Vibrational Dissociation Dynamics of the Methane Clusters of 3-Amino-s-Tetrazine

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The dissociation dynamics of van der Waals clusters formed from 3-amino-s-tetrazine (AT) and methane (CH$_4$) in a supersonic molecular beam shows that the rate of bond breaking of the AT-CH$_4$ van der Waals bond is determined largely by the cluster density of states. Unlike in the case of argon clusters of AT, which were initially investigated by Alfano et al., the nature of initially excited AT vibrational ring mode does not appear to play a major role in the dissociation dynamics of AT-CH$_4$ cluster. The difference in vibrational predissociation rates between AT-Ar ($2 \times 10^6$ s$^{-1}$) and AT-CH$_4$ (> $2 \times 10^{10}$ s$^{-1}$) mirrors the expected increase in cluster density of states that occurs when argon replaces methane as AT’s complexing partner. AT-CH$_4$ is estimated to have a ground-state binding energy of < 270 cm$^{-1}$.

Key words: van der Waals clusters, supersonic jet expansion, Franck-Condon factor, fluorescence quantum yield, extreme mode selectivity

INTRODUCTION

Physical chemists have long been very interested in investigating the possibility of achieving some degree of control over the outcome of chemical reactions by selectively exciting specific vibrational motions of molecules. For this reason, many types of van der Waals clusters, binary clusters in particular, have been extensively studied (Alfano et al. 1989; Alfano et al. 1992; Brumbaugh et al. 1983; Dimopoulou-Rademann et al. 1988; Heppener et al. 1985; Ramaekers et al. 1983; Smalley et al. 1978; Weber et al. 1988). Typically, binary clusters are composed of a parent aromatic molecule that acts as the chromophore (the cluster component that is directly involved in the absorption or emission of radiation) and a complexing partner, which is usually a noble gas or a small molecule such as ammonia, methane, water, etc. Many of these binary clusters were investigated using supersonic jet spectroscopy.

A supersonic jet expansion, as used in the experiment described below, is generated by passing gas at high pressure (for example, He or Ar at a pressure between 50 to 100 atm) through a small pinhole (typically with a diameter of between 25 to 100 microns). The gas is then allowed to expand in a reaction chamber that is under vacuum, and the resulting free jet flows above the speed of sound. Molecules in a free supersonic jet expansion have very cold vibrational and rotational temperatures, which make the technique very useful. For one, it allows the formation of clusters that may not be stable at room temperature. In addition, the resulting spectra of the molecules or clusters are far less congested than ordinary gas-phase spectra, making it easier to investigate the dynamics of a reaction, for example.

Combined with lasers, the use of supersonic jet spectroscopy allows one to study binary clusters whose emission peaks shift by a small, but reproducible, amount (typically about 30 cm$^{-1}$ in the case of an aromatic molecule paired with an argon atom) relative to those of the lone parent molecule. This small, nonetheless real,
shift suggests that a complexing partner such as argon only weakly perturbs the electronic structure of the parent aromatic molecule. This small shift can be easily measured using a set-up that has a spectral resolution of about 6 cm⁻¹, for example, as is the case with the set-up used in the study described in this paper. Such a slight perturbation would thus be expected to give rise to a spectrum essentially identical to that of the lone parent molecule, except that all the peaks due to the cluster are shifted by more or less the same amount relative to the corresponding peaks arising from the lone parent molecule.

For many years, however, the dissociation dynamics of the binary van der Waals clusters that have been investigated using lasers as excitation source have shown little dependence on the nature of the vibrational motion that was initially excited. But in 1992, Alfano et al. found that the argon clusters of 3-amino-s-tetrazine (AT) actually exhibited extreme mode-selectivity, i.e., the rate of bond-breaking of the van der Waals bond (the bond between AT and argon) was found to be extremely sensitive to the nature of the initially-excited aromatic ring vibrational motion (Alfano et al. 1992). Therefore, we wanted to determine what gives rise to the observed extreme mode selectivity of the AT-Ar cluster, which all other previously studied clusters do not exhibit.

The results of studies on AT-CH₄ cluster discussed below demonstrate that a dominant factor—the cluster density of states—effectively overcomes whatever gives rise to the extreme mode selectivity exhibited by the AT-argon cluster. This suggests that molecules with complexing partner larger, or more complex than argon would not be expected to exhibit any extreme mode selectivity because of dominance of the cluster density of states (density of states typically refers to the number of rotational and/or vibrational states in a given energy range) in those cases.

METHODS

Synthesis of AT
Triaminoguanidine hydrochloride (TGH) is first synthesized by simply mixing guanidine hydrochloride and hydrazine. After washing the collected TGH with small amounts of methanol, it is refluxed under nitrogen with formic acid for an hour or more. The viscous, oily compound obtained from refluxing is then mixed with a few milliliters of methanol. This leads to the formation of 4-amino-3-hydrazino-s-triazole hydrochloride (AHT), which is a milky-white solid. AHT is then reacted with HCl, and then NaNO₂ solution is added dropwise (this procedure must be done under nitrogen, with the entire solution constantly stirred and cooled using an ice-acetone mixture). The reaction between AHT and NaNO₂ solution forms 3-azido-4-benzylideneamino-s-triazole (ABT).

ABT is then made into alkaline by adding Na₂CO₃ until the pH has changed to about 9 or 10. Acetonitrile is added to the mixture and stirred overnight to extract ABT. Extraction with acetonitrile is repeated several times. The combined acetonitrile extracts are then gently evaporated using a rotary evaporator in which the solution is immersed in cold water. The ABT obtained after evaporation is then thermally decomposed using chlorobenzene, which leads to the formation of 3-amino-s-tetrazine (AT). The AT is purified using liquid chromatography (2:1 diethyl ether-petroleum ether as solvent) followed by sublimation. The melting point of purified AT is 172°C. (Note: One must be extremely careful when synthesizing AT using the above procedure because the thermal decomposition step using chlorobenzene generates a large amount of N₂ gas over a short period of time. An explosion can occur if the temperature during decomposition is allowed to rise too rapidly or beyond 110°C.)

