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Hindered Internal Rotation and Ortho-H₂ Enrichment in Trans-Stilbene–H₂/D₂ Complexes

Abstract

A supersonic free jet expansion has been used to prepare trans-stilbene–H₂ and D₂ complexes. The cooling in the jet collapses most of the ortho and para H₂ and D₂ rotational population to the lowest rotational levels of a given nuclear spin symmetry: $j = 0$ and $j = 1$. The laser-induced fluorescence excitation spectrum of stilbene–D₂ shows a well-resolved doublet at the origin due to stilbene–D₂($j = 0$) and stilbene–D₂($j = 1$) complexes. The 4.9 cm⁻¹ splitting of these transitions indicates that the D₂ molecule is undergoing hindered internal rotation in the complex and that the barrier to internal rotation changes upon electronic excitation. The relative intensities of the stilbene–D₂($j = 0$) and stilbene–D₂($j = 1$) origins depend on the D₂ concentration in the jet. At low D₂ flows the transitions arising from stilbene–D₂($j = 1$) are favored while at high D₂ flows the ($j = 0$)/($j = 1$) transition intensities approach the 2:1 intensity ratio given by their nuclear spin statistical weights. By contrast, in stilbene–H₂ we observe only a single transition at the origin which we assign to stilbene–H₂($j = 1$). We are able to place an upper bound on the stilbene–H₂($j = 0$) transition intensity of 5% of the stilbene–H₂($j = 1$) intensity. Dispersed fluorescence spectra are used to bracket the binding energies of the stilbene–H₂/D₂ complexes in both ground and excited states.

Hindered internal rotation and *ortho*-H₂ enrichment in *trans*-stilbene-H₂/D₂ complexes

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A supersonic free jet expansion has been used to prepare *trans*-stilbene-H₂ and D₂ complexes. The cooling in the jet collapses most of the *ortho* and *para* H₂ and D₂ rotational population to the lowest rotational levels of a given nuclear spin symmetry: $j = 0$ and $j = 1$. The laser-induced fluorescence excitation spectrum of stilbene-D₂ shows a well-resolved doublet at the origin due to stilbene-D₂ ($j = 0$) and stilbene-D₂ ($j = 1$) complexes. The 4.9 cm⁻¹ splitting of these transitions indicates that the D₂ molecule is undergoing hindered internal rotation in the complex and that the barrier to internal rotation changes upon electronic excitation. The relative intensities of the stilbene-D₂ ($j = 0$) and stilbene-D₂ ($j = 1$) origins depend on the D₂ concentration in the jet. At low D₂ flows the transitions arising from stilbene-D₂ ($j = 1$) are favored while at high D₂ flows the ($j = 0$)/($j = 1$) transition intensities approach the 2:1 intensity ratio given by their nuclear spin statistical weights. By contrast, in stilbene-H₂ we observe only a single transition at the origin which we assign to stilbene-H₂ ($j = 1$). We are able to place an upper bound on the stilbene-H₂ ($j = 0$) transition intensity of 5% of the stilbene-H₂ ($j = 1$) intensity. Dispersed fluorescence spectra are used to bracket the binding energies of the stilbene-H₂/D₂ complexes in both ground and excited states. In the ground state of stilbene-H₂ ($j = 1$) and stilbene-D₂ ($j = 0, 1$) complexes, $169 \leq D'_0 \leq 249$ cm⁻¹, so that the stilbene-H₂ ($j = 0$) transitions cannot be missing by virtue of the complex being unbound. We propose a simple kinetic scheme which supports the possibility that selective exchange reactions, in which more strongly bound H₂ ($j = 1$) preferentially displaces H₂ ($j = 0$) from stilbene, contribute to the enrichment of stilbene-H₂ ($j = 1$) complexes in the jet. We also propose that H₂ ($j = 2$) molecules may contribute to the suppression of stilbene-H₂ ($j = 0$) complexes by virtue of the fact that the H₂ ($j = 2$) level is above the dissociation threshold for the stilbene-H₂ complex while the D₂ ($j = 2$) level is likely not.

I. INTRODUCTION

The very weak binding present in most van der Waals complexes offers the possibility of unusual, large-amplitude motions not afforded most chemically bound molecules. While most of the van der Waals complexes whose geometries have been characterized have possessed well-defined conformations,¹⁻⁴ there are several examples in which the complexes are inherently nonrigid with one of the complexed species undergoing internal rotation with respect to the other species.⁵⁻⁸ Such motions can be especially important in light molecules such as H₂ or D₂ which are capable of tunneling through energetic barriers between more than one energy minimum in the potential energy surface. Past studies of complexes containing H₂ present an interesting range of behaviors. There are several cases in which there is no evidence of internal rotation of the H₂ molecule, either because the barrier to H₂ internal rotation is large enough that tunneling cannot occur or because the barriers to internal rotation in ground and excited states are so similar that the tunneling splittings cannot be resolved in the spectrum. Examples include the tetrazine-H₂⁹ and glyoxal-H₂¹⁰ complexes. In other cases, such as I₂-H₂/D₂¹¹ and H₂-rare gas complexes,¹² distinct transitions due to *ortho*- and *para*-H₂/D₂ complexes are clearly resolved in the spectrum. These

splittings point to significant tunneling by the H₂ or D₂ molecules through a twofold barrier to its internal rotation within the complex. In these cases, the barrier to internal rotation varies enough with electronic¹¹ or vibrational¹² excitation to cause observable shifts of transitions due to $j = 0$ -correlated states (i.e., the lowest rotational level of *para*-H₂) from those due to $j = 1$ -correlated states (i.e., the lowest energy rotational level of *ortho*-H₂) where j is the rotational angular momentum quantum number of the free H₂ or D₂ molecule.

Some of the most intriguing results on H₂-containing complexes have come from recent studies of HF-H₂/D₂ by Lovejoy, Nelson, and Nesbitt (hereafter referred to as LNN).^{7,8} These authors have carried out high-resolution measurements on these complexes in the infrared in the spectral region near the HF fundamental. They have analyzed the vibration-rotation spectrum of HF-H₂ complexes in terms of a hindered internal rotation of H₂ in which the ground internal rotation state is correlated to the $j = 1$ rotational level of the free H₂ molecule. Yet, despite the fact that LNN should be able to detect absorptions some 60 times weaker than the HF-H₂ ($j = 1$) transitions, they have been unable to observe the corresponding HF-H₂ ($j = 0$) transitions. By comparison, in HF-D₂ these authors readily observe HF-D₂ transitions due to both $j = 0$ and $j = 1$ D₂. The anomalous absence of HF-H₂ ($j = 0$) complexes in the supersonic expansion is explained by LNN in terms of the preferential stabilization of HF-H₂ ($j = 1$) complexes by the an-

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isotropy in the HF-H₂ potential which causes them to be formed more efficiently in the expansion than HF-H₂ (*j* = 0) complexes.

