5510 *J. Phys. Chem. A* **2002,** *106,* 5510−5516

Quantitative Representation of Specific Rate Constants *k*(*E*) for the Photoisomerization of Diphenylpolyenes: The Solution of a Longstanding Problem

J. Schroeder, T. Steinel, and J. Troe*

Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany

Received: November 30, 2001; In Final Form: March 19, 2002

Specific rate constants *k*(*E*) of the photoisomerization of four isotopomers of *trans*-stilbene, of 4-chloro- (4CS) and 4-methyl-*trans*-stilbene (4MS), of *all-trans*-1,4-diphenyl-1,3-butadiene (DPB), and of 4-(dimethylamino)-4′-cyanostilbene (DCS) are represented by conventional RRKM theory, using new ab initio calculations of excited state frequencies. Data from supersonic beam experiments are reproduced quantitatively when the barrier heights are fitted to the experiments and activated complex frequencies are taken unchanged from the parent molecules. The main difference to earlier work lies in the smaller frequencies now calculated for the reaction coordinates. The results of this work clearly support an adiabatic mechanism of the reaction which can very well be quantified by statistical unimolecular rate theory.

1. Introduction

The photoisomerization reactions of *trans*-stilbene and of related diphenylpolyenes are model systems on which general concepts of photochemistry have repeatedly been applied and tested. The reactions were found to involve energy barriers such that fluorescence is unperturbed by isomerization at energies below these barriers, whereas fluorescence at higher energies is increasingly quenched by fast barrier crossing, leading via nonfluorescing conformations to isomerization.

Among the many facets of these systems, three central questions have attracted particular attention: (i) what is the origin of the energy barrier in the excited state and which electronic states are involved? (ii) can the barrier crossing in isolated molecules be quantitatively understood? (iii) are measurements on energy-resolved isolated molecules compatible with results for thermally averaged molecules in liquid environments? Early quantum yield measurements[1−5] as well as increasingly realistic quantum-chemical treatments[6−11] have concentrated on the mechanistic aspects of question i. With the advent of first measurements of the specific rate constants *k*(*E*) for barrier crossing,[12] it became clear[13,14] that thermal averaging of *k*(*E*) does not lead to the measured photoisomerization rates of *trans*-stilbene in the liquid phase, whereas the situation is different for diphenylbutadiene.[15−17] Question iii, as a consequence has led to controversial discussions,[13,18−24] which, in particular for the case of *trans*-stilbene, wait for a satisfactory answer.

The investigation of question ii, to which the present article is devoted, took an interesting course. Measurements of *k*(*E*) for isolated jet-cooled molecules qualitatively showed all features of a unimolecular isomerization in the excited electronic state. The specific rate constants increased with energy *E* in the way of a typical unimolecular reaction. Nevertheless, statistical unimolecular rate theory in the form of RRK[25] and RRKM[13] calculations failed on a quantitative level. Such calculations employed the first complete frequency set from Warshel,[26] which was based on a SCF−ELCAO−CI treatment: they fitted the barrier height by the experimentally observed onset of photoisomerization, selected the torsion around the ethylenic bond as the reaction coordinate, and assumed that the other frequencies do not change on the short way from the parent molecule to the activated complex. Measured *k*(*E*)'s were markedly lower than calculated values. A number of possible explanations have been offered and discussed in detail: it was suspected that the barrier crossing might be reversible,[13] that intramolecular vibrational energy redistribution (IVR) would not be complete before barrier crossing,[20,27] that the reaction could be electronically nonadiabatic,[18,28] that the activated complex might be tighter than the parent molecule,[14] etc. The latter assumption from[14] led to optimized RRKM fits which very well reproduced the measurements of the *k*(*E*) and allowed for consistent calculations of thermally averaged rate constants. However, the other possibilities could have produced similarly satisfactory fits of the measurements such that no unique interpretation was possible.

The ambiguity of the situation has led us to a new attempt to solve the dilemma. Improved possibilities to calculate vibrational frequencies for excited electronic states by ab initio methods[29] allowed us to do such calculations for a series of diphenylpolyenes. The surprising accuracy of the calculated frequencies for those vibrations, where a comparison could be made, provides confidence that the calculations are essentially correct. The major changes from the present work in comparison to earlier calculations are in the low frequency torsional modes corresponding to the reaction coordinate. By fitting the barrier height as before and identifying activated complex frequencies with the calculated parent molecule frequencies (except for the reaction coordinate), now conventional RRKM calculations systematically led to very good agreement with the measurements. This is found to be true for deuterated molecules as well as for more complicated substitutions.

We conclude that the simplest explanation of the long standing discrepancy, i.e., inaccurate molecular frequencies in earlier work, is the correct one and speculations about reversible barrier crossing, incomplete IVR, or nonadiabatic reaction mechanisms should be abandoned.