Measurement of Excitation and Emission Spectra
The fluorescence excitation spectra (FES) of the methane clusters of AT were obtained by crossing the cluster-containing supersonic molecular beam with the output of a dye laser (using an argon-ion laser to excite the dye laser). The dispersed emission spectra (DES) of the clusters were then obtained by individually exciting the cluster peaks found in the acquired excitation spectra, and then collecting and recording the resulting molecular or cluster emission that follows excitation.

A FES is equivalent to an absorption spectrum, thus FES peaks correspond to transitions from ground state to various vibrational levels of an excited electronic state. The transitions are almost all from the lowest vibrational level of ground electronic state because most of the molecules and clusters in a supersonic jet expansion populate the lowest vibrational levels of ground electronic state. The peaks in a DES, on the other hand, represent transitions from excited vibronic (vibrational-electronic) state to various vibrational levels of ground electronic state.

The specific cluster giving rise to certain peaks in the excitation spectra can be identified partly by measuring how much the cluster peak intensities increase as a function of methane concentration, and also by measuring the shifts from monomer AT peaks. For example, the rate of formation of AT-CH₄ and AT-(CH₄)₂ clusters would
be expected to be approximately first-order and second-order with respect to methane concentration, respectively, assuming their formation is kinetically determined. Peaks due to methane clusters of AT in FES can be readily distinguished from those of the monomer AT, since cluster peaks do not appear in FES if methane is not introduced in supersonic molecular beam (see Fig. 1).

If a binary cluster is surrounded by solvent molecules such as in the case of samples in liquid state, vibrational relaxation (VR) from an excited vibrational level to a lower vibrational level is fairly rapid due to many molecular collisions that absorb excess vibrational energy. In the clusters studied here, relaxation occurs mostly to the lowest vibrational level (also referred to here as the vibrationless or zero-point level). In a supersonic jet expansion, however, the binary clusters are isolated, so emissions from initially-excited cluster level can be observed partly because of practically non-existent molecular collisions that can drive the relaxation process.

Still, VR involving a cluster in a supersonic molecular beam can occur even in the absence of molecular collisions. This is because various cluster states can absorb excess vibrational energy that was initially injected into the parent aromatic molecule. When emission from the initially-excited cluster is observed, it suggests that the emission process occurs at a rate comparable to that of VR.

A Coherent Innova 400 argon-ion laser set at 477 nm was used to pump a Coherent Model 490 standing wave dye laser. For the dye laser solution, 5 x 10^{-3} M concentration of Coumarin 535 using ethylene glycol as solvent was prepared. The dye solution was diluted with ethylene glycol during optimization of laser power to allow for about 80% absorption. Between 4-6 g of 9-methylantracene per 1.5 L, dye solution was used as a triplet quencher.

With a wavelength range of from about 508.0 nm to about 550.0 nm, the dye laser output was directed to the supersonic molecular beam, which contains AT-(CH₄)ₙ (where n=1, 2, 3, . . .) clusters entrained in the He gas. For the fluorescence excitation experiments, the dye laser output was scanned and the resulting monomer AT or cluster fluorescence was directed using a camera lens to a cooled RCA 8575 photomultiplier tube (PMT) in a photon counting configuration. The laser power was used to normalize the fluorescence excitation spectra. Methane was mixed with He and AT using a UNIT mass flow controller.

In the dispersed emission experiment, emissions resulting from excitation with a fixed laser frequency were directed to a 1-meter Spex monochromator, which was scanned using a 2400 groove/mm grating over the 550.0–508.0 nm (18,182 – 19,685 cm⁻¹) range. The spectral resolution for all the dispersed emission spectra is about 6 cm⁻¹. All of the emission spectra were normalized using simultaneously measured total fluorescence.

RESULTS

We investigated the dissociation dynamics of AT-CH₄, AT-(CH₄)₂, and AT-(CH₄)₃ clusters upon exciting AT's 16b², 16a², 6a¹, 1¹, and 6a² modes (see Fig. 2). These excitations
correspond to the injection of from about 430 cm\(^{-1}\) to 1212 cm\(^{-1}\) excess vibrational energy (measured relative to the lowest vibrational level, i.e., the vibrationless or zero-point level, which has a frequency \(\nu_o\) and vibrational quantum number equal to zero). We also investigated the dissociation dynamics of AT-N\(_2\) and AT-C\(_2\)H\(_6\) clusters.

Due to space limitations, we present and discuss results pertaining mainly to 16b\(^2\), 16a\(^2\), 6a\(^1\), and 6a\(^2\) excitation of the methane clusters of AT. To aid us in our analysis, we made comparisons with extensive amount of data available from previous studies on other clusters.

The first number inside the parentheses in subheadings below refers to vibrational mode frequency of FES peak that was excited, while the second number is the amount of excess vibrational energy relative to chromophore’s vibrationless level in excited electronic state (i.e., \(\Delta\nu_{\text{exc}} = \nu_{\text{exc}} - \nu_o\), where \(\nu_{\text{exc}}\) is the excitation frequency). The cluster emission may occur directly from the initially excited level, or emission may originate from a lower vibrational level (not necessarily the zero-point level) in case where the cluster undergoes non-radiative decay or VR (prior to emission) from the initially-excited vibrational level.

Excite 16b\(^2\) (18 816 cm\(^{-1}\)/431 cm\(^{-1}\))

The DES obtained upon exciting the AT-CH\(_4\) 16\(^2\) peak in the FES at 18 816 cm\(^{-1}\) is shown in Fig. 3(a). The intensity at the excitation frequency is due entirely to scattered light (i.e., no emission from the initially-excited cluster level is observed). All major transitions have the same relative positions and relative intensities as the features in DES obtained upon exciting the free AT 0\(^0\)\(_o\) (the 0\(^0\)\(_o\) transition, also referred to as the origin transition, involves the transition between vibrationless level of ground electronic state and vibrationless level of the excited electronic state). They are, however, shifted by about 14 cm\(^{-1}\) to the red of corresponding AT monomer transitions.

Since the AT-CH\(_4\) 16b\(^2\)\(_o\) peak in the excitation frequency is also red-shifted by about 14 cm\(^{-1}\) to red of the AT 16b\(^2\)\(_o\) transition, the peaks in this DES must originate from the excited electronic state of AT-CH\(_4\) chromophore.
rather than from the AT monomer. The features in the AT-CH$_4$ 16b$^2$ spectrum are quite broad, having linewidths of about 45 cm$^{-1}$, which is several times broader than our instrumental resolution.