We have recently been studying a wide variety of *trans*-stilbene-X van der Waals complexes.^{13,14} Our main focus in those studies was to try to understand vibronic state mixing and predissociation in large-molecule van der Waals complexes. We were particularly interested in the anomalous behavior we observed in stilbene-X van der Waals complexes when the low frequency out-of-plane phenyl ring vibrations of the stilbene chromophore were excited. In the process of such studies we discovered other unusual behavior which is in many ways analogous to that observed in the infrared by LNN. In this paper we will present evidence that while the *trans*-stilbene-H₂ *S*₁ ← *S*₀ vibronic transitions are singlets, the stilbene-D₂ origin is a doublet with a splitting of about 5 cm⁻¹. The body of evidence points to the doublets being distinct transitions due to stilbene-D₂ (*j* = 0) and D₂ (*j* = 1) complexes. However, as in the HF-H₂ complex, only the stilbene-H₂ (*j* = 1) transitions are observed. We determine the binding energy of the ground state stilbene-H₂/D₂ complexes to be sufficient to support bound states of the stilbene-H₂ (*j* = 0) complex and propose kinetic suppression of stilbene-H₂ (*j* = 0) as the cause of its absence in the spectrum.

II. EXPERIMENTAL

The experimental apparatus used in this work is identical to that used in earlier work by our group.¹³⁻¹⁵ As a result, only a brief description will be given here. The stilbene-H₂ and stilbene-D₂ complexes are formed from a 2% H₂ or D₂ in helium mixture which has been passed over a sample of *trans*-stilbene heated to 110 °C. The mixture is then expanded through a pulsed nozzle with 500 μ opening at a total backing pressure of about 10 atm (1 atm = 101.325 kPa). The adiabatic cooling produces the van der Waals complexes of interest. These are subsequently probed by the doubled output of an excimer-pumped dye laser (~10-100 μJ/pulse in the UV, 0.30 cm⁻¹ bandwidth) about 0.5 cm downstream from the nozzle orifice. Fluorescence from the expansion is collected at right angles to the laser and expansion axes. Fluorescence excitation spectra record total fluorescence as a function of laser wavelength. Dispersed fluorescence spectra detect fluorescence resolved by a 3/4 m monochromator (150 μ slits, 9 cm⁻¹ bandwidth) with the laser fixed at a peak wavelength. *Trans*-stilbene was purchased commercially (Kodak, >96% pure) and used without further purification.

III. RESULTS AND ANALYSIS

In Fig. 1(a) we present the fluorescence excitation spectrum in the region near the origin of the *S*₁ ← *S*₀ transition in *trans*-stilbene under free jet expansion conditions in which stilbene-H₂ complexes are present. The stilbene-H₂ origin is clearly visible in the spectrum (labeled as 0₀⁰-H₂) 28 cm⁻¹ red of the parent origin. The low energy region of the *trans*-stilbene excitation spectrum has been completely assigned by Spangler *et al.*¹⁵ Only three modes are involved in this assignment: 25 (*a*_g, ethylenic carbon-ethylenic carbon-phenyl

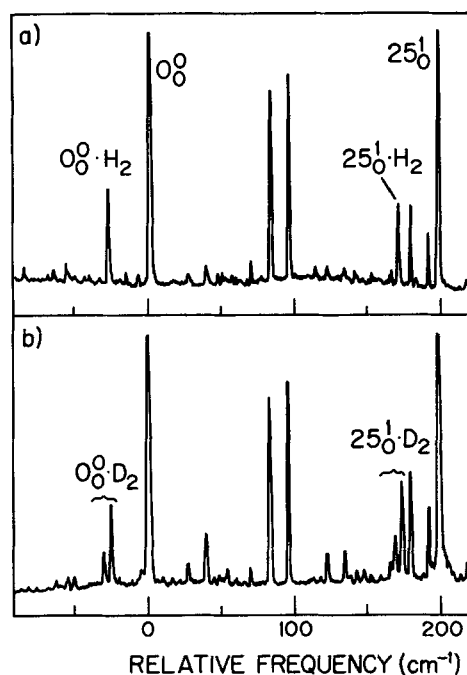


FIG. 1. Partially saturated laser-induced fluorescence excitation spectrum of *trans*-stilbene in the region near the *S*₁ ← *S*₀ origin under expansion conditions in which (a) stilbene-H₂ complexes and (b) stilbene-D₂ complexes are present. Transitions due to the free stilbene molecule are labeled X_n^m while the *trans*-stilbene-H₂ or D₂ complex transitions are labeled as X_n^m-H₂ or D₂.

nyl in-plane bend), 36 (*a*_u, ethylenic carbon-phenyl out-of-plane bend) and 37 (*a*_u, ethylenic carbon-phenyl out-of-plane twist). The 25₀¹-H₂ transition can also be readily observed, possessing an identical shift from the parent transition to that at the origin. The parent transitions 82 and 95 cm⁻¹ above the origin are 36₀¹37₀¹, and 37₀², respectively. As we showed in a recent publication, the stilbene-H₂ transitions associated with these out-of-plane phenyl modes are each split into a series of 5-6 closely spaced transitions due to strong, mode-selective coupling to the van der Waals motions of the complex.¹⁴ In the present paper we will be concentrating for the most part on the stilbene-H₂ and stilbene-D₂ transitions built on the origin. The stilbene-(H₂)₂ origin is located at very nearly twice the frequency shift (-56 cm⁻¹) of the stilbene-H₂ origin. This suggests that the two H₂ molecules occupy equivalent and largely noninteracting sites on stilbene, probably on either side of the stilbene plane.

The corresponding fluorescence excitation spectrum of stilbene-D₂ is shown in Fig. 1b. *To our great surprise, the stilbene-D₂ transition at the origin is split into a doublet.* Furthermore, all higher energy transitions also exhibit a similar doubling, as seen, for example, in the 25₀¹-D₂ transitions marked in the figure.

