structure, the bottom of the conduction band contains three metal–metal bonding levels. For d^3 systems like ZrCl, these bands are completely occupied, whereas for d^2 counts, obviously they are not. Instead of geometrically distorting, interstitial hydrides enter the gaps between adjacent metal atom layers and interact in specific ways with the metal orbitals depending upon the sites they occupy. The effects of other main group atom interstitials are not significantly different.

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Appendix

All of the calculations described in this paper used the Extended Hückel method[37] both for the molecular orbital calculations of the fragment and for the tight-binding computations on the crystalline solids. The atomic parameters are listed in Table II.

The following geometrical parameters were used: (1) all M–M distances were set at 3.82 Å where appropriate; (2) all M–Cl distances were set to 2.81 Å; (3) the interstitial atoms occupied the geometrical centers of each interstice based upon these distances. All lattice sums included third nearest-neighbor cells and were restricted to two dimensions in ZrCl-type phases and three-dimensions for NaCl-type, NiAs-type, and CaHCl phases. To produce the DOS and COOP curves, a special points set for the appropriate irreducible wedge of the Brillouin zone was selected.[38] A total of 64 points were used.

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Communications to the Editor

Direct Observation of a Mode-Selective (Non-RRKM) van der Waals Reaction by Picosecond Photofragment Spectroscopy[†]

David H. Semmes,[‡] J. Spencer Baskin, and
Ahmed H. Zewail*

Contribution No. 7555, Arthur Amos Noyes
Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125

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The idea of directing reactions by selectively exciting particular vibrational modes with lasers (laser-selective chemistry) has stimulated much experimental and theoretical research aimed at exploring its feasibility and the deviation from statistical RRKM behavior in large molecules. In the absence of collisions, the yield and rate of a reaction will be determined by the specific rate of intramolecular vibrational-energy redistribution (IVR) from the initial mode excited to the other modes in the molecule and by the rate of bond breaking (vibrational predissociation). If k_{IVR} is larger than k_{VP}, then the chemistry is from a statistically formed distribution of vibrational states and a statistical behavior (RRKM) may prevail, even if a laser is used to selectively excite the initial state of the reagent. It is this interplay between IVR and VP that determines the mode selectivity of the reaction. Excitation of the molecule with short enough pulses, short compared to k_{IVR}^{-1} and k_{VP}^{-1}, should allow us to view these processes in real time and hopefully establish conditions for nonstatistical behavior.

We report here the direct observation of mode-selective picosecond laser-induced photofragmentation for the reaction

$$\text{stilbene–He} \rightarrow \text{stilbene} + \text{He}$$

Real-time measurements of the reaction rates of the van der Waals molecule stilbene–helium are given as a function of *reagent* and *product* internal energies. We have observed a mode dependent, rather than energy dependent, unimolecular decay rate and a mode dependence in the rate of product formation up to an excess vibrational energy of four times the bond energy.

In picosecond photofragment spectroscopy[1] experiments, a picosecond pulse initiates the reaction in a molecular beam and, in general, a second picosecond pulse, delayed in time, monitors the nascent fragment. Here, the pulse excites the stilbene-type modes of the van der Waals (vdW) molecule (reagent), and the spectrally dispersed fluorescence of the reagent and product is time resolved on the picosecond time scale, as we reported earlier.[2] In this way, we can monitor the reaction dynamics from reagent state to product state.

The excitation spectra of *trans*-stilbene[3] and stilbene–He[4] have been published. Furthermore, the IVR dynamics of stilbene has been characterized,[3a] and recent work on the excitation spectra of the complex shows selective line broadening among the low-energy states.[4b] The stoichiometry of the complexes (1:1 or 1:2) has been determined by using sub-Doppler measurements of the rotational constants of the emitting species,[2,5] which allows us to positively distinguish between stilbene and stilbene–He spectra. We have studied the reaction when the reagent is excited to 83, 95, 198, and 396 cm^{-1} in the excited state (S_1) of the complex. These energies correspond to the vibrational modes $36^1 37^1$, 37^2, 25^1, and 25^2, respectively, where the superscript indicates the number of quanta in the torsion (37) or in the bend (25) mode. The binding energy of He to stilbene in the excited state is determined to be less than 50 cm^{-1}.

