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Extreme mode selectivity in a dissociating van der Waals molecule: Complexes of aminotetrazine and argon

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Since the earliest use of lasers in chemistry, considerable effort has been devoted to mode selective photochemistry where either the rate or the product distribution of a reaction is changed in a nonstatistical way by changing the frequency of the light. These efforts have had very limited success, and when mode selectivity has been postulated, the effect has been small and often ambiguous.

Mode selective effects might be expected in the dissociation of weakly bound complexes where bonds can be broken with relatively little energy. Clear examples of mode selectivity have been observed in van der Waals photochemistry, but even here the effects have been limited. Tetrazine-argon,[1] benzene-argon,[2] and p-difluorobenzene-argon[3] all have levels of similar energy that produce different dissociation rates, but with one exception the differences are within a factor of five and the measured dissociation rates are around 10^8 s^{-1}. Extreme selectivity has been seen in the distribution of product vibrational states where many energetically allowed states are not seen at all. There appears to be no previous example of a state dependent change in the product yield in a van der Waals dissociation.

Here we report van der Waals dissociation rates that vary by over two orders of magnitude depending on which of several vibrational states of similar energy is excited. We also show an example of product distributions that change qualitatively depending on the initially excited state.

The complexes aminotetrazine-Ar and aminotetrazine-Ar$_2$ were studied using methods described previously.[1] The fluorescence lifetimes of several levels of aminotetrazine were measured using a pulsed laser system with instrument response of roughly 20 ns FWHM. The lifetime of the vibrationless level of aminotetrazine was 154 ± 3 ns and the lifetimes of excited vibrational levels decreased monotonically with increasing energy to 54 ± 4 ns at 1406 cm^{-1}. In the analysis that follows, we assume that the fluorescence lifetimes of a given vibrational level are the same for aminotetrazine and aminotetrazine-Ar. These lifetimes are more than two orders of magnitude larger than those of tetrazine.[1]

The fluorescence excitation spectrum of aminotetrazine-Ar has three bands of particular interest at 429, 505, and 606 cm^{-1} relative to the 0_0^0 band at 18 411 cm^{-1}. We tentatively assign them to $16b_0^2$, $16a_0^2$, and $6a_0^1$, respectively. The assignment of the in-plane $6a_0^1$ transition is quite certain while the assignments of the two out-of-plane modes are less certain.

The emission spectra produced when these bands are excited are shown in Fig. 1, and the dissociation rate is inferred from the relative intensities of the bands in the emission spectra. Excitation of $16b^2$ produces only emission from aminotetrazine and none from aminotetrazine-Ar, and the

dissociation rate of $16b^2$ is at least 4×10^8 s^{-1}. Excitation of $16a^2$ produces emission from both aminotetrazine and aminotetrazine-Ar with most of the emission coming from aminotetrazine. The dissociation rate of $16a^2$ is 6×10^7 s^{-1}. When $6a^1$ is excited, emission from both aminotetrazine and aminotetrazine-Ar is observed, but now most of the emission is from aminotetrazine-Ar. Therefore, the dissociation is slow compared to the 82 ns lifetime of $6a^1$. The dissociation rate from $6a^1$ is 2×10^6 s^{-1}, a rate much smaller than previously observed in molecules of this type. The dissociation rate varies by more than two orders of magnitude for three states separated by less than 200 cm^{-1}, with the dissociation rate decreasing with increasing excitation energy.

The dissociation of aminotetrazine-Ar$_2$ produces two products, aminotetrazine and aminotetrazine-Ar. The emission spectra produced by exciting aminotetrazine-Ar$_2$ are shown in Fig. 2. Excitation of $16b^2$ produces no emission from aminotetrazine-Ar$_2$; most of the emission comes from aminotetrazine, with a smaller amount from aminotetrazine-Ar. The production of aminotetrazine means that the average binding energy of argon is less than 215 cm^{-1} in the excited electronic state. This is less than the lower limit of 277 cm^{-1} estimated[1] for tetrazine-Ar.
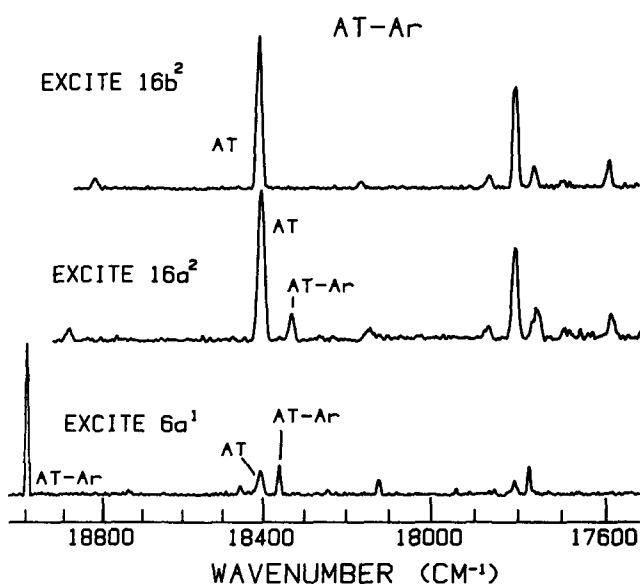