In Fig. 2 we present an expanded view of the origin region of the spectrum. The members of the stilbene-D₂ doublet are split by 4.9 cm⁻¹. The red member of the doublet is 30.0 cm⁻¹ shifted from the stilbene origin so that the two members of the stilbene-D₂ doublet surround the stilbene-H₂ singlet (located -28 cm⁻¹ from the parent origin). A comparison of the stilbene-(H₂)₂ and (D₂)₂ origin transi-

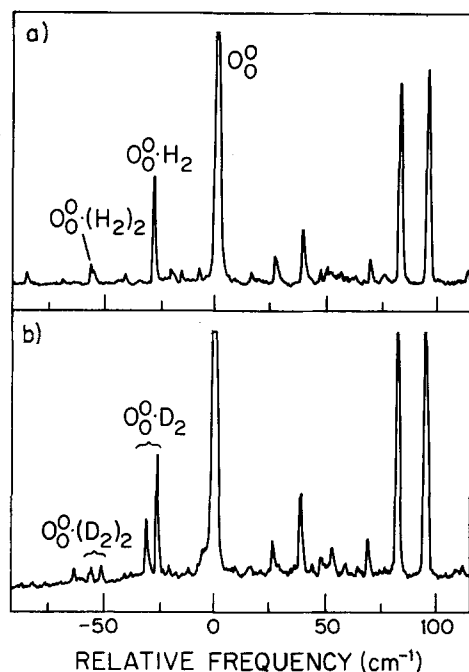


FIG. 2. An expanded region of the total fluorescence excitation spectrum near the origin. (a) Stilbene- H_2 . (b) Stilbene- D_2 . Note that the stilbene- D_2 origin is a doublet while stilbene- H_2 is a singlet. The single stilbene- $(H_2)_2$ origin and doubled stilbene- $(D_2)_2$ origin transitions are also labeled in the spectrum. These possess twice the shift from the parent origin as the stilbene- H_2 and D_2 complexes.

tions shows similar behavior: the $S-(D_2)_2$ transition is split into two transitions separated by 4.9 cm^{-1} while the $(H_2)_2$ analog is a singlet. *The obvious question is, "What is the source of this doubling and why is it present only in stilbene- $(D_2)_n$?"* This question is so intriguing because one would expect near-identical behavior in the isotopic substitution of D_2 for H_2 in a van der Waals complex.

Several causes of this doubling could be imagined. First, the doubling could be an artifact produced by impurities which are present in the D_2 expansion but not in the H_2 expansion. However, for it to be an impurity it would have to be a major impurity of concentration approximately equal to that of D_2 itself, yet our D_2 sample is $>99\%$ pure. Thus we are confident that both members of the doublet are due to a mixed complex of stilbene and D_2 . By virtue of their frequency shifts relative to the origin, both peaks are likely due to the 1:1 complex stilbene- D_2 . Second, one of the peaks could be a stilbene- D_2 van der Waals transition which has a large nonzero Franck-Condon factor (FCF) in stilbene- D_2 but for which the corresponding transition in stilbene- H_2 has a small FCF. Third, the stilbene- D_2 complex might form two distinct geometric conformers which the stilbene- H_2 complex does not form. Fourth, the two transitions in stilbene- D_2 could be due to distinct *ortho*- D_2 and *para*- D_2 complexes with stilbene while one of these forms of the stilbene- H_2 complex is suppressed in the expansion. At first glance, none of these possibilities seems very likely because it is hard to imagine how the isotopic substitution of D for H could have the dramatic effect we observe in the spectrum. However, two sets of experiments have led us to conclude that the last option is that which is actually occurring in the expansion.

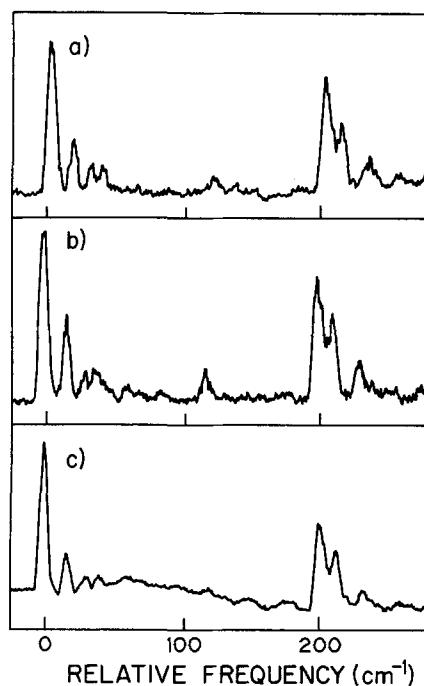


FIG. 3. Dispersed fluorescence spectra of (a) red member of the stilbene- D_2 doublet at the origin, (b) the blue member of the stilbene- D_2 doublet at the origin, and (c) the single peak in the stilbene- H_2 origin. Note the near-identical character of these three spectra.

A. The dispersed fluorescence spectra

In Fig. 3(c) we show the low energy region of the dispersed fluorescence spectrum of the single peak stilbene- H_2 origin. The major peak 200 cm^{-1} red of the resonance peak is the 25_1^0 transition. The smaller peaks 20 and 45 cm^{-1} red of the 0_0^0 transition are 37_2^0 and 37_4^0 while the peak at 38 cm^{-1} is an unassigned peak which is characteristic of the stilbene- H_2 complex.¹⁴ For comparison, the dispersed fluorescence spectra of the red [Fig. 3(a)] and blue [Fig. 3(b)] members of the stilbene- D_2 doublet are shown above it. *It is obvious from the figure that the dispersed fluorescence spectra of the stilbene- D_2 peaks are indistinguishable from that of the stilbene- H_2 origin.* On this basis, stilbene hot bands, impurities, and van der Waals vibrations are ruled out since these would be expected to have easily distinguishable dispersed fluorescence spectra. In particular, we have dispersed the fluorescence from transitions involving van der Waals vibrational excitation in stilbene-Ar, where van der Waals transitions are prevalent in the spectrum, and the spectra are completely different from the spectrum of the stilbene-Ar origin.

The possibility of distinct geometric conformers is harder to eliminate. There are several van der Waals complexes which have been found to be formed in two or more stable geometries in supersonic expansions.¹⁶⁻¹⁹ Such geometric conformers could, in principle, exhibit similar dispersed fluorescence spectra if the two conformations did not effect the dominant stilbene vibrational frequencies very much. Our previous work on stilbene- H_2 and other stilbene-X van der Waals complexes led us to the conclusion that in the stilbene- H_2 complex the H_2 molecule was located above the

plane of the stilbene molecule and experienced nearly free motion between the two phenyl rings.¹⁴ It is hard to imagine an alternative geometry which could successfully compete with this conformation, but, on the basis of the dispersed fluorescence spectrum alone, it is hard to eliminate this possibility. The third option, distinct absorptions due to *ortho*-D₂ and *para*-D₂, is also still viable since the origins of complexes from these two forms of D₂ would be expected to have near-identical dispersed fluorescence spectra.

