Relative Effects of Cluster Geometry and Density-of-States on s-Aminotetrazine Cluster Dissociation Dynamics

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The rates of bond breaking of the van der Waals bond in the aminotetrazine (AT)-methane, aminomethyltetrazine (AMT)-argon, and dimethyltetrazine (DMT)-argon clusters are measured and compared using fluorescence emission spectroscopy. The results suggest that the rate of breaking of the van der Waals bond depends largely on the cluster density of states and is more or less independent of the cluster geometry. Thus, the rates of bond breaking are quite similar for all three van der Waals clusters even though the AT-methane cluster has a different effective geometry compared to those of the AMT-argon and DMT-argon clusters. The relative rates of AMT-argon and DMT-argon clusters, which have similar geometries, are consistent with the differences in their cluster density of states.

Keywords: van der Waals bond, supersonic jet expansion, Franck-Condon factor, fluorescence quantum yield

INTRODUCTION

Physical chemists have long been 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. A class of van der Waals clusters that have been widely investigated are binary clusters composed of a parent aromatic molecule, which is bound via a van der Waals bond to a smaller complexing partner [1-10]. The parent aromatic molecule acts as the chromophore (the cluster component that directly interacts with the incident radiation) while the complexing partner is usually a noble gas or a small molecule such as methane, ammonia, and water. These binary van der Waals clusters are formed only in a supersonic jet expansion since their very weak binding energies prevent them from forming at room temperature. In a supersonic jet expansion, the clusters are stabilized because their rotational and vibrational energies can be as low as a few tenths Kelvin and a few tens Kelvin, respectively [11].

Generally, the rates of breaking of the van der Waals bond of these binary clusters have not been observed to exhibit any extreme sensitivity to the nature of the initially excited vibrational mode of the chromophore. Measured rates have

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typically varied by a factor of two at the most. But in 1992, Alfano et al. observed that the argon clusters of s-aminotetrazine (AT) exhibited extreme mode selectivity [2]. Instead of just varying by a factor of two, the van der Waals bond-breaking rates varied by as much as two orders of magnitude depending on which chromophore vibrational mode was excited (Fig. 1 shows the various vibrational ring modes of AT).

In a previous paper, the calculated dissociation (van der Waals bond breaking) rates upon excitation of the different AT vibrational modes of the AT methane clusters and the proposed mechanism consistent with these rates were presented [12]. In this paper, the dependence of the dissociation rates as a function of geometry of two types of binary clusters containing either:

with argon as complexing partner or (b) a methane molecule as a complexing partner of AT will be discussed. With AT as the chromophore in the type (b) cluster, the rates of breaking of the $AT\text{-}CH_4$ van der Waals bond are measured and compared with the previously reported dissociation rates of the binary clusters AMT-Ar and DMT-Ar [2]. Fig. 2 shows the geometries of the binary clusters typically observed in a supersonic jet expansion.

METHODOLOGY

The fluorescence excitation spectra of the methane cluster of AT ($AT\text{-}CH_4$) is obtained using argon-ion and dye lasers. The fluorescence emission spectra of $AT\text{-}CH_4$ is then obtained by individually exciting the different
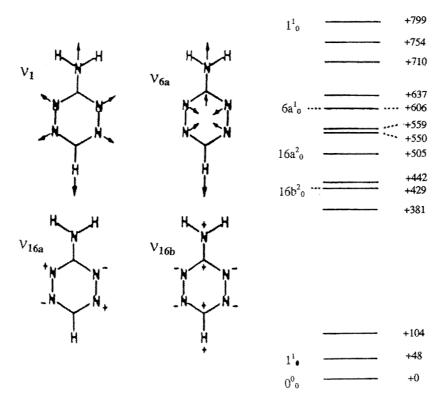

Fig. 1. *Some AT ring normal modes alongside an energy level diagram of the low energy vibrations seen in the AT excitation spectrum.*