2. Computational Details

2.1. Molecular Frequencies. For each examined molecule, a ground state geometry optimization was carried out using a

10.1021/jp014387j CCC: $22.00

sequence of semiempirical (AM1) and density functional theory methods (B3LYP). Polarized split valence basis sets with diffuse functions were used, namely 6-311G+(d). The optimized ground state geometries served as the starting geometry for the excited state optimization, which was performed using a configuration interaction method with singly excited configurations (CIS) and an as large basis set as practically possible. The basis sets were increased from 6-31g to 6-31g(d), 6-31g(d,p), 6-31+g(d,p), 6-311g, 6-311g(d), 6-311g(d,p) and 6-311+g(d). In the case of the substituted stilbenes, diffuse functions were not used in the excited state due to unstable convergence behavior of the optimization routine. All calculations were carried out using the GAUSSIAN98 suite of programs.[30] The second derivatives of the resulting force fields yield the vibrational frequencies of the harmonic normal modes of the equilibrium geometry. Transition state frequencies were not calculated for two reasons. First, localization of the transition state is not a straightforward task, since multiple configurations contribute to the electronic structure of the transition state[10] such that CIS methods will not be adequate. More elaborate methods, such as CASSCF or MRCI, are still too demanding to apply them to large molecules such as diphenylpolyenes. Second, the assumption that the vibrational frequencies do not change from the equilibrium geometry to the transition state seems to be a very good one for all examined molecules rendering the calculation of transition state frequencies unnecessary.

Four isotopomers (D0, D2, D10,and D12) of *trans*-stilbene were investigated, D0 denoting the undeuterated species, D2 the molecule with the ethylenic hydrogens replaced by deuterium, D10 the molecule with the phenyl hydrogens replaced by deuterium, and D12 the completely deuterated isotopomer. In addition, *all-trans*-1,4-diphenyl-1,3-butadiene (DPB), 4-(dimethylamino)-4-cyano-stilbene (DCS), 4-chloro-*trans*-stilbene (4CS), and 4-methyl-*trans*-stilbene (4MS) were studied.

Raw frequencies computed on the CIS level contain known systematic errors, because Hartree−Fock based methods neglect the electron correlation. An empirical scaling factor of 0.9, introduced by Pople et al. is used to compensate for this error.[31,32] Our notation of the normal modes follows that used by Mulliken[33] and Herzberg.[34]

To judge the quality of our ab initio calculations of excited-state frequencies, our results are compared with experimental results from a variety of investigations.[35−38] As spectroscopic data for *trans*-stilbene are particularly complete, we concentrate our comparison on this molecule. The assignment of the fluorescence excitation bands of *trans*-stilbene has been a difficult task which still has not been solved unambiguously, but three normal modes have been identified as the main contributors to the features of the fluorescence excitation spectrum. Excellent results were obtained for these modes, see below. A fluorescence excitation study especially at high energies of the deuterated isotopomers D2, D10, and D12 from[39] provided further data for a comparison, see below.

The calculated frequencies were found to be in very good agreement with the experimental data, the mean errors being only 1.0 ± 0.8%. This good agreement supports the scaling factor for Hartree−Fock based frequencies introduced by Pople et al.[32]

A basis set analysis for *trans*-stilbene with respect to the normal-mode frequencies shows that the reaction coordinate is the most sensitive frequency. Demanding a deviation of less than 1 cm^{-1} while increasing the basis, we find that 6-31+g(d) achieves this limit for the model chemistry and basis sets we employed. In the case of DPB the reaction coordinate frequency reaches a constant value already with the 6-31g(d) basis set. Table 1 demonstrates this basis set dependence.

TABLE 1: Basis Set Dependence of the Frequency of the Reaction Coordinates $V(\nu_{\mathrm{TC}}[\mathrm{cm}^{-1}])$ for *trans*-stilbene (tSt) and *all-trans*-1,4-Diphenyl-1,3-butadiene (DPB), See Text

	6-31g	6-31g(d)	6-31+g(d)	6-311+g(d)
tSt	20.4	25.0	24.0	24.2
	6-31g	6-31g(d,p)	6-31+g(d,p)	6-311g(d,p)
DPB	31.3	31.7		31.9

2.2. Specific Rate Constants. The specific rate constants $k(E)$ for barrier crossing are calculated by the standard expression from statistical unimolecular rate theory:

$$k(E) = \frac{W^{\ddagger}(E - E_0)}{h\rho(E)} \tag{1}$$

where E_0 is the barrier height, E is the vibrational energy, $W^{\ddagger}(E - E_0)$ is the number of activated complex states below the energy E, and $\rho(E)$ is the vibrational density of states of the reacting molecule at the energy E. $W^{\ddagger}(E - E_0)$ as well as $\rho(E)$ are calculated using the Beyer−Swinehart counting algorithm.[40] To compare gas and liquid-phase data, we also calculated k_∞ such as given by

$$k_\infty = \int_{E_0}^{\infty} k(E) f(E)\, \mathrm{d}E \tag{2}$$

where $f(E)$ is the thermal distribution function.

The expression for $k(E)$, in the standard rigid activated complex RRKM version of eq 1, is evaluated assuming that the frequencies of the transition state are equal to the frequencies of the parent molecule in its equilibrium geometry and that one mode can clearly be identified as the reaction coordinate. A scaling of transition state frequencies such as proposed in refs 14 and 15 was not required anymore. The mode corresponding to the reaction coordinate was determined by visualization of the normal modes with the program GAUSSVIEW.[41] Only out-of-plane modes can be considered as potential reaction coordinates, since breaking the planar symmetry is essential for the isomerization. An obvious choice is that mode which comprises the ethylenic double bond torsion and which is accompanied by the phenyl ring motion necessary for isomerization. This is in accordance with the MNDO−CI investigations of the isomerization barrier in ref 10. This is an important point since there are also modes involving ethylenic double bond torsion without out-of-plane motion of the phenyl rings. These modes lead to a twisting of the molecule but not to *trans*-*cis*-isomerization. As sufficiently precise ab initio calculations of the barrier height are still out of our reach today, the threshold energy E_0 remains as the only parameter to fit the experimental results.