B. The dependence of peak intensities on D₂ flow

Figure 4 presents a series of fluorescence excitation spectra taken with increasing D₂ concentration in the expansion. The top-most trace is taken with a 1% D₂, the middle trace with a 2% D₂, and the bottom trace a 5% D₂ in helium mixture as the expansion medium. All other conditions were held constant. The peak just to the red of the parent origin in Fig. 4(a) is due to stilbene-He and is absent at higher D₂ flows because helium is displaced by the more strongly bound D₂ at higher flows. In concentrating on the stilbene-D₂ doublet, note first that we can change the relative intensities of the members of the doublet over a wide range simply by varying the D₂ concentration. Thus, the sources for the two absorptions must be chemically distinct species with different rate constants and binding energies associated with their formation in the expansion. Second, as the D₂ flow is increased, the blue member of the doublet grows by comparison to the red member. At high flows the relative ratio of

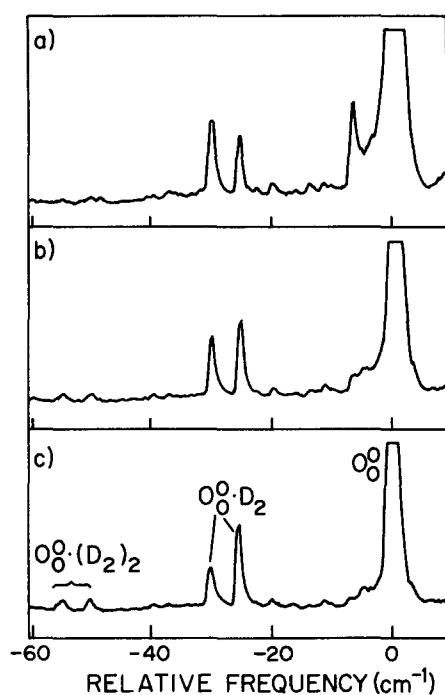


FIG. 4. Total fluorescence excitation spectra in the region near the stilbene origin taken with varying D₂ concentrations in the free jet expansion. (a) 1% D₂ in helium expansion mixture, (b) 2% D₂ in helium mixture, and (c) 5% D₂ in helium mixture. Note that at low D₂ concentrations the red member of the doublet is favored while at high D₂ concentrations the doublet asymptotically approaches a red:blue intensity ratio of 1:2, precisely the D₂ *para:ortho* population ratio in the expansion.

intensities of red to blue asymptotically approaches a 1:2 ratio. We have gone to D₂ concentrations several times higher than that shown in Fig. 4(c) without any significant change in the 1:2 ratio. Furthermore, as can be seen in Fig. 4(c), in that same limit of high D₂ concentration, the members of the stilbene-(D₂)₂ doublet go to a 1:1 intensity ratio. These intensity ratios are precisely those we would expect if the doublet were due to *ortho*- and *para*-D₂ complexes with stilbene in which the transition intensities are determined solely by the *ortho:para* nuclear spin statistical weights for D₂. Recall that, as a homonuclear diatomic, D₂ possesses two interleaved sets of rotational energy levels (*j* odd and *j* even) with different nuclear spin symmetries.²⁰ These two sets of levels are only very weakly coupled to one another since collisions are so ineffective in changing nuclear spin states. However, the collisional cooling in the early portion of the supersonic expansion will collapse the *j* even population (*ortho*-D₂) into *j* = 0 and the *j* odd population (*para*-H₂) into *j* = 1. The populations of the *j* = 0 and *j* = 1 D₂ states in the expansion will thus reflect the nuclear spin statistics, i.e., the *j* = 0/*j* = 1 population ratio will be 2:1. This is precisely the blue/red intensity ratio in the stilbene-D₂ doublet we have observed at high D₂ concentrations in the supersonic expansion. The correspondence must be more than coincidence and would lead us to assign the red member of the doublet with the larger shift from the parent to stilbene-D₂(*j* = 1) and the blue member to stilbene-D₂(*j* = 0). A similar intensity ratio was observed for the I₂-D₂ *ortho:para* doublets observed by Kenny *et al.*¹¹

The stilbene-(D₂)₂ peaks confirm this assignment. If the stilbene-(D₂)₂ complexes are being formed with D₂(*j* = 0) and D₂(*j* = 1) represented in the complexes at a weight determined by nuclear spin statistics, then the stilbene-(D₂)₂ origin should be an equally spaced triplet with intensities from blue to red of $I(j=0, j=0):I(j=0, j=1):I(j=1, j=1) = 4:4:1$. Experimentally [Fig. 4(c)] we see equal intensities for the two readily observable members of the triplet. The red-most (*j* = 1, *j* = 1) peak is difficult to pick out due to its weak intensity, although Fig. 2(b) shows some hint of a peak which appears as a shoulder on a stilbene hot band.

We thus conclude that the doubling we see in the stilbene-D₂ S₁ ← S₀ vibronic transitions is due to slightly different absorption frequencies for stilbene-D₂(*j* = 0) and stilbene-D₂(*j* = 1). The red member of the doublet we assign to stilbene-D₂(*j* = 1), the blue member to D₂(*j* = 0). The 4.9 cm⁻¹ splitting between the members of the doublet points to different barriers to internal rotation of the D₂ molecule in the ground and first excited singlet electronic states of the stilbene-D₂ complex. The fact that the S-D₂(*j* = 0) origin transition possesses a smaller shift from the parent origin than S-D₂(*j* = 1) is entirely consistent with our expectation, based on the work of LNN,^{7,8} that the D₂(*j* = 0) molecule will interact less strongly with stilbene than will D₂(*j* = 1). We will focus at greater length on these conclusions in the discussion section.

If our assignment of the doublet in stilbene-D₂ is correct, we are immediately faced with a further quandary. If the doublet is due to distinguishable transitions of stilbene-

$D_2(j=0)$ and stilbene- $D_2(j=1)$, then why do we not see a similar doubling in the stilbene- H_2 spectrum? Put another way, "Where is the other stilbene- H_2 peak at the origin?" By analogy with $HF-H_2$,⁷ it is very likely that the peak we observe is the more strongly bound ($j=1$) correlated state while stilbene- $H_2(j=0)$ is missing. We might expect that, in the high H_2 concentration limit, the stilbene- $H_2(j=0)$ and $H_2(j=1)$ integrated intensities at the origin should approach their spin statistical limit (as they did in stilbene- D_2) of $I(j=0)/I(j=1) = 1/3$.²⁰ Obviously, there is nothing in the spectrum in the region near the single $0_0^0-H_2$ peak which is close to one-third the intensity of the observed peak. We have taken an extensive series of scans over a wide range of expansion conditions and H_2 flows without seeing any evidence of a second transition. Furthermore, we have been able to eliminate even the small peaks we can observe in the region of interest as either stilbene hot bands, stilbene-He transitions, or stilbene- $(H_2)_2$ transitions. We conclude that the stilbene- $H_2(j=0)$ transition is less than 5% the intensity of the stilbene- $H_2(j=1)$ transition. This is at least six times smaller than it should be based on nuclear spin statistics.