(a) one or more methyl groups attached to the parent aromatic molecule (tetrazine, in this case)

peaks in the excitation spectra that correspond to $AT\text{-}CH_4$.
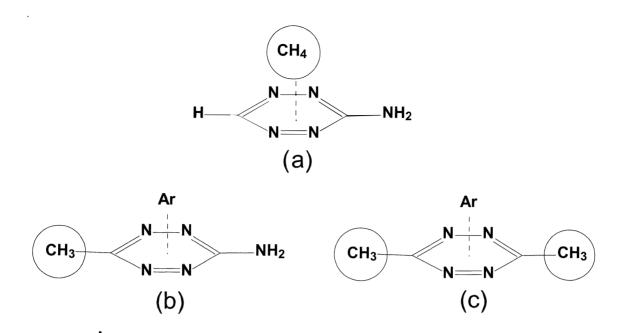
Fig. 2. *Geometries of the (a) AT-CH$_4$ cluster; (b) AMT-Ar cluster; and (c) DMT-Ar cluster.*

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 the laser power to allow for about 80% absorption. Between 4-6 g of 9-methylanthracene 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 the AT-CH$_4$ clusters entrained by He gas. For the fluorescence excitation experiments, the dye laser output was scanned and the resulting monomer AT or AT-CH$_4$ 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, the fluorescence resulting from excitation with a fixed laser frequency was 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 the simultaneously measured total fluorescence. AT was synthesized by N. P. Quevada.

RESULTS

Fig. 3 shows the fluorescence excitation spectrum in the vicinity of the $6a^1_0$ AT monomer vibration obtained upon mixing AT and 1.0% CH$_4$ using He as a carrier gas. (Here, the numerical superscript on a vibrational mode such as $6a^1_0$ corresponds to the excitation from the ground (S$_0$) state to the AT 6a mode in the excited (S$_1$) electronic state with vibrational level $\upsilon = 1$ (hence the superscript "1"), while the numerical subscript "0" corresponds to the zero point level ($\upsilon = 0$) of the ground electronic state. The excitation spectrum shows peaks attributed to AT-CH$_4$, AT-(CH$_4$)$_2$, AT-(CH$_4$)$_3$ clusters. These peaks do not appear when no methane is mixed with AT. The assignment of the peaks to

binary, ternary, and quaternary clusters was based on the rate of increase of the peak intensities with methane concentration.

Fig. 4 shows the dispersed emission spectra obtained by fixing the laser at a frequency corresponding to the excitation of the AT-CH$_4$ 16b^2, 16a^2 , 6a^1, and 6a^2 ring mode, respectively (here, excitation of the ring mode means excitation of the AT molecule in the AT-CH$_4$ cluster). The bars over the peaks' vibrational assignments in Fig. 4 indicate that the peaks are those of the undissociated AT-CH$_4$ cluster.

DISCUSSION

The intensity of each peak in the dispersed emission spectra is directly proportional to the product of the: (a) number density of the bare AT fragment or the undissociated AT-CH$_4$ cluster; (b) fluorescence quantum yield, which in this case is assumed to be the same for both the AT and the AT-CH$_4$ cluster; and (c) Franck-Condon factor for a given transition. Thus, from the known values of the fluorescence quantum yield and the Franck-Condon factor for a given transition, one obtains the number density of either the bare AT fragment or the undissociated AT-CH$_4$ cluster. The number density of the AT fragment divided by the total number density (taken as the sum of the AT fragment and the AT-CH$_4$ cluster number densities) is equal to the cluster dissociation yield for a given excited level. From the calculated yield and the known fluorescence quantum yield, one obtains the cluster dissociation rate for a given excited level.

In a previous paper, it was shown that the van der Waals bond-breaking process is consistent with a three-step serial mechanism: vibronic (vibrational-electronic) excitation, followed by vibrational relaxation, and then breaking of the cluster van der Waals bond [12]. Based on the calculated dissociation rates, which was discussed in detail in the paper, the vibrational relaxation step corresponds to the slow or rate determining step.