3. Results

3.1. Specific Rate Constants. Our calculated frequencies for *trans*-stilbene as the prototype molecule are listed in Table 2 whereas the low-frequency modes are illustrated in Figure 1. When we compare previously used sets of S_1-frequencies of *trans*-stilbene with our present results, see Table 2, we find that the semiempirical frequencies from ref 26 and ref 28 on average are 7.1% and 6.3%, respectively, higher than our frequencies, while the empirical frequencies from ref 23 are substantially lower (mean deviation of 28.7%). The largest deviations are found in the group of low frequency modes, especially in the

TABLE 2: Calculated S_1-Frequencies of *trans*-Stilbene[a]

this work		ref 26		ref 28		ref 23		this work		ref 26		ref 28		ref 23	
mode	ν [cm^{-1}]	$\Gamma_{v'}$	ν [cm^{-1}]	$\Gamma_{v'}$	ν [cm^{-1}]	$\Gamma_{v'}$	ν [cm^{-1}]	mode	ν [cm^{-1}]	$\Gamma_{v'}$	ν [cm^{-1}]	$\Gamma_{v'}$	ν [cm^{-1}]	$\Gamma_{v'}$	ν [cm^{-1}]
ν_{37}	24.2	a_u	41	a_u	41	a_u	40.4	ν_{66}	983	b_u	1046	b_u	1034	b_g	543
ν_{36}	47.4	a_u	55	a_u	54	a_u	49.8	ν_{65}	1059	b_u	1086	a_g	1082	a_g	570
ν_{72}	81.8	b_u	88	b_u	97	b_u	63.8	ν_{18}	1061	a_g	1090	b_u	1086	b_u	607
ν_{48}	119	b_g	131	b_g	132	b_g	71.2	ν_{64}	1113	b_u	1155	a_g	1151	a_g	614
ν_{25}	199	a_g	230	a_g	229	a_g	130	ν_{17}	1115	a_g	1157	b_u	1152	b_u	648
ν_{35}	212	a_u	238	a_u	239	a_u	168	ν_{16}	1142	a_g	1174	b_u	1166	b_u	660
ν_{24}	275	a_g	289	b_g	284	b_g	182	ν_{63}	1148	b_u	1177	a_g	1171	a_g	667
ν_{47}	277	b_g	309	a_g	305	a_g	201	ν_{15}	1167	a_g	1264	a_g	1217	a_g	701
ν_{34}	397	a_u	396	a_u	403	a_u	213	ν_{62}	1188	b_u	1306	b_u	1270	b_u	711
ν_{46}	409	b_g	401	b_g	407	b_g	215	ν_{14}	1224	a_g	1321	a_g	1294	a_g	820
ν_{45}	439	b_g	445	b_g	454	b_g	217	ν_{61}	1267	b_u	1377	b_u	1334	a_g	830
ν_{71}	457	b_u	469	a_u	475	a_u	227	ν_{13}	1272	a_g	1392	a_g	1335	b_u	1020
ν_{33}	474	a_u	548	b_u	542	b_u	250	ν_{60}	1288	b_u	1396	b_u	1349	b_u	1064
ν_{70}	514	b_u	593	b_u	583	b_u	255	ν_{12}	1331	a_g	1460	a_g	1396	b_u	1146
ν_{23}	591	a_g	603	b_g	619	b_g	257	ν_{59}	1343	b_u	1484	b_u	1397	a_g	1160
ν_{69}	597	b_u	611	a_u	629	a_u	266	ν_{11}	1416	a_g	1500	a_g	1452	a_g	1194
ν_{22}	613	a_g	654	a_g	646	a_g	270	ν_{58}	1431	b_u	1523	a_g	1483	b_u	1423
ν_{44}	634	b_g	668	b_u	662	b_u	276	ν_{10}	1456	a_g	1535	b_u	1488	a_g	1456
ν_{34}	640	a_u	700	a_g	698	a_g	285	ν_{57}	1460	b_u	1543	b_u	1494	b_u	1490
ν_{43}	713	b_g	715	b_g	716	b_g	303	ν_{56}	1513	b_u	1566	a_g	1519	b_u	1492
ν_{31}	737	a_u	721	a_u	735	a_u	306	ν_{9}	1519	a_g	1581	b_u	1521	a_g	1624
ν_{30}	775	a_u	797	a_u	757	b_g	313	ν_{8}	1545	a_g	1606	a_g	1545	a_g	1625
ν_{68}	779	b_u	800	b_g	814	a_u	321	ν_{55}	1562	b_u	1662	b_u	1562	b_u	1638
ν_{42}	786	b_g	834	b_g	818	b_g	335	ν_{7}	1615	a_g	1671	a_g	1632	a_g	1713
ν_{29}	809	a_u	862	b_u	832	a_u	338	ν_{6}	2998	a_g	3078	a_g	3077	a_g	3028
ν_{41}	818	b_g	888	a_u	843	b_u	350	ν_{54}	2998	b_u	3080	a_g	3085	b_u	3035
ν_{21}	831	a_g	903	b_g	903	a_g	360	ν_{53}	3003	b_u	3084	b_u	3087	a_g	3035
ν_{40}	879	b_g	906	a_u	910	a_u	391	ν_{5}	3004	a_g	3086	a_g	3088	a_g	3037
ν_{28}	880	a_u	915	a_g	910	b_g	401	ν_{4}	3014	a_g	3087	b_u	3088	b_u	3038
ν_{67}	941	b_u	999	a_u	1018	b_u	415	ν_{52}	3016	b_u	3088	a_g	3088	b_u	3039
ν_{20}	958	a_g	1003	b_g	1021	a_g	421	ν_{3}	3023	a_g	3088	b_u	3089	a_g	3041
ν_{27}	969	a_u	1006	a_u	1024	b_u	462	ν_{51}	3024	b_u	3090	a_g	3090	b_u	3041
ν_{39}	970	b_g	1012	b_g	1025	a_u	500	ν_{2}	3028	a_g	3090	b_u	3091	a_g	3043
ν_{38}	979	b_g	1021	b_u	1025	b_g	521	ν_{50}	3030	b_u	3091	b_u	3092	b_u	3044
ν_{26}	980	a_u	1036	a_g	1033	a_g	524	ν_{1}	3048	a_g	3092	a_g	3093	a_g	3045
ν_{19}	982	a_g	1041	a_g	1034	a_u	532	ν_{49}	3049	b_u	3095	b_u	3095	b_u	3045