Excite 16a$^2$ (18 875 cm$^{-1}$/ 510 cm$^{-1}$)

The DES obtained upon exciting the FES peak of AT-CH$_4$ at 18 875 cm$^{-1}$ displays features that exhibit relative positions and intensities similar to those in free AT 0$^0_o$ DES (see Fig. 3(b)). This again indicates that the transitions, whose linewidths are similar to those in 16b$^2_o$ DES, also originate from the vibrationless level of the cluster chromophore. However, cluster emission features are red-shifted by about 15 cm$^{-1}$, instead of the expected 30 cm$^{-1}$ red-shift. The feature at the excitation frequency is due entirely to scattered light.

Excite 6a$^1$ (18 977 cm$^{-1}$/ 609 cm$^{-1}$)

Excitation of the AT-CH$_4$ 6a$^1_o$ transition at 18 977 cm$^{-1}$ leads to a dramatic departure from the preceding observations. The DES peaks are all sharp and intense. At the excitation frequency, only about 15% of intensity is due to resonance fluorescence (emission involving the same two vibrational levels as in the excitation process, i.e., emission is not preceded by relaxation). Moreover, the features in this DES shown in Fig. 3(c) have frequencies and relative intensities that match those of the free AT 0$^0_o$ DES. There is an extremely weak feature that may be attributed to the 0$^0_o$ transition of AT-CH$_4$ cluster, but otherwise the spectrum shows a practically complete VP of the cluster.

Excite 6a$^2$ (19 583 cm$^{-1}$/ 1212 cm$^{-1}$)

Going up to 1212 cm$^{-1}$ of excess vibrational energy, we excited the AT-CH$_4$ 6a$^2_o$ transition at 19 583 cm$^{-1}$. The DES is shown in Fig. 3(d). In contrast to the 6a$^1_o$ and 1$^0_o$ emission spectra, the 6a$^2_o$ DES is somewhat congested. The feature at the excitation frequency is due entirely to scattered light. The major features arise from the vibrationless level of the AT fragment, but there are additional features assignable to 16b$^1_i$ and 16a$^2_i$ transitions of the AT fragment in addition to free AT combination bands built upon each of the 16b$^1_i$ and 16a$^2_i$ transitions. The strongest feature lies at a frequency that matches exactly that of the free AT 6a$^1_o$ transition.

AT-(CH$_4$)$_2$

Excite 6a$^1$ (18 947 cm$^{-1}$/ 609 cm$^{-1}$)

The DES obtained upon exciting the 6a$^1_o$ transition of
AT-(CH₄)₃ at 18 947 cm⁻¹ is shown in Fig. 4(a). The feature at the excitation frequency arises entirely from scattered light. Strong features originate from the vibrationless level of AT-(CH₄) (the emission being denoted by mode of transition labels with a single bar above each of them), indicating an efficient VP of AT-(CH₄) to form AT-(CH₂). Weak emissions due to 0ₖ, 6a₀, and 1₀, transitions of the AT-(CH₃)₂ cluster are also observed in this spectrum.

Excite 6a² (19 547 cm⁻¹/ 1213 cm⁻¹)

Exciting the AT-(CH₄)₂ 6a² transition at 19 547 cm⁻¹, as shown in Fig. 4(b), generates strong and sharp emissions from the vibrationless level of the free AT fragment. Thus, applying two quanta of excitation in 6a mode leads mainly to the breaking of both AT-(CH₄) bonds.

We also observed relatively weak and broad emissions due to 0₁, 6a¹, 1¹, and 6a² transitions of AT-CH₄ fragment, which partly overlap AT fragment features. The presence of 6a¹ transition due to the free AT fragment sets an upper limit to the binding energy of about 270 cm⁻¹. Resonance fluorescence (RF) is absent at the excitation frequency.

AT-(CH₄)₂

Excite 6a¹ (18 916 cm⁻¹/ 609 cm⁻¹)

Figure 4(c) shows the DES obtained by exciting the AT-(CH₄)₂ 6a¹ transition at 18 916 cm⁻¹. The spectrum displays emissions principally from the vibrationless level of AT-(CH₄) (the emission being denoted by mode or transition labels with double bars above them), which means the dominant process here is VP of AT-(CH₄) to form AT-(CH₂). No RF is observed at the excitation frequency. There is some overlap between features due to AT-(CH₃), and AT-(CH₂) giving rise to base widths of more than 60 cm⁻¹.

Excite 6a² (19 524 cm⁻¹/ 1212 cm⁻¹)

The DES obtained subsequent to exciting the AT-(CH₄)₂ 6a² transition at 19 524 cm⁻¹ is shown in Fig. 4(d). The feature at excitation frequency is due entirely to scattered light. The spectrum reveals emissions primarily from the vibrationless level of AT-CH₄, which shows the dominant process here is VP of AT-(CH₄) to form AT-CH₂, i.e., both AT-CH₄ van der Waals are broken with about 1212 cm⁻¹ amount of vibrational excitation energy. In this spectrum, the respective 0₁ and 6a¹ transitions of AT-CH₄ and AT-(CH₂) overlap resulting in broad transitions with base widths of about 50 cm⁻¹.

**DISCUSSION**

**Aminotetrazine-CH₄ Dynamics**

The emission peaks obtained upon exciting the cluster 16b² and 16a² features originate from the vibrationless level (i.e., from the 0⁰ level, instead of 16b² or 16a² level) of the cluster, which shows that vibrational relaxation (VR) of the cluster is the dominant process following 16b² and 16a² excitation. If vibrational predissociation (which involves the breaking of cluster van der Waals bond) occurs at this level, it must be slower than VR because we did not observe distinct features that can be attributed to free AT produced upon cluster fragmentation. It is possible, however, that some free AT fragment features are buried underneath the broad peaks in the DES.

The observation of intermolecular VR in AT-CH₄ cluster upon excitation of the two lowest vibronic levels (16b₂ and 16a₂) sets it apart from the AT-Ar cluster. In the AT-Ar cluster, the dominant competing processes are vibrational predissociation (VP) and RF. Excitation of AT-Ar 16b₉ transition leads to an essentially complete VP to AT monomer.