The behavior we have observed is found in other related H_2 - and D_2 -containing complexes. In Fig. 5 we show a close-up view of the region near the origin of the $S_1 \leftarrow S_0$ transition of *p*-methyl-*trans*-stilbene. Our group has recently made a near-complete assignment of the low energy region of this molecule.²¹ The doublet at the origin is made up of the $0a_1$ and $1e$ transitions of the hindered methyl rotor. In the upper trace we show the total fluorescence excitation spectrum of *p*-methyl-*trans*-stilbene with a 2% H_2 in helium expansion mixture. The *p*-methyl- H_2 origin is clearly visible in the spectrum as a doublet shifted 21 cm^{-1} red of the parent transitions, which is comparable to the 28 cm^{-1} shift observed in stilbene- H_2 . In addition, as in stilbene- H_2 , there is no evidence for a second doublet which could be ascribed to *p*-methyl- $H_2(j=0)$. The lower trace shows the corresponding spectrum of *p*-methyl- D_2 . Here we clearly see two sets of doublets, due to *p*-methyl- $D_2(j=0)$ and ($j=1$), which are split by 5.8 cm^{-1} . The ($j=0$) and ($j=1$) doublets show the same behavior with respect to D_2 flow as we outlined earlier in stilbene- D_2 ; namely, that at high D_2 flows the *p*-methyl- $D_2(j=0)/(j=1)$ intensity ratio approaches the nuclear spin statistical weight limit of 2.0. Furthermore, the *p*-methyl- $(D_2)_2$ transitions which are labeled in the figure form an evenly spaced triplet of doublets due to ($j=0, j=0$), ($j=0, j=1$), and ($j=1, j=1$) combinations. These have an intensity distribution which favors ($j=1$)-containing complexes at low D_2 flow and tend toward the nuclear spin statistical weight limits at high D_2 flow (4:4:1). Thus *p*-methyl-*trans*-stilbene- H_2 and D_2 complexes show completely analogous behavior to stilbene- H_2 and D_2 .

The dispersed fluorescence spectra of Figs. 6 and 7 provide us with bounds on the excited state binding energy of the stilbene- H_2 and D_2 complexes. In Fig. 6 we show the dispersed fluorescence spectra of the 25_0^1 transitions in the (a) stilbene- H_2 and (b) stilbene- $D_2(j=0)$ complexes, 197 cm^{-1} above the origin. Both spectra contain a set of peaks near zero on the relative frequency scale due to resonance

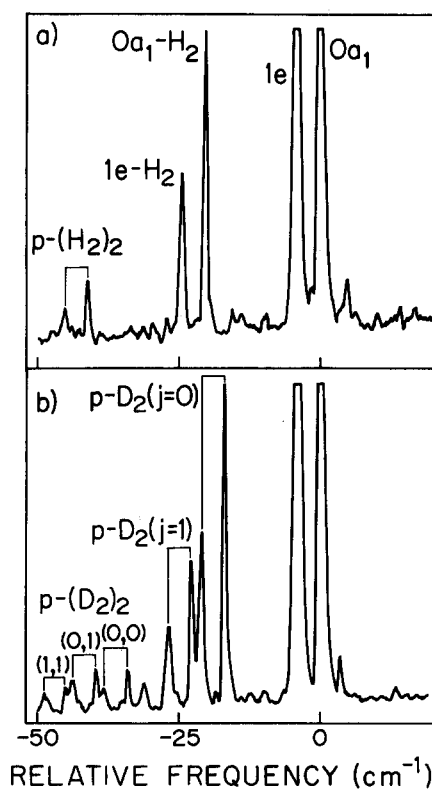


FIG. 5. Fluorescence excitation spectrum of *p*-methyl-*trans*-stilbene in the region near the origin taken with (a) 5% H_2 in helium and (b) 5% D_2 in helium as expansion mixture. The parent origin in *p*-methyl-*trans*-stilbene is a $0a_1/1e$ doublet caused by the internal rotation of the methyl group. The *p*-methyl-*trans*-stilbene- H_2 origin is also a doublet while the *p*-methyl-*trans*-stilbene- D_2 origin is composed of two doublets separated by 5.8 cm^{-1} .

emission from the level carrying the oscillator strength in absorption, the 25^1 level of the complex. The broad bands to the right in the spectra are centered around the major transitions from the 0^0 level of the complex, but are at least 50 cm^{-1} FWHM. These peaks can be ascribed^{14,22,23} to state mixing of the 25^1 level with background levels of the complex containing large amounts of van der Waals mode excitation. Each of these background levels possesses its own unique set of transitions to the ground state which, when summed with the other background emissions, results in the broadened emissions we observe. The emissions are centered around 0^0 transitions since the dominating contributor to the density of states at 197 cm^{-1} excess energy (i.e., at the energy of the 25^1 level) are of character 0^0-vdW^m . Since all the observed emission is from the intact complexes, the excited state binding energy of both the stilbene- H_2 and stilbene- D_2 complexes is almost certainly greater than 197 cm^{-1} .

Figure 7 presents the dispersed fluorescence spectra from two major transitions of stilbene- $D_2(j=0)$ and ($j=1$) in the closely spaced groupings of peaks near $25_0^1 36_0^1 37_0^1$, 277 cm^{-1} above the origin.^{13,14} Here we see emission entirely from the origin of the parent stilbene molecule following predissociation of the complex. The small peak far to the left in the spectrum is entirely due to scattered laser light. The corresponding spectra of stilbene- D_2 transi-

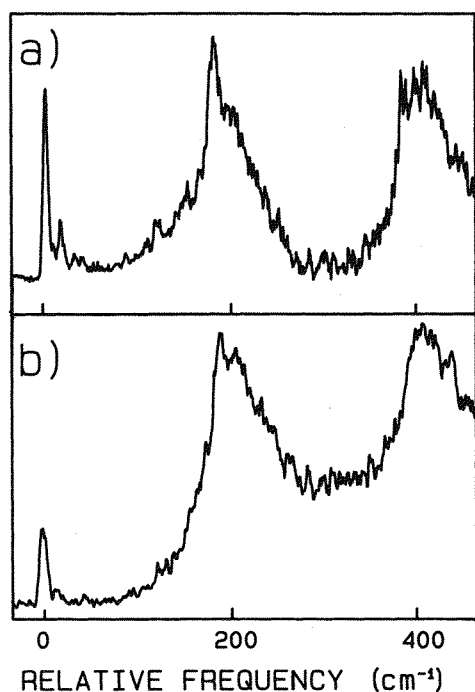


FIG. 6. Dispersed fluorescence spectrum of the $25_0^1 37_0^2$ transition in (a) *trans*-stilbene- H_2 and (b) *trans*-stilbene- $D_2(j=0)$. The peaks furthest to the left in each spectrum are resonance fluorescence while the broadened features can be ascribed to vibronic state mixing of the 25^1 level with background van der Waals levels.