FIG. 1. Emission spectrum produced by exciting the $16b^2$ (top), $16a^2$ (middle), and $6a^1$ (bottom) levels of aminotetrazine-Ar. Emission bands assigned to aminotetrazine are labeled AT while those assigned to aminotetrazine-Ar are labeled AT-Ar. In the top two traces, the weak feature at the excitation wavenumber is entirely scattered light. In the bottom trace less than 15% of the intensity of the feature at the excitation wavenumber is due to scattered light.
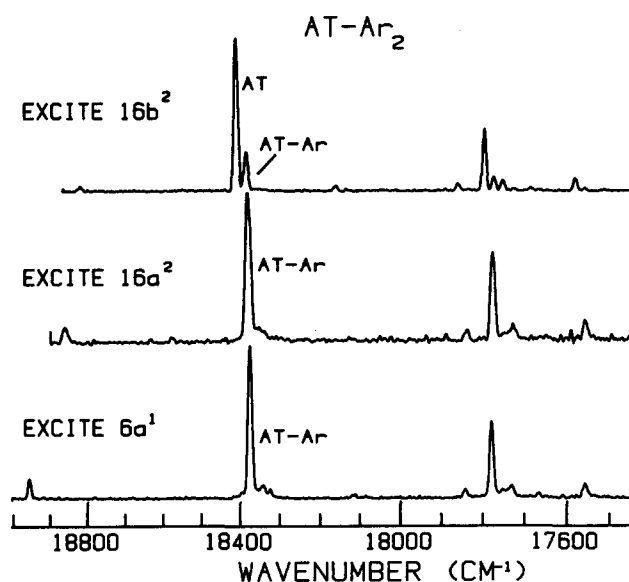
FIG. 2. Emission spectrum produced by exciting the $16b^2$ (top), $16a^2$ (middle), and $6a^1$ (bottom) levels of aminotetrazine-Ar_2. Emission bands assigned to aminotetrazine are labeled AT while those assigned to aminotetrazine-Ar are labeled AT-Ar. The band labeled AT-Ar is the 0_0^0 transition and other unlabeled bands of AT-Ar are also from the 0^0 level. In the top two traces, the weak feature at the excitation wavenumber is entirely scattered light. In the bottom trace some of the intensity at the excitation wavenumber is due to fluorescence from aminotetrazine-Ar_2.

Excitation of $16a^2$ also produces complete dissociation. Here all of the emission is from aminotetrazine-Ar with no emission from aminotetrazine. Excitation of $6a^1$ produces a little emission from aminotetrazine-Ar_2, a very little emis-

sion from aminotetrazine (not visible in Fig. 2), and a great deal of emission from aminotetrazine-Ar. Changing the originally excited state produces drastic changes in the product branching ratio with the more highly fragmented product being favored by excitation to the lowest energy state.

The mechanism responsible for the extreme mode selectivity in complexes of aminotetrazine and argon is not understood. An understanding of this mechanism is important since it certainly has relevance for mode selective van der Waals chemistry and may also have some bearing on mode selectivity in chemically bound molecules.

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NOTES

An accurate evaluation of the stationary points of the LiFH potential energy surface

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The Li + HF → LiF + H reaction is of great interest from both experimental and theoretical points of view. To investigate this reaction cross sections have been measured using crossed molecular beam techniques[1] and reactive probabilities evaluated by classical and quantum methods.[2,3]

This has stressed the importance of providing an accurate functional representation of the potential energy surface (PES) for this reaction. Available fits of the LiHF PES come

from the detailed ab initio study of Ref. 4: Li approaches HF going through a well of 4.5 kcal/mol located early on the minimum energy path; the transition state is 10 kcal/mol above the reactant asymptote and is located in the exit channel. Such a barrier to reaction was found to be too high to explain the large reactivity measured at low collision energy.

For a realistic description of the intramolecular motion, scaling factors are nowadays routinely introduced in the