In the case of AT-CH₄, the dominance of intermolecular VR over VP at 16b² level can be explained in terms of cluster density of states and binding energy. The methane cluster has a greater density of van der Waals states (also referred to here as cluster states) because of the six degrees of freedom resulting from methane complexation, three of which correspond to the van der Waals stretch and bending modes, and the other three to methane rotational degrees of freedom relative to a fixed AT framework. The methane cluster, owing to methane’s greater polarizability (2.593 Å³) (Kirouac et al. 1973; Orcutt et al. 1967) compared to argon’s (1.641 Å³) (Kirouac et al. 1976; Newell et al. 1965) is also expected to have a larger binding energy.

The behavior of AT-CH₄ upon excitation of 16b² and 16a² levels is similar to that of aniline-CH₄. When excited with 494 cm⁻¹ excess energy, the aniline-CH₄ emission features are broadened by as much as 120 cm⁻¹, the broad peaks being built around the cluster chromophore’s zero-point level transitions (Nimlos et al. 1989). The calculated density of states for aniline-CH₄ at 700 cm⁻¹ excess energy is 3 x 10⁴ states per cm⁻¹, and only about 15 states per cm⁻¹ for aniline-Ar (Nimlos et al. 1989). Hence, the intermolecular VR rate is expected to be at least three orders of magnitude faster in aniline-CH₄ than in aniline-Ar because of the former’s greater cluster density of states (everything else being equal, the VR rate should increase with increasing density of states).

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Our estimated average AT-CH$_4$ binding energy is $< 272$ cm$^{-1}$ based on observation of the free AT 6a$^1$ excitation upon exciting the AT-(CH)$_4$ 6a$^2$ level with 1212 cm$^{-1}$ excess energy (The difference between 6a$^2$ and 6a$^1$ levels is 606 cm$^{-1}$). Since both AT-(CH)$_4$ completely fragments into AT, which corresponds to the breaking of both AT-CH$_4$ bonds, we divide 606 cm$^{-1}$ by two to obtain an estimate of the excited state binding energy of AT-CH$_4$, which is $< 303$ cm$^{-1}$. From the observed red-shift of about 31 cm$^{-1}$ corresponding to the frequency difference in the peak positions of AT and AT-CH$_4$ cluster in the FES, we obtain a ground state binding energy estimate of $< 272$ cm$^{-1}$ for the AT-CH$_4$ cluster. Since the ground electronic state binding energy is lower ($< 272$ cm$^{-1}$) than that in excited electronic state ($< 303$ cm$^{-1}$), the cluster is more stable in the excited state than in the ground electronic state.

The above estimated binding energy for AT-CH$_4$ is a lower limit because if the binding energy is $> 272$ cm$^{-1}$, we would not expect to observe any fragmentation features at all. This value is comparable to the lower limits of the binding energy of argon clusters of tetrazine (277 cm$^{-1}$) and AMT (274 cm$^{-1}$) (Brumbaugh et al. 1983).

To obtain estimates of VP constants from dispersed emission spectra, we determine the relative yield of AT fragment from the number densities of the AT fragment and the cluster. The intensity of an AT fragment or cluster DES peak, as shown in equation (1) below,

$$\text{Intensity} \propto \eta \times \Phi \times \text{F.C.}$$

is directly proportional, for a given transition, to the product of fragment or cluster number density ($\eta$), fluorescence quantum yield ($\Phi$), and Franck-Condon factor (F.C.). Thus, from the intensities of the DES features and experimentally known values of $\Phi$’s and F.C.’s for those features, one obtains the number densities of the bare AT fragment or AT cluster. The ratio of the number density of AT fragment to the combined number densities of AT fragment and those due to all AT cluster transitions in the emission spectra is defined as the relative yield of VP ($Y_{VP}$).

In the case of the 6a$^1$ excitation of AT-CH$_4$, for example, the relative yield is given by equation (2) below

$$Y_{VP} = \eta_{AT}/(\eta_{AT} + \eta_{AT-CH4})$$

where $\eta_{AT}$ denotes the AT fragment number density and $\eta_{AT-CH4}$ represents the AT-CH$_4$ cluster number density.

As discussed below, complexation with a noble gas or a nonpolar molecule normally produces a weak perturbation of the vibronic structure of the parent aromatic molecule. Thus, for the purpose of calculating estimates of VP rates, the $\Phi$’s and F.C.’s that we use for the clusters are based on known values for free AT. Differences in the number densities of monomer and cluster therefore reflect differences in their corresponding peak intensities in the DES.

We calculate the lower limits of VP rate constants only for those cases where features due to AT or other fragmentation products (e.g., AT-CH$_4$ from AT-(CH)$_4$ excitation) are clearly observed in the DES. For instance, we do not attempt to estimate the lower limits of VP rates for the 16b$^2$ and 16a$^2$ emission spectra of AT-CH$_4$ cluster because the broad features in those spectra make it impossible to clearly identify AT fragment features. As can be seen below, this omission does not preclude one from deducing the correct mechanism involved in the fragmentation of various clusters of AT.

We consider two mechanisms shown in Fig. 5, and then compare the resulting rate constants with those already known for similar systems. The first mechanism assumes that the different processes that take place upon excitation of a given cluster transition – RF, VR, and VP – occur in parallel. The second mechanism involves a serial intermolecular VR/VP process competing in parallel with RF. These mechanisms and resulting rate equations are shown below.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mechanisms.png}
\caption{Two possible mechanisms involving the vibrational predissociation of AT-CH$_4$}
\end{figure}
For a parallel mechanism in which the only two competing processes are RF and VP, solving the rate equation yields a simple expression given by equation (3) below

(3) \( Y_{vp} = k_{vp} / (k_{vp} + k_f) \) (parallel mechanism)

where \( k_{vp} \) corresponds to the VP rate constant and \( k_f \) refers to the fluorescence rate constant. The equation allows one to calculate the rates of VP from the calculated relative yield of dissociation product (free AT fragment) and the known fluorescence lifetimes of AT.

For the sequential mechanism shown in Fig. 5, we arrive at the simple expression below because no emission features are observed from the relaxed levels of the cluster. Thus, we can ignore the process associated with the relaxed cluster emission. The resulting equation differs from that corresponding to the parallel mechanism in that \( k_{vr} \), the VR rate constant, has now replaced \( k_{vp} \).

