (c), represent the A_1 and E type bands and the solid line their sum.

3.2. Propyne

The spectral signatures of the first to fourth C–H methyl stretch overtone regions of propyne [9–11], employing room temperature PA and jet-cooled action spectroscopy, are shown in figure 2. The intensity profiles of the action spectra, figure 2b, show good correspondence to those of the PA spectra, figure 2(a), and it was thus assumed that the photodissociation cross-section for all vibrational levels associated with a given stretch manifold, *V*, is the same. Since propyne is a symmetric-top belonging to the C_{3v} point group, its infrared-active vibrational levels of A_1 symmetry should be expected to exhibit parallel type bands, while the degenerate levels of *E* symmetry perpendicular type; and indeed, the apparent bands in the spectra correspond to these types.

Comparison of the PA and action spectra in the corresponding manifolds clearly shows that the former represent broader features. The band contraction of the parallel bands and appearance of fewer transitions in the perpendicular ones are a consequence of rotational cooling (15-20 K) and reduction of the contribution of the inhomogeneous structure in the action spectra. The importance of narrowing and consequently of the improved resolution is exemplified by the PA, figure 2(A)(a), and action, figure 2(A)(b), spectra of the first overtone, where the very broad feature in the 5725-5875 cm⁻¹ region of the former is resolved to signatures of four features of different symmetries in the latter. These features are the result of parallel bands exhibiting contours with definable P-, Q- and R-branches and perpendicular bands with well separated ${}^{P}Q$ and ${}^{R}Q$ transitions.

As for the higher overtones, dominant bands are observed in each range with some smaller bands at the high frequency tail of the second and third overtones. The action spectra clearly show that the dominant bands in each region are overlaid by some sharp features, related to the contribution of the perpendicular transitions. Based on these observations, it is obvious that action spectroscopy provides an appealing means for tracing cold overtone spectra of the vibrational manifolds, reducing the spectral congestion and improving the spectral resolution. These characteristics were found to be crucial for identifying the band shapes and for performing band simulations, shown in figure 2(c), and consequently retrieving the band types, band origins and homogeneous linewidths $(0.3 \pm 0.1, 3.0 \pm 0.5, 6 \pm 1 \text{ and } 7 \pm 1 \text{ cm}^{-1}$ for the main bands of the V = 2-5 manifolds, respectively).

The action spectra, figure 2(b), were modelled using a joint local mode/normal mode (LM/NM) Hamiltonian and an equivalent NM Hamiltonian for the C–H methyl moiety, while considering the Fermi resonances between stretch and deformations (the overtones of the symmetric CH₃ deformation mode, $2v_4$, and the doubly degenerate CH₃ deformation mode, $2v_7^0$) [9–11]. Diagonalization of the matrices of the vibrational Hamiltonians in both models resulted in eigenvalues and corresponding eigenvectors. The use of the LM approach for description of the C–H oscillators benefited from reduced number of model parameters, and enabled computation of the intensities [10] via calculation of the dipole moment functions [18]. These intensities together with the calculated band positions (see below) are exhibited by the sticks of figure 2(d).



Figure 3. Time-dependent populations of the $|200, 00\rangle$ (A), and $|300, 00\rangle$, $|400, 00\rangle$ and $|500, 00\rangle$ (B) states as determined from the simplified LM/NM Hamiltonian for the coupled C–H methyl stretches and deformations in propyne and the exponential decays. The insets show the shorter timescale for the corresponding states. In panel (A) the blue, green, black, and red lines represent the $|200, 00\rangle$ and $|110, 00\rangle$ states, and the $|100, 20\rangle$ and $|100, 02\rangle$ doorway states, respectively. In panel (B) the green, red, and blue lines show the populations of the $|300, 00\rangle$, $|400, 00\rangle$ and $|500, 00\rangle$ states, respectively.

Diagonalization of the vibrational Hamiltonian through least square fittings of the eigenvalues to the action spectra peak positions and consideration of the correspondence between calculated intensities and simulated band areas revealed model parameters [10]. These parameters allowed us to obtain a good correlation between predicted and experimental band positions of the methyl C–H bonds and an assignment of the observed bands [10]. It is clearly seen that the calculations predict the methyl pure LM transitions to be the dominant ones over all the manifolds, and in particular in the V = 5 manifold region, where they carry almost all the intensity.

In addition, the obtained Hamiltonian, accounting for the relatively strong couplings between the initially prepared states and the doorway states, and the retrieved linewidths, which reflect the exponential decay of the initially prepared states to the bath states, allowed us to uncover the overall temporal evolution of the C-H manifold states [10]. Our findings, figure 3, imply that the decay of the population is rapid, meaning that the specificity of the C-H excitation is lost in picoseconds (ps), but still differs for the different overtones. In particular, the time dependent population up to 20 ps of the pure C-H methyl stretch states $|V 0 0, 0 0\rangle$ for the first overtone is displayed in figure 3(A) and for the second to the fourth overtones in figure $3(B) [10]^2$. Also, in the corresponding insets the temporal behaviour of the $|V 0 0, 0 0\rangle$ states on a shorter timescale, up to 2 ps, is displayed. The inset of figure 3(A) also includes the time-dependent behaviour of the initially slightly populated $|1 \ 1 \ 0, \ 0 \ 0\rangle$ state and the

² The eigenstates are denoted by five quantum numbers: n_1 , n_2 , n_3 , d_1 and d_2 , where the first three quantum numbers represent the distribution of the excitation between the identical three bonds of the CH₃ group, and d_1 and d_2 are the number of quanta in the symmetric and antisymmetric CH₃ deformation modes, respectively.

 $|1 0 0, 2 0\rangle$ and $|1 0 0, 0 2\rangle$ doorway states (dark states containing one quantum of C–H stretch and two quanta of v_4 and ν_7^0 deformations, respectively) which are most strongly mixed via Fermi resonance with the bright states. The energy redistribution plots were obtained by taking into account the oscillations due to energy flow inside the methyl group, obtained from the derived Hamiltonian and the corresponding exponential decay of the population with a time constant τ (derived from the linewidths) for each overtone. The inset of figure 3(A) clearly shows that the doorway states acquire and lose population during sub-picosecond oscillations of the $|2 0 0, 0 0\rangle$ state. Also, figure 3(A) shows that the $|2 0 0, 0 0\rangle$ state lives about an order of magnitude longer than the |3 0 (0, 0, 0), $|4, 0, 0, 0\rangle$, and $|5, 0, 0, 0\rangle$ states, figure 3(B), although on the shorter timescale the population of the $|5\ 0$ (0, 0, 0) state decays less than that of the $|2, 0, 0, 0\rangle$ state. This behaviour might be attributed to the weaker Fermi resonances in the V = 5 manifold region and the different coupling with the bath states in the two regions. Consequently, in low-Vstates the coupling is doorway dominated, while at high-Vthe increased density of bath states overwhelms the detuning from doorway states, except at the very earliest time. The time evolution of C-H methyl stretches implies rapid IVR, meaning that the specificity of the C-H excitation is lost in ps.

The dynamical behaviour of the two molecules differs not only because of the various C–H oscillator environments, but also due to the different density of states in the region of the C–H fundamentals and overtones of methylamine and propyne, respectively. These examples shed light on the importance of the VMP method for understanding molecular processes and speak to its utility as a new 'window' providing a different view of vibrational dynamics.

Acknowledgments

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