[a] The present *ab initio* calculations used the configuration interaction method and the 6-311+g(d) basis set. Our notation in the first column follows that used by Herzberg and Mulliken. Frequencies from other calculations[26,28,23] are displayed for comparison. Symmetry races $\Gamma_{v'}$ of the normal modes are also specified when available.

mode with the lowest frequency, which we found to be the reaction coordinate in all examined cases. The reaction coordinates, ν_{rc}, are a_u-modes (out-of-plane, out-of-phase), corresponding to the ethylenic double bond and phenyl torsion. In *trans*-stilbene the reaction coordinate corresponds to the mode ν_{37} with $\nu_{rc} = 22-24$ cm^{-1} depending on the isotopomer, see Table 3. This is considerably less than previously calculated for *trans*-stilbene using a semiempirical QCFF/PI Hamiltonian (52−56 cm^{-1})[28] or a semiempirical SCF−LCAO−CI scheme (88 cm^{-1}).[26] Reaction coordinates of *trans*-stilbene corresponding to higher frequencies, such as 410[18] and 903 cm^{-1} ,[20] or even 1392 cm^{-1},[20] are in clear contrast to our findings. According to our calculations, all modes above 980 cm^{-1} are in-plane a_g- or b_u-modes, the only out-of-plane mode in the vicinity of a proposed 903 cm^{-1} mode corresponds to the out-of-plane motion of the hydrogens, while the proposed 410 cm^{-1} mode is a phenyl wagging mode without contribution of the ethylenic bond torsion.

For 4CS, 4MS, and DCS, the equivalent a_u-modes identified as the reaction coordinates ν_{rc} are 13, 17, and 16 cm^{-1}, respectively. In the case of DPB, an a_u-mode can be identified as the reaction coordinate as well with $\nu_{rc} = 29$ cm^{-1}, comprising torsion around the two double bonds and phenyl ring torsion.

Calculated specific rate constants $k(E)$ were fitted to experimental results from supersonic beam experiments for deuterated isotopomers of *trans*-stilbene (D0,[42] D2 and D10,[43] D12[44]), DPB[16] as well as DCS,[45] 4CS,[46] and 4MS.[46] Figures 2−7 show the results. In all cases, very good agreement is found by treating E_0, which cannot yet be calculated sufficiently well, as the only adjustable parameter. The threshold energies E_0 obtained are included in Table 3. The threshold energies of the different isotopomers of *trans*-stilbene are expected to be practically identical, since the difference in zero point energies of the reaction coordinates of the examined isotopomers is only ≈1 cm^{-1}. Indeed, we find that the fitted threshold energies of D0, D2, and D12 are all practically identical (1155 ± 10 cm^{-1}): only the fit of D10 has led to a significantly smaller barrier of 1060 cm^{-1}. This discrepancy could be caused by an experimental artifact because, for an unknown reason, the D10 results show considerably larger scatter near to the threshold than the other isotopomers. Further experiments should improve the accuracy of the D10 data. The internal consistency of the D0, D2 and D12 data is taken as a strong support for the present results. Early thermal gas-phase data at high excess energies from refs 47−49 are included in Figure 2 for *trans*-stilbene. Including these data, Figure 2 shows that the RRKM representation of $k(E)$ holds very well from 1000 up to 9000 cm^{-1}.

The specific rate constants for the isomerization of DCS are also fitted well, yielding a threshold energy of 835 ± 10 cm^{-1}, while the curves for 4CS and 4MS are reproduced with threshold energies of 1000 ± 30 and 980 ± 30 cm^{-1}, respectively. In the case of DPB, the experiments provide specific rate constants up to 7500 cm^{-1} excess energy and again all experiments can