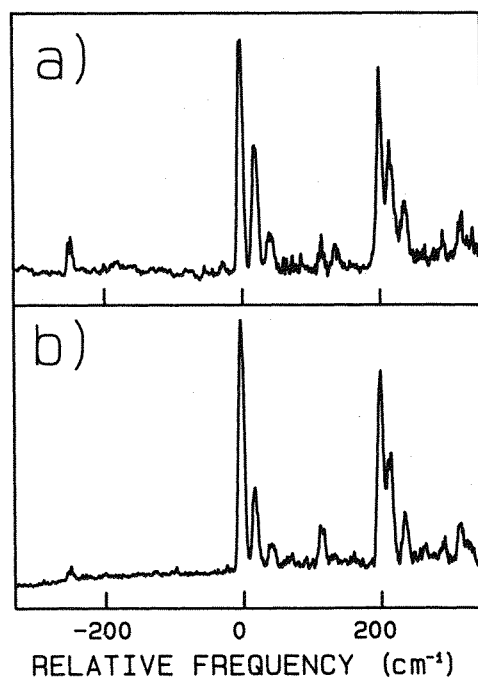


FIG. 7. Dispersed fluorescence spectra of two major transitions of (a) stilbene- $D_2(j=0)$ and (b) stilbene- $D_2(j=1)$ in the closely spaced grouping of peaks near $25_0^1 36_0^1 37_0^1$, about 277 cm^{-1} above the origin transitions. In both spectra, the observed emission is entirely from the origin of the stilbene parent following dissociation of the stilbene- D_2 complex.

tions built on $25_0^1 37_0^2$ look identical to those in Fig. 7. We conclude that both the stilbene- $D_2(j=0)$ and stilbene- $D_2(j=1)$ complexes have binding energies less than 277 cm^{-1} . As we showed in an earlier paper,¹⁴ the stilbene- H_2 complex also predissociates from these levels. Thus the dispersed fluorescence spectra allow us to bracket the excited state binding energy of $H_2(j=1)$, $D_2(j=1)$, and $D_2(j=0)$ to *trans*-stilbene between 197 and 277 cm^{-1} . Combining this result with the shift of the complex transitions from the parent transitions yields ground state binding energies bracketed by $169 < D_0'' < 249\text{ cm}^{-1}$. It is likely that the missing stilbene- $H_2(j=0)$ complex also possesses similar bounds on its binding energy.

IV. DISCUSSION

In the preceding section we have presented evidence that the doublets we observe in the fluorescence excitation spectrum of stilbene- D_2 are due to distinct transitions from stilbene- $D_2(j=0)$ and stilbene- $D_2(j=1)$. At the same time, in the stilbene- H_2 spectrum we only observe the stilbene- $H_2(j=1)$ transition and can place an upper bound on the stilbene- $H_2(j=0)$ transition intensity of 5% of the stilbene- $H_2(j=1)$ intensity. In reaching these conclusions, we have been emboldened by the recent elegant studies of LNN on the HF- H_2 and HF- D_2 complexes.^{7,8} Despite the wholesale differences in the nature of the chromophore (HF vs stilbene) and the type of excitation (vibrational vs electronic) in the two studies, our results are remarkably similar to theirs.

The recognition of H_2/D_2 internal rotation in the stilbene- H_2/D_2 complexes presents us with an unusual physical picture of the large amplitude motions present in the stilbene- H_2 or D_2 complexes. Our previous work on stilbene- H_2 pointed to the van der Waals bending motions being more nearly pseudotranslations of the H_2 molecule moving along the plane of the stilbene molecule than localized vibrations.¹⁴ More precisely, in order to account for the unusual vibronic structure of several transitions involving out-of-plane phenyl ring motion, we proposed that in the excited state of the complex the van der Waals bending modes involve nearly free motion of H_2 between the two phenyl rings. A similar motion is also likely in the stilbene- D_2 complex. Now our observation of well-resolved *ortho* and *para* transitions points to a second large amplitude motion of the complex: hindered internal rotation of the H_2 or D_2 molecule. By virtue of the small mixing of j levels (due to their large separations in D_2), the $D_2(j=0)$ wave function of the complex is nearly that of free $D_2(j=0)$; that is, nearly isotropic. We might approximate it pictorially as a billiard ball. By contrast, the $D_2(j=1)$ Π state wave function is at a maximum with the D_2 molecule lying down on the stilbene plane. The internal rotation of this state then approximates a molecular frisbee. The combined pictures of the large amplitude motions of the D_2 molecules in the stilbene- D_2 complexes is an amusing one. In the case of $D_2(j=0)$ we are viewing a billiard ball rolling back and forth along the molecular pool table presented by the π cloud of the planar stilbene molecule. On the other hand, the large-amplitude motion of $D_2(j=1)$ is more like that of a frisbee or hockey puck skit-

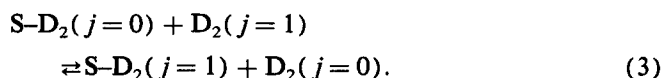
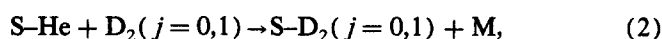
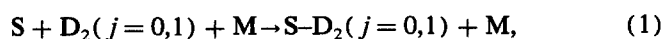
tering back and forth along the flat surface of the stilbene molecule. It is the orientational preference of the complexed D_2 molecule in the $D_2(j=1)$ -correlated state which results in a stronger interaction with the stilbene molecule than the isotropic ($j=0$) interaction.

Ideally we would be able to determine from our spectra the height of the barrier to internal rotation of the H_2 or D_2 molecule in both the ground and excited electronic states. We know that the stilbene- D_2 doublets are nominally $\Delta j = 0$ transitions from $j'' = 0$ and $j'' = 1$ (or more precisely, $\Sigma \rightarrow \Sigma$ and $\Pi \rightarrow \Pi$ transitions). By virtue of the observed splitting in stilbene- D_2 (4.9 cm^{-1}), the barrier to internal rotation is changing upon electronic excitation. However, we have not been able to observe any higher transitions to sets of levels correlated to $\Delta j = \pm 2, \pm 4, \dots$ free rotor transitions. This fact suggests that the (presumably) twofold barrier to internal rotation is not changing very much upon electronic excitation since the internal rotor wave functions in the two states are still nearly orthogonal. Our spectra simply do not have either a large enough set of internal rotation transitions or the rotational resolution within a single transition to be able to determine quantitative internal rotor barrier heights for these complexes.

We must still account for the fact that stilbene- $H_2(j=0)$ complexes appear to be missing from the supersonic jet. One intriguing option is that put forward as a possibility in HF- H_2 by LNN; namely, that the ground state stilbene- $H_2(j=0)$ complex is simply not bound because it is not stabilized by the hindered rotor potential to the same extent as the $H_2(j=1)$ state. However, we can clearly rule out this option in our case since the dispersed fluorescence spectra of stilbene- $H_2(j=1)$ and stilbene- $D_2(j=0,1)$ show that all three observed complexes possess excited state binding energies between 197 and 277 cm^{-1} . Combining this result with the 28 cm^{-1} shift of the complex's origin from that of the parent leads to bounds on the ground state binding energies between 169 and 249 cm^{-1} . There is no reason to believe that the stilbene- $H_2(j=0)$ complex will be any different. Thus even though the stilbene- $H_2(j=0)$ ground state binding energy is probably somewhat less than that of stilbene- $H_2(j=1)$, it is still easily large enough to support many bound states.