Depending on the mechanism assumed, one obtains an estimate of either \( k_{vp} \) or \( k_{vr} \) from the experimentally determined \( Y_{vp} \) and \( k_f \). In a sequential (i.e., serial) mechanism in which intermolecular VR is the rate determining step, the rate of VP would be, by definition, faster than the rate of VR. Hence, one can estimate the lower limit for the rate of VP in a sequential mechanism based on calculated \( k_{vr} \).

In our calculations, we assume that the fluorescence lifetime \( (\tau_f) \) of any given vibrational level is unchanged by complexation. This is a reasonable assumption considering that complexation of AT with methane has little effect on vibronic level structure of AT as evidenced by the \( 0^s \) DES of various AT-CH\(_4\) clusters. Also, Hager and Wallace have found that non-polar partners of 2-amino pyridine (2AP) such as Ar, CH\(_4\), CF\(_4\), and CCl\(_4\) have negligible effect on 2AP’s fluorescence lifetimes (Hager & Wallace 1985). Even polar solvents such as ammonia and 1,4-dioxane have been found to exert little effect on parent molecule’s decay dynamics (Hager & Wallace 1985).

Assuming the cluster dissociation dynamics is described by a parallel mechanism, and using \( \Phi_f = 0.1 \), F.C. = 0.67, and \( \tau_f = 90 \text{ ns} (\tau_f = 1/k_f) \) for the 6a\(^1\) level of AT-CH\(_4\), we obtain an estimate for the VP constant (Alfano et al. 1992; Shauer et al. 1985). In the case of AT-CH\(_4\) 6a\(^1\) excitation, we see from the DES that the VP of AT-CH\(_4\) to the AT monomer is essentially complete since the features, with the exception of the peak at excitation frequency, are all due to the AT fragment. Thus, we can estimate that the binding energy of AT-CH\(_4\) must be less than 606 cm\(^{-1}\), which is the amount of excess vibrational energy injected into the 6a\(^1\) mode above the zero-point vibrational level.

Using equation (1) to calculate the number densities from relative intensities, and assuming \( \Phi_f \) and F.C. to be the same for AT fragment and AT-CH\(_4\) cluster, the relative yield of VP becomes equal to \( Y_{vp} = \eta_{AT} / (\eta_{AT} + \eta_{AT-CH4}) = 20.155 / (20.155 + 10) = 0.9995 \). (The values \( \eta_{AT} = 20.155 \) and \( \eta_{AT-CH4} = 10 \) correspond to the photon counts of AT fragment and AT-CH\(_4\) cluster in the supersonic jet, which were obtained using the photon-counting configuration described in part B. of “Methods” section above.) We then use equation (3) \( Y_{vp} = k_{vp} / (k_{vp} + k_f) \) to calculate \( k_{vp} \) (the VP rate constant). In this case, we use \( k_f = 1/\tau_f = 1/(90 \times 10^9 \text{ s}) \), where \( \tau_f \) was based on the measured value for the 6a\(^1\) level of AT-CH\(_4\). Thus, using \( Y_{vp} = 0.9995 \) and \( k_f = 1.1 \times 10^{-7} \text{ s} \), we obtain a lower limit for \( k_{vp} \) equal to \( 2.2 \times 10^{-9} \text{ s} \).

If we assume a serial mechanism, we have to use equation (4). However, equation (4) contains the quantity \( k_{vr} \) whose value we do not know. On the other hand, we can see from 6a\(^1\) spectrum that the features are entirely due to the VP of the cluster (since the excitation of the cluster produces only AT monomer peaks produced from the fragmentation of initially-excited AT-CH\(_4\) cluster). This shows that \( k_{vp} \) is much greater than \( k_{vr} \).

If intramolecular VR occurs at a rate comparable to those of other competing processes, one should see peaks due to cluster emission from vibrational levels lower than the initially-excited cluster vibrational level. Since we do not see peaks due to emission from the relaxed cluster vibrational levels, we can safely assume that \( k_{vp} \) is much greater than \( k_{vr} \). Thus, if we substitute \( k_{vp} \) with \( k_f \) in equation (4), we get a lower limit to the value of \( k_{vp} \) since the spectrum shows that \( k_{vp} \) is much smaller that \( k_{vp} \) at least in the case of AT-CH\(_4\) 6a\(^1\) excitation. Thus, using either equation (3) or (4), we obtain a value of \( > 2.2 \times 10^{-9} \text{ s} \) for the \( k_{vp} \) of AT-CH\(_4\) at the 6a\(^1\) level.

This calculated value of the VP rate constant is just an order of magnitude greater than the calculated 6a\(^1\) level VP rate constants for aminomethytetrazine-argon (AMT-Ar) and dimethyltetrazine-argon (DMT-Ar) (<1.6 x 10\(^9\) s\(^{-1}\) and 3 x 10\(^9\) s\(^{-1}\), respectively) (Alfano et al. 1992). The calculated VP rate constant for AT-Ar from the same vibrational level, on the other hand, is only 2 x 10\(^9\) s\(^{-1}\). This increase in the VP rate upon substitution of argon with methane mirrors the three orders of magnitude increase in the cluster density of states at 700 cm\(^{-1}\) excess vibrational energy upon changing the complexing partner of aniline from argon to methane (Nimlos et al. 1989). Everything else being equal, this implies that the increase in the VP rate is due mainly to increase in the cluster density of states.
An intermolecular VR process competing in parallel with VP is not compatible with these results. In a parallel mechanism with two competing processes, an increase in the rate of one process can only occur at the expense of the other. Because VR depends on the density of cluster states, an increase in density of states (as would occur when argon replaces methane as AT complexing partner) would be expected to result in an enhancement of the VR rate. In turn, this should lead to a decrease in the rate of competing bond-breaking process (i.e., VP) involving the AT-CH₄.

The DES and calculated rates for AT-CH₄ are, however, consistent with a two-step serial process where the first step involves VR (from the initially-excited vibrational mode of aromatic parent molecule into the cluster modes), followed by VP. In this process, VP occurs only when the amount of vibrational energy that flows into the cluster modes exceeds the binding energy of the cluster. This mechanism has been proposed by Kelley and Bernstein to explain the VP process of AT-(CH₄)₂ (Kelly & Bernstein 1986).