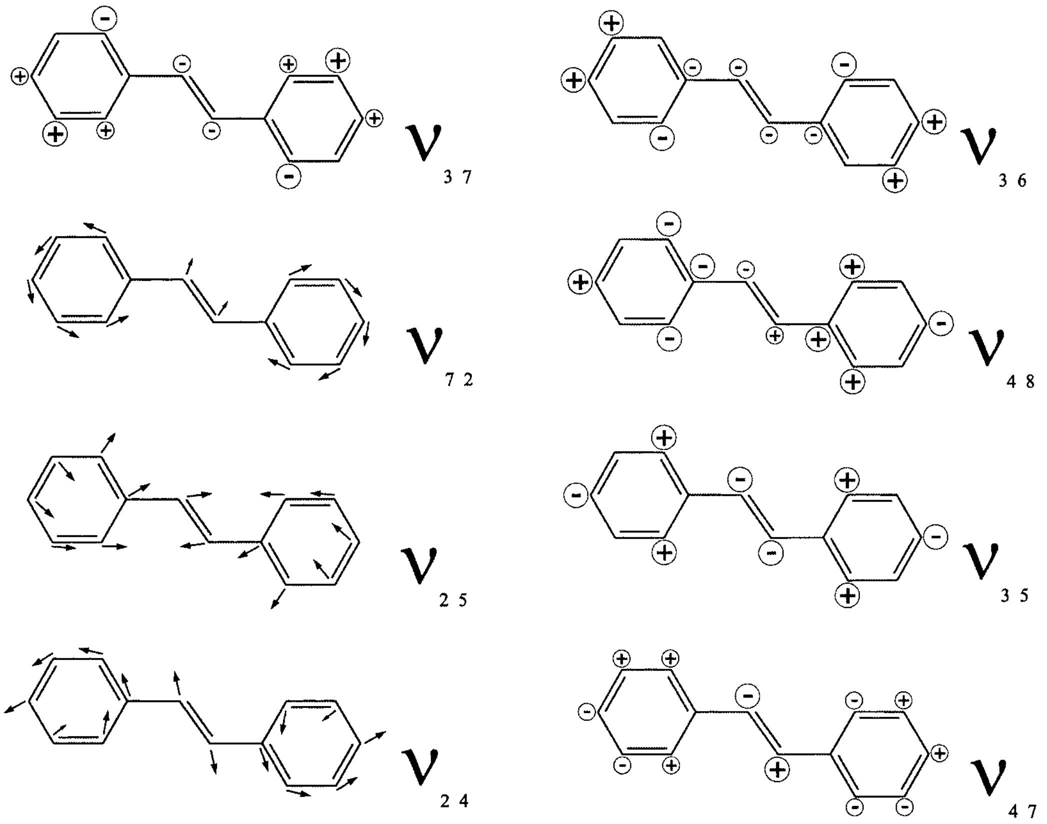

Figure 1. Low frequency modes of S1-*trans*-stilbene, ν_{37} is the reaction coordinate, comprising ethylenic double bond and phenyl ring torsion, ν_{36} and ν_{35} represent butterfly motions, ν_{48} is a wagging mode, while ν_{72}, ν_{25}, and ν_{24} clearly are in-plane modes.

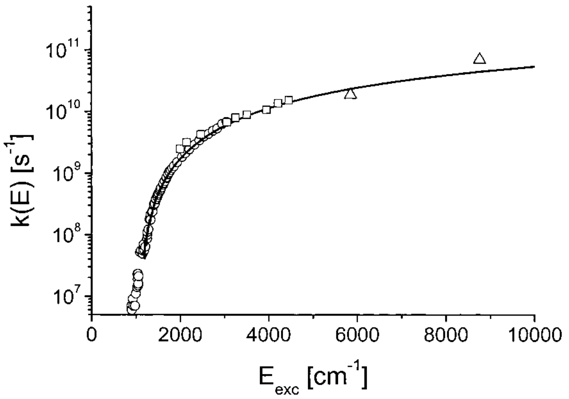

Figure 2. Specific rate constants k(E) for the photoisomerization of D0 *trans*-stilbene (○: supersonic beam experiments from ref 42. Additional data from experiments in low-pressure gases from refs 47 and 48 at 390 K (△) and ref 49 at 296 K (□). Full line: RRKM calculations from this work).

TABLE 3: Barrier Heights, E_0 and Frequencies of Reaction Coordinates ν_{rc} Used in the Calculations of k(E)

	tSt D_0	tSt D_2	tSt D_{10}	tSt D_{12}	DPB	DCS	4CS	4MS
E_0 [cm^{-1}]	1155	1160	1065	1150	1000	835	1000	980
ν_{rc} [cm^{-1}]	24	24	22	22	29	16	13	17

be represented very well with a threshold energy of $E_0 = 1000 \pm 10$ cm^{-1} being the only fit parameter. One notices that deuteration practically does not change E_0 in *trans*-stilbene which supports the assumption that vibrational frequencies do not change from the parent molecule to the activated complex, while other substitutions lead to lower values of E_0.

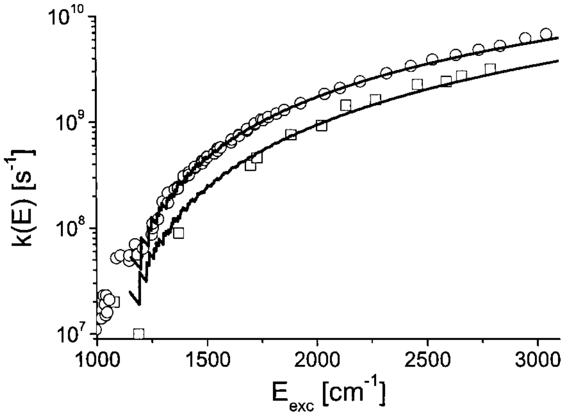

Figure 3. Specific rate constants $k(E)$ for the photoisomerization of 2 isotopomers of *trans*-stilbene (supersonic beam experiments, ○: D0 from ref 42. □: D12 from ref 44. Full lines: RRKM calculations from this work).