To obtain the state distribution of the product, dispersed fluorescence spectra were measured at each excitation energy studied. For 37^2 reagent excitation, most of the fluorescence intensity is from vibrationless product stilbene (0^0); the rest is from the S_1 + 47 cm^{-1} state of stilbene (37^1). The fluorescence spectrum

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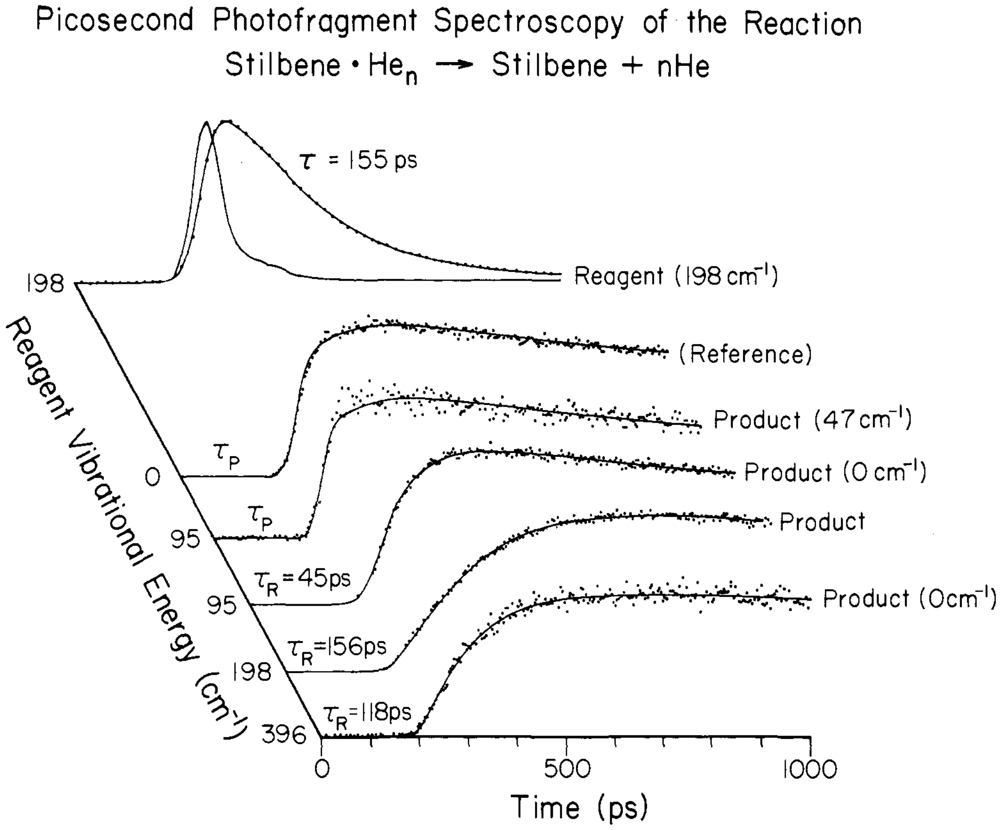

Figure 1. Picosecond time-resolved fluorescence of reagent and product states, formed in the reaction stilbene–He$_n$ → stilbene + nHe [$n = 2$ for the decay from 25^2 (396 cm^{-1}) and $n = 1$ for all other data]. τ_p identifies the temporal resolution (pulse width 15 ps; response ~ 50 ps). The decay at 0 cm^{-1}, where no reaction occurs, is a reference curve with which the reader may compare curves that have rises slower than the response. At 83 cm^{-1} (not shown) only vibrationless stilbene is formed in the reaction, with a 34-ps rise time. Note the distinction between reagent and product excess vibrational energies.

of the reagent molecule excited to 25^1 is stilbene emission but cannot be assigned as a mixture of known stilbene bands. The observed bands are probably dark in transitions from the ground state and are reached by redistribution. When the stilbene–He$_2$ complex is excited to 25^2, emission is observed from the 0^0 and 25^1 states of stilbene.

The picosecond time-resolved fluorescence measurements are shown in Figure 1. The rise times of stilbene emission clearly show that *product stilbene is formed in the reaction more rapidly at lower excitation energies of the reagent.* Furthermore, when exciting the reagent to 37^2 we have measured different rates for the formation of stilbene in the different product states, *with the higher internal energy product formed substantially faster.* On the other hand, when the reagent is excited to 25^1 the fluorescence from each line studied in the emission spectrum has the same formation rate,[6] which is equal to the measured decay rate of the complex (Figure 1). The results show the mode selectivity of the reaction, contrary to statistical RRKM behavior. Earlier work[7] on time-integrated product state distributions in the photodissociation of tetrazine–Ar has shown that even though IVR is selective, no mode-selective effects could be attributed to the initial level of excitation. In the case of tetrazine–Ar, there is a fast photochemical reaction in tetrazine itself and this feature was cleverly used as an internal clock to estimate the VP rate relative to the photochemical rate. There is no photochemistry in stilbene at the energies studied here[3a,b] and the mode selectivity observed is purely a vibrational problem.