In the case of methane clusters of AT upon excitation of the 6α‘ mode, results are consistent with VR being the rate determining step in a serial VR/VP process. Because the rate of VR depends on the cluster density of states, an increase in density of states would hasten intermolecular VR and thus enhance the overall rate of the VR/VP process.

The similar order of magnitude increase in both VP rates and density of states (from about 10⁸ s⁻¹ for AT-Ar to about 10¹⁰ s⁻¹ for AT-CH₄ for kᵥ, and from about 10 cm⁻¹ for AT-Ar to about 10⁴ cm⁻¹ for AT-CH₄ for the density of states, based on the calculated density of states for aniline-Ar and aniline-CH₄) supports a serial mechanism for the methane cluster of AT. Moreover, the argon and methane clusters of perylene and indole have also been observed to exhibit a very similar dependence of the VP rates on cluster density of states (Outhouse et al. 1991; Wittmeyer et al. 1989).

The results of studies on AT-N₂ and AT-C₂H₆ clusters further support a serial mechanism involving the VP of AT-CH₄ and AT-C₂H₆. VP is found to be more efficient at the 16b level of AT-C₂H₆ than that of AT-CH₄ (based on the apparent presence of AT fragment peaks in the DES of AT-C₂H₆ upon excitation of cluster 16b level). This would be expected if a serial mechanism, where VR is the rate-determining step, is involved in both AT-CH₄ and AT-C₂H₆. AT-C₂H₆ has a greater cluster density of states than AT-CH₄, and so the VP of the cluster would be faster if the slow step (VR) is enhanced by increasing the cluster density of states. The observed dynamical behavior of AT-N₂ is also consistent with a serial mechanism and with it having a cluster density of states less than both that of the AT-CH₄ and AT-C₂H₆ clusters.

**Aminotetrazine-(CH₄)₂ Dynamics**

To calculate the VP rates for the AT-(CH₄)₂ and AT-(CH₄)₄ clusters, we consider four different possible mechanisms in Figure 6. The first two mechanisms assume that VR from the initially excited ring mode to the cluster modes occurs prior to VP. In the other two mechanisms, VR from initially excited ring mode to the cluster modes is assumed to occur in parallel with VP.

The constant expressions shown in Figure 7 can all be derived using similar arguments and assumptions. Due to space limitations, we show the calculation of the rate constant for one mechanism only. The other rate constant expressions can be derived using similar arguments and assumptions. For the mechanism shown in Fig. 6(a), one obtains the expression below using steady-state approximation.

\[
\frac{dA}{dt} = k_{iv}^f [AT - CH_4] - k_{vp} [AT^4] = 0
\]

Figure 6. Four possible mechanisms involving the vibrational predissociation of AT-(CH₄)₂
We assume that the fluorescence rate constant, $k_{fl}$, is the same for the bare AT and the cluster. Hence by multiplying the numerator and denominator on the right side of equation (6) by $k_{fl}$, we obtain the ratio of the rates of formation of AT$^8$ and AT$^8$-CH$_4$ (see Mech. a). This ratio is equal to the ratio of the number density of AT$^8$ to the number density of AT$^8$-CH$_4$. Dividing both numerator and denominator of this ratio by the total number density (which we obtain by combining all the number densities from all species that show emission in the DES), we obtain the ratio of the relative yield of AT$^8$ to the relative yield of AT$^8$-CH$_4$ (see Mech. a).

Mechanism a:

$$k_{vp}^1 = (k_{fl} + k_{vp}^2) \frac{Y(\text{AT}^4 - \text{CH}_4)}{Y(\text{AT}^8 - \text{CH}_4)_2}$$

$$k_{vp}^2 = k_{fl} \frac{Y(\text{AT}^8)}{Y(\text{AT}^4 - \text{CH}_4)}$$

Mechanism b:

$$k_{vp}^1 = k_{fl} \frac{Y(\text{AT}^8 - \text{CH}_4)}{Y(\text{AT}^4 - \text{CH}_4)_2}$$

$$k_{vp}^2 = k_{fl} \frac{Y(\text{AT}^8)}{Y(\text{AT}^4 - \text{CH}_4)}$$

Mechanism c:

$$k_{vp}^1 = (k_{fl} + k_{vp}^2) \frac{Y(\text{AT}^4 - \text{CH}_4)}{Y(\text{AT}^8 - \text{CH}_4)_2}$$

$$k_{vp}^2 = k_{fl} \frac{Y(\text{AT}^8)}{Y(\text{AT}^4 - \text{CH}_4)}$$

Mechanism d:

$$k_{vp}^1 = k_{ivr} \frac{Y(\text{AT}^8 - \text{CH}_4)}{Y(\text{AT}^8 - \text{CH}_4)_2}$$

$$k_{vp}^1 = k_{ivr} \frac{Y(\text{AT}^8)}{Y(\text{AT}^8 - \text{CH}_4)_2}$$

Equation (7) allows us to calculate $k_{vp}$ (the VP rate constant corresponding to the fragmentation of AT-CH$_4$ to form AT) from the experimentally known values of $k_{fl}$ and the relative yields of AT$^8$ and AT$^8$-CH$_4$ represented by $Y(\text{AT}^8)$ and $Y(\text{AT}^8 - \text{CH}_4)$. Following the same procedure above, we obtain the expression for $k_{ivr}$ (the VP rate constant corresponding to the fragmentation of AT-(CH$_4$)$_2$ to form AT-CH$_4$):

$$k_{vp}^2 = \frac{Y(\text{AT}^8 - \text{CH}_4)}{Y(\text{AT}^8 - \text{CH}_4)}$$

The ratio of the relative yield of AT$^8$ to the relative yield of AT$^8$-CH$_4$ is determined from the transitions due to the relaxed AT-(CH$_4$)$_2$ cluster levels in the DES. In the 6a$^1$ DES of AT-(CH$_4$)$_2$, for instance, the AT$^8$-(CH$_4$)$_2$ features correspond to AT-(CH$_4$)$_2$ 0$^0$-$^0$, 6a$^0$-1$^0$, and 1$^0$-$^0$ transitions. However, in cases in which no AT$^8$-(CH$_4$)$_2$ emissions are observed, only an estimate of the lower limit to $k_{vp}$ will be obtained by assuming a small value for $Y(\text{AT}-(\text{CH}_4)_2)$. Using the same argument as above for the three other mechanisms, we obtain different expressions for $k_{vp}^1$ and $k_{vp}^2$, which are shown in Figure 7.