3.2. Thermally Averaged Rate Constants. The transition from specific rate constants $k(E)$ of eq 1 to thermally averaged rate constants k_∞ of eq 2 in the present case is trivial. As the frequencies of the reaction coordinates all are very low with $hc\nu_{rc}/kT \ll 1$, one has

$$k_\infty = A_\infty \exp(-E_0/kT) \qquad (3)$$

with $A_\infty = c\nu_{rc}$, see Table 4. As an internal consistency check Arrhenius parameters were also calculated numerically using eq 2. Table 4 includes the corresponding Arrhenius parameters.

The data derived for k_∞ allow for a comparison with thermal photoisomerization rate constants k_{nr} such as measured in low viscosity, nonpolar, liquid solvents. For DPB we calculate $k_\infty = 6.2 \times 10^9$ s^{-1} at 295 K, while $k_{nr} = 6.1 \times 10^9$ s^{-1} was measured in liquid ethane.[17] For DCS we calculate $k_\infty = 5.6 \times 10^9$ s^{-1} at 273 K, while $k_{nr} = 5.5 \times 10^9$ s^{-1} was obtained in

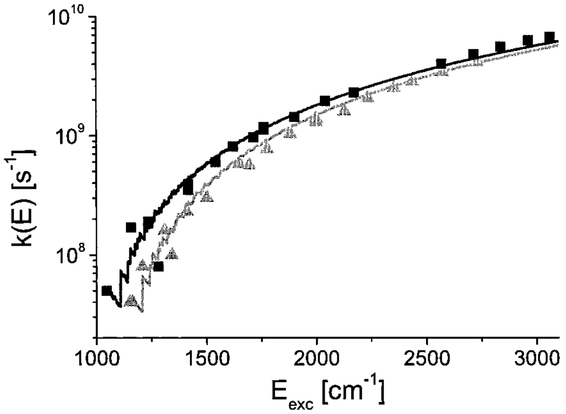

Figure 4. Specific rate constants k(E) for the photoisomerization of 2 isotopomers of *trans*-stilbene (supersonic beam experiments, ▲: D2. ■: D10 from ref 43. Full lines: RRKM calculations from this work).

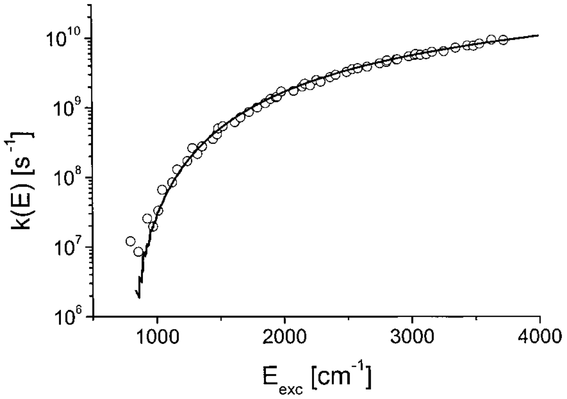

Figure 5. Specific rate constants *k*(*E*) for the photoisomerization of DCS (○: supersonic beam experiments from ref 45. Full line: RRKM calculations from this work).

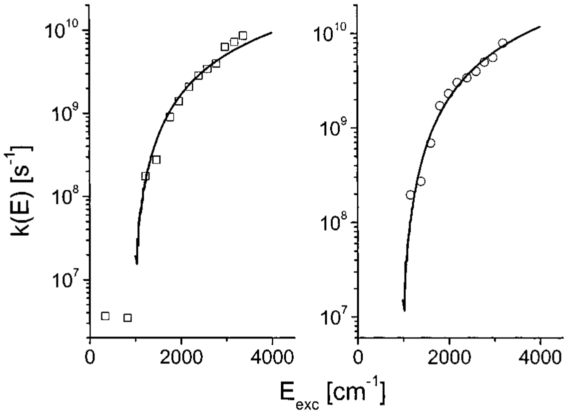

Figure 6. Specific rate constants *k*(*E*) for the photoisomerization of 4-chloro-trans-stilbene (□) and 4-methyl-*trans*-stilbene (○) (supersonic beam experiments from ref 46); full lines: RRKM calculations from this work).

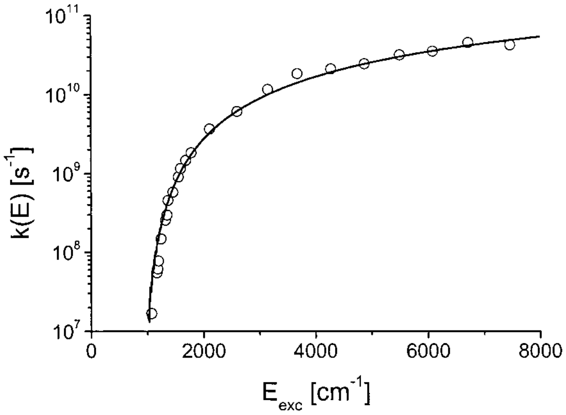

Figure 7. Specific rate constants k(E) for the photoisomerization of DPB (○: supersonic beam experiments from ref 16. Full line: RRKM calculations from this work).