The energy difference between the initially populated vibrational level and the vibrational level populated upon vibrational relaxation represents the maximum amount of energy available for breaking the van der Waals bond. Since the rate of vibrational relaxation increases with increasing density of states (which refers to the number of vibrational/rotational levels for a given energy range), the overall bond-breaking rate would be expected to increase when the cluster density of states is increased (since this would increase the rate of the slow step, which is vibrational relaxation).

Fig. 4 shows that injecting 445 cm^{-1} excitation energy into the 16b20 level of the AT-CH4 cluster does not lead to cluster fragmentation. As Fig. 4 shows, however, injecting 606 cm^{-1} excitation energy into the 6a10 level (this value being obtained by subtracting the 6a10 vibrational energy relative to that of 000 vibrational energy, which is set at 0 cm^{-1}; see Fig. 2) of the cluster results in complete cluster dissociation to produce AT monomer fragment. In the AT-Ar studies by Alfano et al. [2], they showed that these results arise from mode selectivity (i.e., from the nature of the initially-excited vibrational level) rather than from the differences in the amount of excitation energy.
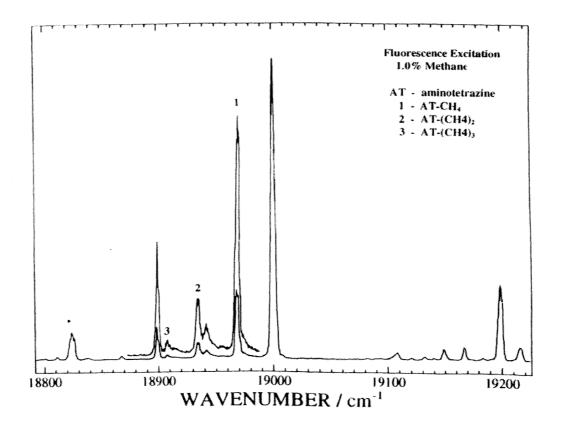
Fig. 3. *Fluorescence excitation spectrum of AT mixed with 1.0% methane showing magnified peaks due to AT-CH₄, AT-(CH₄)₂ and AT-(CH₄)₃.*

For the $6a^1$ vibrational level of AT-CH$_4$ and AT-(CH$_4$)$_2$, the calculated cluster dissociation rate constants are more than 2.3×10^{10} and between 3.1×10^8–3.7×10^8, respectively. These calculated dissociation rates differ by just an order of magnitude from the calculated rates at the $6a^1$ level of AMT-Ar and DMT-Ar, which are 1.6×10^9 and 3×10^9 s^{-1}, respectively [2]. The calculated dissociation rate constant for AT-Ar, on the other hand, is only 2×10^6 s^{-1} [2].

The increase in the dissociation rate of the binary AT cluster upon substitution of argon with methane mirrors the between three to four 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 [8]. Everything else being equal, this implies that the increase in the dissociation rate is due mainly to the increase in the cluster density of states.

The similarity of the vibrational dissociation (breaking of the cluster bond upon vibrational excitation of the cluster) rate of AT-CH$_4$ at the $6a^1$ level with those of AMT-Ar and DMT-Ar suggests that the effective cluster density of states is more important in determining the dissociation rates of the van der Waals bond than the overall cluster geometry. Those clusters with argon as complexing partner has a smaller nominal cluster density of states than those with methane as a complexing partner. Yet, those clusters with methyl group covalently bonded to the parent molecule (and with argon as complexing partner) have dissociation rates similar to those of clusters with methane as a complexing partner.