The general model for describing the dissociation in our case invokes a dynamic IVR. The initial chemical bond state excited in the reagent is not the reaction coordinate and energy flow in the molecule is important for dissociation to take place. Accordingly, the deposited energy in the reagent vibration (stilbene-type) redistributes to a bath of states involving both stilbene and van der Waals vibrations (including the reaction coordinate). These states then predissociate with rates which depend on how their internal energy is distributed. Modeling this with a kinetic scheme provides the following picture. The dynamics of the reagent excited to 37^2 can be explained as occurring via two channels: rapid (<10 ps) IVR followed by a slower (45 ps) predissociation to the 0^0 state and a direct fast VP to 37^1 of product stilbene. The latter is consistant with theoretical calculations based on propensity rules[8] and basically reflects the near match between reagent and product state quantum numbers. When 25^1 is excited, the IVR is slower (150 ps) and is the rate-determining step in the entire dissociation process. The dynamics of the 1:2 complex excited to 25^2 appear to be similar to that of the 1:1 complex at 37^2, IVR preceding slower VP. The kinetic model used here accounts for the measured rise and decay times, their relative amplitudes in each decay, and the relative product-state distributions.

The question now is what determines the mode-selectivity? As mentioned earlier, the initial reagent state may decay by IVR to a number of intermediate states (because of their high density) which undergo VP. The IVR rate is determined by coupling strengths and by vibrational state densities. The state density increases monotonicaly with energy,[8] so the coupling strength must be mode dependent. The observed rapid IVR at the relatively low energies is due to strong coupling with the van der Waals modes. The 95-cm^{-1} state has been assigned to 37^2, an out-of-plane torsion of the phenyl rings.[3c,d] The helium atom in the complex lies above one of the phenyl rings[2,5] and it is perhaps not surprising that this mode (based on character and also energetics) couples more efficiently than mode 25, an in-plane bend.

The above measured rates of reaction can now be compared with measurements of spectral line widths, a point of relevance

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to many previous studies of dissociation. Our time-resolved results predict a homogeneous line broadening of the transitions to 83 and 95 cm^{-1} that is much larger than the one to 198 cm^{-1}, consistent with the observed broadening in the excitation spectra.[4b] It is important, however, to note that while these large line widths predict fast decay of the initially excited state, the rate with which the predissociated stilbene is produced is much lower (τ = 34–45 ps) and is limited by the VP rate from the intermediate state to which energy has been redistributed. Thus, the line width (if homogeneous) reflects the initial decay process (e.g., IVR) which may not be the rate-determining step of the reaction. This is consistent with the proposal of ref 4b for the description of the line broadening of the stilbene–helium excitation spectra. Line-width measurements have been used previously for deducing predissociation rates[9a] and their dependence on the mode excited[9b] in the ground electronic state of relatively smaller molecules. The separation of IVR from VP made here for large molecules could also be important in describing the dissociation dynamics of these systems, as discussed recently.[10]

Real-time studies of IVR,[11] VP,[12,2] and reaction rates[1,13] will certainly improve our understanding of dynamics and hopefully find general conditions for nonstatistical reactions such as those reported here.

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Hexakis(1,3-dithiol-2-ylidene)cyclohexane with Two Different Conformations of the Six-Membered Ring

Toyonari Sugimoto, Yohji Misaki, Tohru Kajita, and
Zen-ichi Yoshida*

Department of Synthetic Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan

Yasushi Kai and Nobutami Kasai*

Department of Applied Chemistry, Osaka University
Yamadaoka, Osaka 565, Japan

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Since Reppe discovered the synthesis of cyclooctatetraene by the tetramerization of acetylene using nickel catalyst,[1] active investigation has been continuing toward cyclooligomerization of many olefins, acetylenes, and cumulenes catalyzed by nickel and the other transition-metal complexes.[2] However, it was quite unknown whether cyclooligomerization of cumulenes bearing sulfur substituents occurs by a transition-metal complex catalyst. Recently we succeeded in the synthesis of tetrakis(1,3-dithiol-2-ylidene)cyclobutane, a promising electron donor for organic metals, by Ni(0)-catalyzed reductive cyclodimerization of 2,2′-(1,2-dibromoethanediylidene)bis(1,3-dithiole).[3] By using DMF as a medium of the reaction in place of THF, cyclotrimerization was found to proceed preferentially to provide a new type of [6]radialene, hexakis(1,3-dithiol-2-ylidene)cyclohexane (**1**). Very interestingly, the central six-membered ring of **1** was found to be in a twisted-boat conformation, which was converted to a thermodynamically more stable chair one by heating in solution or by electrochemical two-electron oxidation at room temperature. In this paper we wish to report the synthesis, structural feature, and characteristic properties of dodecacarbomethoxy- and hexabenzo-substituted derivatives of **1**, **1a** and **1b**, respectively.