TABLE 4: Arrhenius Parameter A_∞ and E_0 for Equation 3 and Arrhenius Parameter A and E_a Calculated from Eq 2

	tSt	DPB	DCS	4CS	4MS
A_∞ [10^{11} s^{-1}]	7.3	8.6	4.8	3.9	5.2
E_0 [cm^{-1}]	1155	1000	835	1000	980
A [10^{11} s^{-1}]	7.5	8.7	4.5	3.9	5.1
E_a [cm^{-1}]	1165	1015	840	1005	1000

diethyl ether.[50] In striking contrast to this, our calculated value of $k_\infty = 2.5 \times 10^9$ s^{-1} at 295 K for *trans*-stilbene, which agrees reasonably well with the value of $k_\infty = 1.8 \times 10^9$ s^{-1} from the optimized RRKM fit from ref 14, is about 1 order of magnitude lower than $k_{nr} = 2.8 \times 10^{10}$ s^{-1} such as measured in liquid ethane.[17] On the other hand, k_∞ is in perfect accordance with the experimental gas phase thermal average given by Fleming[51] where $k(296\text{ K}) = 2.5 \times 10^9$ s^{-1} in methane was extrapolated to zero pressure. We also determined the thermal rate constant k_{nr} for *trans*-stilbene in helium at 323 K which, in this weakly interacting environment, only shows a slight pressure dependence.[24] Extrapolated to zero pressure we obtained a thermally averaged value of $k_{nr} = 4.5 \times 10^9$ s^{-1} which compares very well with a calculated $k_\infty = 4.3 \times 10^9$ s^{-1} at this temperature.

Recently, we presented a similar comparison between measurements of k(E) and the corresponding calculated k_∞ with measured thermal rate coefficients k_{nr} in low viscosity solutions for the trans- and *cis*-conformers of benzocyclobutenyliden-benzocyclobutene.[29] While, for the *cis*-isomer, the two rate constants agreed to within better than 10% (1.2 and 1.3 × 10^{10} s^{-1}, respectively), for the *trans*-isomer there was a factor of 2−3 discrepancy (1.8 versus 4.6 × 10^9 s^{-1}) which may be considered as still close to the experimental uncertainty. This supports the view that, among the studied systems, *trans*-stilbene is the only species that exhibits the puzzling solvent effect.

3.3. Excited-State Frequencies. We complete the representation of our results by providing the derived frequency sets for all molecules treated and by comparing calculations and spectroscopic observations as far as available. Table 5 gives all calculated frequencies including also the data for *trans*-stilbene from Table 2. The results from Table 5 form the basis for our RRKM calculations of k(E). Table 6 compares the frequencies of three modes for *trans*-stilbene from spectroscopic determinations[35−37] with our calculations, while Table 7 provides a comparison of spectroscopic results for the isotopomers of *trans*-stilbene from ref 39 with our calculations. In both cases the agreement between experiment and calculation is very good.

4. Conclusion

We have demonstrated that ab initio calculations of vibrational frequencies of electronically excited diphenylpolyenes today can be made with very satisfactory accuracy. A comparison with spectroscopic measurements allows for a proper assignment. At the same time, the corresponding molecular motions can be visualized which helps to identify reaction coordinates of photoisomerizations.

On the basis of the calculated frequencies, standard rigid activated complex RRKM calculations of specific rate constants

TABLE 5: Calculated Vibrational Frequencies of the Electronically Excited S_1-State (in cm^{-1})[a]