Assuming that the covalently bound methyl group's internal rotation couples effectively with van der Waals modes in the AMT-Ar and DMT-Ar clusters, this coupling could enhance the rate of intermolecular vibrational relaxation the same
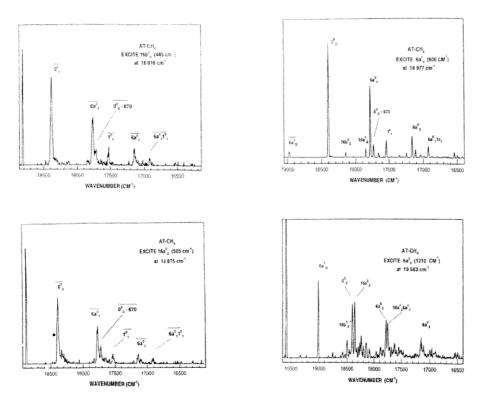
Fig. 4. *Dispersed emission spectra obtained upon exciting the AT-CH$_4$ cluster's: (a) 16b$^2_0$ transition at 18 816 cm^{-1}; (b) 16a$^2_0$ transition at 18 875 cm^{-1}; (c) 6a$^1_0$ transition at 18 97 cm^{-1}; and (d) 6a$^2_0$ transition at 19 583 cm^{-1}.*

way the methyl group's internal rotation enhances intramolecular vibrational relaxation in p-fluorotoluene, for example.

Coupling between the methyl internal rotation with the van der Waals modes is feasible if the frequencies are similar for these modes. Okuyama et al. and Zhao et al. have measured a value of 33 cm^{-1} for the methyl internal rotation frequency in p-fluorotoluene using dispersed emission spectroscopy in the jet [13,14]. On the other hand, the measured ground state cluster stretch mode for the AT-CH$_4$ is around 30 cm^{-1} while for benzene-CH$_4$ [15] and toluene-CH$_4$ [16], the excited state cluster stretch mode were measured to be 32 cm^{-1}. The corresponding value for AMT-Ar is 28 cm^{-1} [2]. Thus, coupling between the methyl internal rotation and the cluster stretch mode is quite feasible. This coupling would give rise to an increase in the effective density of states of the AMT-Ar and DMT-Ar so that instead of having a nominal density of states expected of a cluster with argon

as partner, they would instead have a density of states similar to that of a cluster with methane as a complexing partner.

The decrease in the cluster dissociation rate from the 6a^1 level of AT-(CH$_4$)$_2$ (3.3 x 10^8) relative to that of AT-CH$_4$ (2.3 x 10^{10}) must be due to the switch in the rate determining step (from vibrational relaxation to vibrational predissociation) in a serial mechanism proposed for AT-CH$_4$. The switch to vibrational predissociation as the rate determining step in a serial mechanism is driven by the substantial increase in the cluster density of states when the methane partner of AT is increased from one to two. Since the rate of vibrational relaxation increases with an increase in the vibrational density of states, the increase in the latter must be enough to cause the rate of vibrational relaxation to surpass the rate of vibrational predissociation. Thus, in the case of AT-(CH$_4$)$_2$, RRKM (Rice-Ramsperger-Kassel-Marcus) dynamics govern the bond-breaking process,

that is, the bond-breaking process is statistical, and this is what is actually observed. For example, above the vibrational level where a practically complete dissociation is observed, the observed dissociation products are those expected solely from the amount of the excess vibrational energy injected into the cluster.

Thus, the results above suggest that as long as the effective density of states are similar, differences in the cluster geometry matter little, if at all. In this case, it does not matter whether the CH_4 sits directly on top of the AT ring or whether it sits on the side of the AT ring (as a covalently bound $-CH_3$ group). This would explain why the cluster dissociation rates of AMT-Ar and DMT-Ar clusters are similar to those of AT-CH_4 cluster, rather than the being similar to AT-Ar. Unlike the AMT and DMT, the AT in the AT-Ar cluster does not have a methyl group that can increase the cluster density of states and thus speed up the cluster dissociation rates. In addition, argon, which is the complexing partner of AT in AT-argon cluster, does not have the rotational degrees of freedom that CH_4 has.

The offshoot then is that the density of states dominates any effect geometry differences exert when it comes to cluster dissociation rates, at least when the aromatic ring's partner is a molecule such as methane, rather than an atom such as argon. In fact, not only does the cluster density of states dominate any effect cluster geometry has on the cluster dynamics, it also dominates any effect exerted by the nature of the initially-excited vibrational level.

ACKNOWLEDGMENT

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