As mentioned earlier, in cases in which relaxed AT-(CH$_4$)$_2$ emissions are not observed, one can only obtain estimates of the lower limits to $k_{vp}^1$ and $k_{vp}^2$ by assuming a small value for $Y(\text{AT}-(\text{CH}_4)_2)$. Also, in this case, $k_{ivr}$ cannot be directly determined from the DES. Hence, we can only obtain a lower limit to $k_{ivr}$ using $k_{fl}$ in those cases in which we observe fluorescence from the relaxed levels of the initially excited cluster. In the 6a$^1$ DES, for example, the only cluster emissions we observe originate from the cluster zero-point level. We thus assume in that case that VR is fast compared to fluorescence. We then use that assumption as a basis for substituting $k_{ivr}$ with $k_{fl}$. Also, in derivation of the equation for $k_{vp}^1$ in the case of mechanism c, we also replace $k_{ivr}$ by $k_{fl}$ using the same assumption.

Upon exciting the 6a$^1$, 1$^1$, and 6a$^0$ transitions of the AT-(CH$_4$)$_2$ cluster, we observe the same behavior that AT-Ar$_2$ exhibits in this energy region (We were unable to obtain the dispersed emission spectra of the AT-(CH$_4$)$_2$. 16b$^2$, and 16a$^0$. 142.
transitions. Exciting the AT-(CH$_3$)$_3$ 6a$^1 \nu_3$ transition leads primarily to the breaking of one of two AT-CH$_3$ bonds, while exciting the AT-(CH$_3$)$_2$ $1^\nu_6$ transition generates emissions exclusively from AT-CH$_4$.

However, in the case of AT-Ar$_2$, the calculated rates for 6a$^1$ and 1$^2$ excitation are very similar ($24 \times 10^5$ s$^{-1}$ and $> 25 \times 10^5$ s$^{-1}$, respectively). In contrast, regardless of the mechanisms assumed for AT-(CH$_3$)$_3$ dissociation, the VP rates always differ by two orders of magnitude ($10^8$ versus $10^{10}$ for 6a$^1$ and 1$^2$, respectively). While it may be tempting to attribute this two orders of magnitude change to extreme mode selectivity, it is unclear whether this difference indeed arises from extreme mode selectivity or simply from the fact that a greater amount of excess vibrational energy was injected into the 1$^2$ ($798$ cm$^{-1}$) mode compared to the energy that went into the 6a$^1$ mode ($606$ cm$^{-1}$).

Upon exciting the 6a$^2$ cluster feature with about $1212$ cm$^{-1}$ excess energy, we observe strong emission from the free AT fragment, although some emissions from the AT-CH$_3$ fragment are apparent. Depending on the mechanism assumed, one obtains from one to two orders of magnitude increase in the cluster fragmentation rates. Thus, starting with about $606$ cm$^{-1}$ excess energy and moving upwards to $1212$ cm$^{-1}$, the efficiency of breaking of each AT-CH$_3$ bond increases with increasing number of quanta of excitation deposited into the 6a$^2$ mode excitation (one in 6a$^1$ and two in 6a$^2$). These results mirror those that were obtained upon excitation of the 6a$^1$ and 6a$^2$ transitions of AT-Ar$_2$.

### AT-(CH$_3$)$_3$ Dynamics

In calculating VP rate constants in the case of AT-(CH$_3$)$_3$ excitation, the mechanisms and forms of equations used are the same as those for AT-(CH$_3$)$_2$. The mechanisms and equations for AT-(CH$_3$)$_3$ differ from AT-(CH$_3$)$_2$, only in that each of the cluster labels in the equations and mechanisms for the former has one extra CH$_4$ molecule.

In AT-Ar$_2$, the features in the DES of the 6a$^1$ level do not match any of the known AT vibrational frequencies. Excitation of the 6a$^2$ level of AT-Ar$_2$ yields a spectrum identical to that of 1$^2$ level DES of AT-Ar$_2$, whose features do not correspond to any known AT vibrational frequencies (Alfano et al. 1992).

In contrast, the spectra obtained upon excitation of the 6a$^1$ and 6a$^2$ levels of AT-(CH$_3$)$_3$ exhibit a different dynamical behavior from that of AT-Ar$_2$. The dissociation dynamics of AT-(CH$_3$)$_3$ subsequent to exciting the 6a$^1$ and 6a$^2$ levels is very similar to that of AT-(CH$_3$)$_2$. In both the AT-(CH$_3$)$_2$ and AT-(CH$_3$)$_3$ clusters, one AT-CH$_3$ bond breaks upon excitation of the 6a$^1$ level, and two AT-CH$_3$ bonds break subsequent to excitation of the 6a$^2$ level. Hence, when exciting the 6a vibrational mode, the type of product formed (whether AT or AT-CH$_3$) depends on the number of quanta of excitation energy initially deposited in the 6a mode.

Table 1 shows the calculated VP rate constants for the AT-CH$_3$, AT-(CH$_3$)$_2$, and AT-(CH$_3$)$_3$ clusters upon exciting various cluster vibrionic levels. Because of the

### Table 1. Calculated VP rates for the various vibrational levels of AT-CH$_3$, AT-(CH$_3$)$_2$, and AT-(CH$_3$)$_3$. The letters in teh rate constant column correspond to the mechanisms in Figure 6.