Under argon atmosphere the reaction of 2,2′-(1,2-dibromoethanediylidene)bis(4,5-dicarbomethoxy-1,3-dithiole) (**2a**)[4] with 5 equiv of Zn–Cu[5] in the presence of 0.3 equiv of $Ni(PPh_3)_4$ in dry DMF (room temperature, 0.5 h) gave **1a** (orange crystals, mp > 300 °C)[6] in 35% yield together with the corresponding [4]radialene (yield 5%). In a similar manner **1b** was obtained as yellow crystals (mp > 300 °C) from 2,2′-(1,2-dibromoethanediylidene)bis(1,3-benzodithiole) (**2b**)[4] in 72% yield[7] (Scheme I). Of the two [6]radialenes, **1b** was successfully obtained as single crystals by recrystallization from CS_2/chlorobenzene/ether,[8] and the molecular structure was determined by the X-ray crystallographic analysis (see Figure 1).[9] The remarkable structural feature of **1b** is the twisted-boat conformation of the central

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(4) The dibromo derivatives were synthesized in almost quantitative yields by the reaction of the corresponding 2,2′-(ethanediylidene)bis(1,3-dithiole)s with 2 equiv of NBS in CH_2Cl_2 at room temperature.

(5) $Ni(PPh_3)_4$ was generated in situ by the reaction of $Ni(PPh_3)_2Br_2$ with 20 equiv of Zn–Cu couple in the presence of 2 equiv of PPh_3 and immediately used for the reductive cyclotrimerization of **2**. By use of the other Ni(0) complexes, e.g., $Ni(1,5\text{-cyclooctadiene})_2$ and $Ni(PPh_3)_2(CO)_2$, in place of $Ni(PPh_3)_4$, **1** was also obtained and showed the same ^{13}C NMR and electronic spectra. Attempts to isolate 2,2′-(ethenediylidene)bis(1,3-dithiole)s (cumulenes substituted with 1,3-dithioles) under several conditions were unsuccessful.

(6) Decarbomethoxylation of **1a** was carried out by heating with $LiBr{\cdot}H_2O$ in HMPA at 95–155 °C. However, the targeted parent system was not obtained.

(7) The corresponding [4]radialene was also obtained in 5% yield. All the [4]- and [6]radialenes showed satisfactory elemental analyses and mass spectra.

(8) When **1a** was recrystallized from CS_2/benzene/hexane, apparently single crystals were formed in the solution. However, isolation of the crystals from the solution was unsuccessful, because the crystals became powdered as a result of ready evaporation of the solvents.

(9) Crystal data of **1b**: $C_{48}H_{24}S_{12}$, FW = 985.5, monoclinic, space group $P2/n$, a = 20.978 (5) Å, b = 12.318 (2) Å, c = 21.887 (4) Å, β = 117.58 (1)°, U = 5013 (2) $Å^3$, D_x = 1.305 g cm^{-3}, Z = 4. X-ray diffraction data were measured on a Rigaku four-circle diffractometer using nickel-filtered Cu $K\alpha$ radiation. A total of 8066 reflections were collected up to $2\theta = 120°$ by the θ–2θ scan technique. The crystal structure was solved by the direct method (MULTAN-78) (Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN-78: A System Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, England, and Louvain, Belgium, 1978) and refined by the full-matrix least-squares (XRAY-76) (Stewart, J. M. "XRAY-76"; Report TR-446, University of Maryland, 1976) by using the 6182 observed reflections $[|F_o| > 3\sigma(F_o)]$ to the R index of 0.134 including non-hydrogen atoms with anisotropic temperature factors and hydrogen atoms with isotropic ones. The limited accuracy of the refinement resulted from the difficulty of the assignment for some diffused electron densities which may be from the disordered packing of the crystal solvent, CS_2, chlorobenzene, or ether. The second crystal obtained from the mixed solution of CS_2, chlorobenzene, and hexane is isomorphous with the present crystal (a = 20.985 (5) Å, b = 12.341 (2) Å, c = 21.896 (4) Å, β = 117.47 (1)°). The full set of data on the second crystal were collected by the use of graphite monochromatized Mo $K\alpha$ radiation up to $2\theta = 50°$. The structure analysis gave the same difficulty as the present one. The detailed molecular structure of **1b** should await the X-ray analysis on the other form of the crystal.

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