A second, more likely possibility is that the stilbene- $H_2(j=0)$ population is suppressed in the expansion for kinetic reasons. In order to assess this possibility, we will first try to understand the changes we have observed in the ratio of stilbene- $D_2(j=0)$ to stilbene- $D_2(j=1)$ intensities with changing D_2 concentration in the expansion. Recall that at high D_2 flows the observed intensity ratio reached a limiting value of $I(j=0)/I(j=1)$ of 2:1. This is precisely the ratio of the $D_2 j=0$ (*ortho*) to $j=1$ (*para*) nuclear spin statistical weights, which in turn, is also the expected ratio of $j=0$ to $j=1$ populations in the supersonic jet. At lower D_2 flows this ratio decreased so that under the lowest D_2 flow conditions the ($j=1$) intensity exceeded the ($j=0$) intensity, i.e., low D_2 concentrations favor ($j=1$) formation.

The kinetic processes governing stilbene- D_2 formation in the supersonic jet are shown below:



Reaction (1) involves three-body collisions in which M is usually helium. Reaction (2) is a two-body replacement reaction in which stilbene-He complexes are initially formed (by virtue of helium being present in the expansion at 100 times the density of the D_2) and subsequently replaced by D_2 . Reaction (3) is a $D_2(j=0) \leftrightarrow D_2(j=1)$ exchange reaction which becomes increasingly important as the D_2 concentration is increased in the jet. In the limit as $[D_2]$ gets very large, an equilibrium of sorts will be established between the exchange processes of reaction (3) at each localized region of the early portion of the expansion. The observed ratio of $S-D_2(j=0)$ to $S-D_2(j=1)$ populations will be given by

$$\begin{aligned} [S-D_2(j=0)]/[S-D_2(j=1)] &= (g_1/g_0)\exp(-\Delta E/kT_{\text{eff}}) \\ &= 2 \exp(-\Delta E/kT_{\text{eff}}), \end{aligned}$$

where ΔE is the difference in binding energies between the $j=0$ and $j=1$ $S-D_2$ complexes and T_{eff} is the local temperature in the jet. If we can use HF- D_2 as a guide,⁸ ΔE will be of order $10\text{--}20 \text{ cm}^{-1}$. The effect of the different binding energies of the complexes on the observed population ratio will depend both on the magnitude of ΔE and on the important temperature range over which $S-D_2$ formation and exchange processes can occur. Since the $S-D_2$ complex is bound by about 200 cm^{-1} , stable complexes can be formed at temperatures less than or of order 200 K (i.e., $kT \leq 140 \text{ cm}^{-1}$). Under our expansion conditions (10 atm backing pressure of 1% D_2 in helium), $T_{\text{eff}} = 200 \text{ K}$ occurs already at 1 nozzle diameter downstream ($x/D = 1$) from the nozzle orifice.²⁴ By 3 nozzle diameters the temperature is already at 30 K. Over this range, the single molecule collision frequency²⁴ drops by a factor of 30. We estimate that at $x/D = 1$, $S-D_2$ complexes will experience about ten collisions with D_2 molecules in the expansion per mm travel down the expansion axis. By $x/D = 3$ the complexes will be experiencing only one D_2 collision in 3 mm travel. Thus, at high D_2 flows, the $S-D_2$ formation may be dominated by processes occurring in the very early portion of the expansion where the great majority of two-body (and three-body) collisions take place but where the cooling is still relatively moderate. Under these conditions, $\Delta E \ll kT_{\text{eff}}$ and $[S-D_2(j=0)]/[S-D_2(j=1)] = 2$, as we observe.

On the other hand, as we lower the D_2 concentration in the jet, we will extend complex formation into the colder portions of the jet and simultaneously reduce the importance of exchange processes. Both these factors will serve to select for the complex with stronger binding energy, the $S-D_2(j=1)$ complex. This, too, is consistent with experiment.

In stilbene- H_2 , the differences in binding energy between $S-H_2(j=0)$ and $S-H_2(j=1)$ are magnified by the larger rotational constant of H_2 . A larger ΔE will yield a larger deviation of the population ratio from that given by nuclear spin statistics in a direction which weights the

stronger binding complex more heavily. The three-body formation rates will also be more sensitive to this binding energy difference in S-H₂ than in S-D₂. The combined result must be that, even if a "local" equilibrium is established in the jet, the more strongly bound S-H₂ ($j = 1$) complex is present at a level many times its nuclear spin statistical weight. In essence, the kinetics of complex formation has enriched the stilbene-H₂ complexes in *ortho*-H₂.

All in all, the dramatic suppression of S-H₂ ($j = 0$) in the expansion is still quite surprising. We have shown that the S-H₂ ($j = 1$), S-D₂ ($j = 0$), and S-D₂ ($j = 1$) complexes all possess ground state binding energies between 169 and 249 cm⁻¹. Thus, even though the H₂ ($j = 1$) molecules are expected to be more strongly bound than H₂ ($j = 0$) molecules, the latter's binding energy is still expected to be comparable in size. The extent of selection of the S-H₂ ($j = 1$) complex in the expansion is then somewhat surprising in light of the fact that our expansion often contains more than one cluster which possess quite different binding energies. In these cases the selection will be toward the species of greater binding energy, but not necessarily to the exclusion of other species. For instance, we observe both S-H₂ and S-He complexes in our 1% H₂ in helium expansions [see Fig. 4(a)], even though helium atoms bind to stilbene with less than 50 cm⁻¹ binding energy.