<table>
<thead>
<tr>
<th>Level</th>
<th>Complex</th>
<th>$\Delta v$(cm$^{-1}$)</th>
<th>$\tau_{v}$(ns)</th>
<th>VP</th>
<th>$k_{s}^{\nu}$</th>
<th>$k_{c}^{\nu}$</th>
</tr>
</thead>
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<tr>
<td>6a$^1$</td>
<td>AT-(CH$_3$)$_3$</td>
<td>606</td>
<td>90</td>
<td>20 155 / 10</td>
<td>2.2 $\times 10^{8}$</td>
<td></td>
</tr>
<tr>
<td>1$^2$</td>
<td>AT-(CH$_3$)$_3$</td>
<td>798</td>
<td>85</td>
<td>24 203 / 12</td>
<td>$&gt; 2.2 \times 10^{8}$</td>
<td></td>
</tr>
<tr>
<td>6a$^1$</td>
<td>AT-(CH$_3$)$_2$</td>
<td>606</td>
<td>90</td>
<td>18 288 / 125</td>
<td>3.1 $\times 10^{8}$ (a)</td>
<td>7.6 $\times 10^{6}$ (a)</td>
</tr>
<tr>
<td>6a$^1$</td>
<td>AT-(CH$_3$)$_2$</td>
<td>606</td>
<td>90</td>
<td>18 288 / 125</td>
<td>3.1 $\times 10^{8}$ (b)</td>
<td>2.1 $\times 10^{6}$ (b)</td>
</tr>
<tr>
<td>6a$^1$</td>
<td>AT-(CH$_3$)$_2$</td>
<td>606</td>
<td>90</td>
<td>28 888 / 125</td>
<td>$&gt; 7.7 \times 10^{8}$ (c)</td>
<td>7.6 $\times 10^{6}$ (c)</td>
</tr>
<tr>
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<td>AT-(CH$_3$)$_2$</td>
<td>606</td>
<td>90</td>
<td>18 288 / 125</td>
<td>$&gt; 3.1 \times 10^{9}$ (d)</td>
<td>$&gt; 2.1 \times 10^{6}$ (d)</td>
</tr>
<tr>
<td>1$^2$</td>
<td>AT-(CH$_3$)$_2$</td>
<td>798</td>
<td>85</td>
<td>14 544 / 0</td>
<td>$&gt; 4.2 \times 10^{9}$ (a)</td>
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<td>85</td>
<td>14 544 / 0</td>
<td>$&gt; 4.2 \times 10^{9}$ (b)</td>
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<tr>
<td>1$^2$</td>
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<td>798</td>
<td>85</td>
<td>14 544 / 0</td>
<td>$&gt; 4.2 \times 10^{9}$ (d)</td>
<td></td>
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<tr>
<td>6a$^2$</td>
<td>AT-(CH$_3$)$_2$</td>
<td>1212</td>
<td>62</td>
<td>2347 / 11 414</td>
<td>$&gt; 3.2 \times 10^{9}$ (a)</td>
<td>7.8 $\times 10^{7}$ (a)</td>
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<tr>
<td>6a$^2$</td>
<td>AT-(CH$_3$)$_2$</td>
<td>1212</td>
<td>62</td>
<td>2347 / 11 414</td>
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<td>62</td>
<td>2347 / 11 414</td>
<td>$&gt; 8.7 \times 10^{8}$ (c)</td>
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<td>62</td>
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<td>$&gt; 5.4 \times 10^{9}$ (d)</td>
<td>$&gt; 2.6 \times 10^{9}$ (d)</td>
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<td>6a$^3$</td>
<td>AT-(CH$_3$)$_2$</td>
<td>606</td>
<td>90</td>
<td>36 930 / 132</td>
<td>$&gt; 2.3 \times 10^{9}$ (a)</td>
<td>4.0 $\times 10^{6}$ (a)</td>
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<tr>
<td>6a$^3$</td>
<td>AT-(CH$_3$)$_2$</td>
<td>606</td>
<td>90</td>
<td>36 930 / 132</td>
<td>$&gt; 2.3 \times 10^{9}$ (b)</td>
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</tr>
<tr>
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<td>AT-(CH$_3$)$_2$</td>
<td>606</td>
<td>90</td>
<td>36 930 / 132</td>
<td>$&gt; 1.9 \times 10^{9}$ (c)</td>
<td>4.0 $\times 10^{6}$ (c)</td>
</tr>
<tr>
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<td>36 930 / 132</td>
<td>$&gt; 2.3 \times 10^{9}$ (d)</td>
<td>$&gt; 8.2 \times 10^{6}$ (d)</td>
</tr>
<tr>
<td>6a$^3$</td>
<td>AT-(CH$_3$)$_2$</td>
<td>1212</td>
<td>90</td>
<td>1770 / 18288</td>
<td>$&gt; 3.3 \times 10^{9}$ (a)</td>
<td>1.7 $\times 10^{6}$ (a)</td>
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<tr>
<td>6a$^3$</td>
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<td>1212</td>
<td>90</td>
<td>1770 / 18288</td>
<td>$&gt; 2.9 \times 10^{9}$ (b)</td>
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<td>$&gt; 3.0 \times 10^{8}$ (d)</td>
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</table>
approximations used, most of the rate constants given in the table correspond to lower limits.

**SUMMARY**

The results of study of the dissociation dynamics of methane clusters of AT underscore the role played by the density of states in cluster dynamics. In AT-Ar, the dominant processes are RF and VP. In the same cluster, the VP rates decrease by as much as two orders of magnitude in going from 446 cm\(^{-1}\) (16b\(^2\) excitation) to 505 cm\(^{-1}\) (16a\(^2\) excitation) excess vibrational energy, a variation in VP rates unheard of in other similar type of clusters that have been previously investigated. Thus, in the case of AT-Ar, the difference in bond-breaking rates appears to depend mainly on the nature of initially-excited vibrational mode. If it were due to the amount of excess vibrational energy injected into the cluster, a faster, instead of a slower, bond-breaking rate would be observed for the 16a\(^2\) excitation.

Replacing the argon atom with methane molecule drastically changes the AT cluster dissociation dynamics. VR now becomes important, and in fact dominates the dynamics at the 16b\(^2\) and 16a\(^2\) levels. Upon reaching the 6a\(^1\) level, however, VP takes over as the dominant dynamical process. From the 6a\(^1\) level of AT-CH\(_4\), the emissions not only arise from the zero-point level of the fragments, but free AT transitions due to 16a\(^2\), 16b\(^1\), and their combination bands now have intensities comparable to emissions from zero-point level of free AT fragment. Based on appearance of the free AT 6a\(^1\), transition in the AT-(CH\(_4\))\(_2\) DES, we deduce an upper limit to the AT-CH\(_4\) ground-state binding energy of < 270 cm\(^{-1}\).

Overall, our experimental results appear to be consistent with a sequential intermolecular VR/VP mechanism in which the initial step, which is also the rate determining step, is intermolecular VR.

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**REFERENCES**