There is one further potential contributor to the suppression of S-H₂ ($j = 0$) formation in the expansion relative to S-H₂ ($j = 1$). Since the rotational constant for H₂ is so large ($B = 60.8$ cm⁻¹), the $j = 1$ level is already 120 cm⁻¹ above $j = 0$ while $j = 2$ is 360 cm⁻¹ up. As a result, even at room temperature, the H₂ population is restricted largely to $j \leq 3$. At the same time, nuclear spin symmetry restrictions will force deactivation to occur via $\Delta j = -2$ state changes which must remove at least 360 cm⁻¹ of energy per collision. We do not have a direct measure of the rotational temperature of H₂ in the jet under our expansion conditions ($\sim 1\%$ H₂ in helium). However, studies of pure H₂ expansions by Winkelmann²⁵ have shown H₂ rotational temperatures of 120 K even with cooling parameters²⁶ about five times that in our expansion. Thus it is quite possible that the H₂ rotational distribution in our expansion is near room temperature due to inefficient deactivation by helium. In Table I we have listed the rotational energies and the relative 300 K Boltzmann populations of the first several rotational levels of H₂ and D₂. The lines in the table separate those levels which are clearly above the dissociation energy for the complex from those which are either certainly or probably bound. Note that approximately 50% of the H₂ (j even) population is in $j = 2$ and thus cannot support a bound van der Waals complex with stilbene. By comparison, only 10% of the H₂ (j odd) population is in such levels. Hence if the H₂ rotational distribution is ineffectively cooled in the region of the expansion where complex formation occurs, the energy level structure and binding energy parameters of H₂ will select against stilbene-H₂ ($j = \text{even}$) formation, just as we observe experimentally. By comparison, in stilbene-D₂, the fraction of D₂ j even and j odd populations above the dissociation energy for the complex is much lower: about 20% for D₂ (j even) and at most 35% for D₂ (j odd), which, if anything should favor

TABLE I. Relative rotational level populations and energies of H₂ and D₂. The dashed lines in the table separate those levels which have energy greater than the ground state stilbene-H₂/D₂ binding energy from those which do not. In the case of stilbene-D₂, the $j = 2$ level is just above the lower bound for the dissociation energy.

<i>Para</i> -H ₂ ^a			<i>Ortho</i> -H ₂ ^a			<i>Ortho</i> -D ₂ ^a			<i>Para</i> -D ₂ ^a		
j^b	E_j^c	f_j^d	j	E_j	f_j	j	E_j	f_j	j	E_j	f_j
0	0	0.131				0	0	0.186			
2	365	0.115	1	122	0.661	2	182	0.386	1	61	0.208
4	1216	0.003	3	730	0.083	4	608	0.089	3	365	0.112
									5	912	0.013

^a Since the H nucleus is a fermion with $I = 1/2$ and the D nucleus is a boson with $I = 1$, *para*-H₂ has j even, *ortho*-H₂ has j odd while *para*-D₂ has j odd and *ortho*-D₂ has j even.

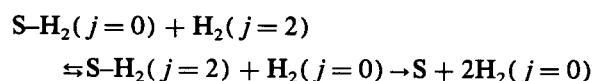
^b H₂ or D₂ rotational quantum number.

^c H₂ or D₂ rotational energy for the j th rotational energy level.

^d Fraction of H₂ or D₂ molecules in a given rotational energy level at 300 K.

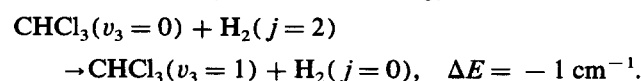
stilbene-D₂ ($j = 0$) complexes in the jet. Furthermore, D₂ is probably more efficiently cooled in the expansion than H₂ by virtue of its rotational constant being 1/2 that of H₂.

The H₂ ($j = 2$) molecules not only are unavailable for three-body formation of complexes, but they also present an additional loss mechanism for S-H₂ ($j = 0$) complexes via exchange processes. The interaction of the H₂ ($j = 2$) with stilbene will split the $j = 2$ state into several levels. Some of the $m_j = \pm 1, \pm 2$ levels will likely be stabilized by the interaction with stilbene more strongly than will H₂ ($j = 0$) molecules. As a result, the ($j = 2$) ↔ ($j = 0$) exchange process



would favor S-H₂ ($j = 2$) formation, which would subsequently rotationally predissociate. The net result would be the destruction of an S-H₂ ($j = 0$) complex by H₂ ($j = 2$). Of course, these mechanisms can only account for a factor of two suppression of S-H₂ ($j = 0$) unless the $j = 2$ molecules contribute disproportionately to S-H₂ ($j = 0$) formation due to a greater formation rate constant than that for H₂ ($j = 0$).

In an effort to determine the presence and importance of H₂ ($j = 2$) in the jet, we seeded into the jet some CHCl₃ along with the H₂. CHCl₃ possesses a ν_3 vibrational mode²⁷ which is a symmetric deformation of the CCl₃ unit with fundamental frequency 363 cm⁻¹. This is very nearly the $j = 2 \rightarrow j = 0$ energy difference in H₂ (364.8 cm⁻¹). It was hoped that CHCl₃ would provide a very efficient deactivation route for H₂ ($j = 2$) via the energy transfer:



We could readily identify the stilbene-CHCl₃ complex in the spectrum, shifted about 40 cm⁻¹ red of the stilbene-H₂ absorption. Unfortunately, no new absorption features appear in the presence of CHCl₃ in the region near the stilbene-

$H_2(j=1)$ absorption. Similar behavior is observed with CCl_4 present, which possesses vibrations with 218 and 314 cm^{-1} vibrational frequencies. Thus, if our hypothesis regarding the importance of $H_2(j=2)$ is correct, it is so despite our inability to increase the stilbene- $H_2(j=0)$ intensity by adding a gas which should efficiently deactivate $H_2(j=2)$ to $H_2(j=0)$. We hope to pursue this problem further in the near future by using pure *para*- H_2 [i.e., $H_2(j\text{ even})$] in the expansion as a means of removing the $(j=0) \leftrightarrow (j=1)$ exchange processes.

V. CONCLUSION

We have presented evidence that the stilbene- D_2 complex exists in the jet in two distinct forms whose ground states are correlated to stilbene- $D_2(j=0)$ and stilbene- $D_2(j=1)$. The $S_1 \leftarrow S_0$ vibronic transitions of stilbene- D_2 are thus split into doublets which are separated by 4.9 cm^{-1} and can be assigned to stilbene- $D_2(j=0)$ and stilbene- $D_2(j=1)$. The relative intensities of these transitions can be changed, but under high D_2 concentrations, the relative intensities approach their nuclear spin statistical weights in the jet. By contrast, in stilbene- H_2 there is only a single transition visible which we assign to stilbene- $H_2(j=1)$. We can bracket the stilbene- H_2 and stilbene- D_2 binding energies between 169 and 249 cm^{-1} , thus eliminating the possibility that the stilbene- $H_2(j=0)$ transitions are missing simply because the complex does not possess a bound ground state. We have proposed a kinetic scheme which can account for our data in terms of a selective exchange process involving replacement of $H_2(j=0)$ by $H_2(j=1)$ in stilbene- H_2 complexes. However, a detailed explanation of why H_2 is so much more selective in such exchange processes is still lacking. In any event, we have demonstrated that the anomalous behavior observed by LNN in the infrared spectrum of HF- H_2 and HF- D_2 complexes^{7,8} is much more general than might have been expected since we have observed similar behavior in the electronic spectrum involving a 26-atom chromophore in *trans*-stilbene- H_2/D_2 complexes. We hope to pursue similar investigations in other X- H_2/D_2 complexes in order to further characterize this unusual behavior.

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