tSt D_0	tSt D_2	tSt D_{10}	tSt D_{12}	4CS	4MS	DPB	DCS	tSt D_0	tSt D_2	tSt D_{10}	tSt D_{12}	4CS	4MS	DPB	DCS	4MS	DPB	DCS
24.2	23.8	22.4	22.1	12.9	17.4	28.7	16.1	983	981	831	822	984	979	962	792	3002	2983	1479
47.4	47.2	44.2	44	37.1	40.9	34.2	26.3	1059	983	834	824	984	981	976	799	3005	2983	1484
81.8	81	76.7	76	63.3	62.3	46.2	48.2	1061	983	836	834	1049	991	976	840	3013	2987	1490
119	118	110	110	87.1	67.7	81.8	48.4	1113	1069	845	835	1059	993	985	840	3016	2988	1494
199	197	190	189	160	100	133	53.2	1115	1078	851	845	1088	1038	985	854	3019	2992	1504
212	204	199	192	177	164	166	68	1142	1113	918	918	1111	1065	990	928	3021	2997	1507
275	238	259	232	228	194	167	120	1148	1116	925	924	1142	1103	990	942	3031	3001	1521
277	275	268	259	251	250	219	129	1167	1130	1021	934	1146	1120	1056	963	3044	3001	1568
397	396	346	345	299	259	247	171	1188	1157	1022	984	1162	1143	1059	971	3044	3013	1592
409	405	356	353	313	307	285	180	1224	1167	1121	1021	1172	1153	1098	972		3013	1644
439	420	391	375	400	339	307	204	1267	1232	1153	1040	1211	1174	1109	977		3024	2293
457	434	417	408	407	402	404	207	1272	1238	1201	1107	1245	1188	1140	979		3024	2873
474	460	442	420	410	410	407	237	1288	1272	1211	1197	1268	1194	1146	1060			2880
514	509	495	494	447	452	437	278	1331	1320	1239	1211	1280	1227	1160	1103			2920
591	587	496	496	462	465	462	288	1343	1321	1257	1211	1315	1270	1171	1116			2922
597	597	502	497	476	473	471	340	1416	1414	1298	1276	1336	1278	1178	1121			2985
613	603	568	566	562	479	477	372	1431	1417	1323	1295	1396	1294	1225	1124			3004
634	606	574	573	596	585	585	406	1456	1437	1342	1321	1423	1326	1233	1145			3023
640	630	590	575	612	600	599	413	1460	1460	1373	1358	1449	1348	1233	1165			3026
713	642	608	583	643	619	602	433	1513	1502	1452	1444	1460	1391	1247	1182			3031
737	669	612	595	658	650	610	435	1519	1511	1460	1454	1482	1414	1264	1186			3035
775	754	632	625	676	681	656	459	1545	1528	1510	1485	1516	1435	1305	1197			3042
779	766	637	628	732	734	657	486	1562	1562	1517	1509	1538	1445	1316	1202			3050
786	772	705	645	768	736	735	492	1615	1608	1591	1575	1558	1452	1364	1215			3056
809	780	724	675	771	773	744	535	2998	2232	2212	2211	1620	1464	1403	1247			3063
818	789	725	717	779	781	784	541	2998	2238	2212	2212	2984	1480	1434	1268			3074
831	792	761	733	786	786	804	558	3003	2998	2219	2218	2990	1499	1453	1302			3075
879	876	776	742	812	794	804	616	3004	2998	2219	2219	2996	1529	1466	1313			
880	877	782	764	830	817	824	633	3014	3004	2233	2230	3001	1559	1472	1338			
941	928	804	787	837	836	830	688	3016	3004	2233	2231	3005	1579	1531	1362			
958	948	804	789	883	843	840	690	3023	3016	2243	2233	3009	1639	1533	1375			
969	957	814	813	946	882	869	709	3024	3016	2243	2238	3015	2844	1566	1424			
970	969	817	816	948	948	889	717	3028	3027	2251	2243	3017	2885	576	1435			
979	970	823	819	968	955	895	778	3030	3027	2251	2244	3026	2935	1619	1455			
980	979	823	819	972	967	937	787	3048	3041	3027	2252	3031	2997	2970	1470			
982	979	827	821	974	977	941	789	3049	3041	3034	2253	3037	3000	2972	1471			

[a] The calculations used the 6-311+g(d) basis for *trans*-stilbene D0, D2, D10, and D12, 6-311g(d,p) for 4CS, 6-31g(d,p) for 4MS, 6-311g(d,p) for DPB, and 6-311g(d) for DCS, see text.

TABLE 6: Comparison of the Frequencies for the Modes with the Most Prominent Features of the Fluorescence Excitation Spectrum of *trans*-Stilbene (in cm^{-1})[a]

from ref 38	from ref 37	from ref 36	from ref 35	this work
47.5	47.5	48.0		47.4
	198	198	198	199
280	280		280	275

[a] These modes are assigned to ν_{36}, ν_{25}, and ν_{24} (from top to bottom).

$k(E)$ for barrier crossing in the considered photoisomerization reactions were made. After the reaction coordinates were indentified and their frequencies calculated, experimental $k(E)$ could all be reproduced very well by choosing activated complex frequencies identical to those of the parent molecules and fitting the threshold energies E_0 only. At present, fitting of E_0 cannot be avoided as sufficiently precise ab initio calculations of this quantity still appear too demanding. The agreement of the derived E_0 for different isotopomers of *trans*-stilbene, such as found in our work, is an important consistency check of the present treatment.

The present analysis of the measured $k(E)$ is much simpler and much more logical than all earlier attempts to rationalize the results. As a matter of fact, it is the simplest interpretation of the experiments which one may think of. It, therefore, apparently casts considerable doubt on earlier suggestions such as reversible reaction, incomplete IVR, electronically nonadiabatic reaction, or other mechanisms. The series of $k(E)$ measurements and their analysis given in the present work, are particularly fine examples for the power of statistical unimolecular rate theory in its RRKM version and they are certainly of textbook quality.

TABLE 7: Comparison of Experimentally Obtained Frequencies for a_g-Modes from Reference 39 with the Present ab Initio Frequencies (in cm^{-1})[a]

	D0		D2		D10		D12	
mode	exptl cm^{-1}	calcd cm^{-1}	exptl cm^{-1}	calcd cm^{-1}	exptl cm^{-1}	calcd cm^{-1}	exptl cm^{-1}	calcd cm^{-1}
ν_{25}	198	199	197	197	192	190	188	189
ν_{24}	276	275	–	275	–	259	–	259
ν_{23}	588	591	590	587	570	568	566	566
ν_{22}	621	613	623	603	611	590	580	575
ν_{21}	849	831	793	780	780	761	741	733
ν_{20}	970	958	969	957	944	925	934	924
ν_{19}	993	982	999	979	873	851	829	835
ν_{18}	1069	1061	–	1069	803	823	–	819
ν_{17}	–	1115	–	1116	792	817	778	816
ν_{16}	1157	1142	1148	1130	1125	1121	1125	1107
ν_{15}	1162	1167	1159	1167	849	845	859	845
ν_{14}	1244	1224	987	981	1246	1201	–	934
ν_{13}	1269	1272	1226	1238	–	1239	–	1211
ν_{12}	1333	1331	1347	1320	–	1298	990	1021
ν_{11}	–	1416	1454	1414	1358	1342	–	1276
ν_{10}	–	1456	–	1437	1430	1460	1406	1321
ν_9	1533	1519	1522	1502	1508	1517	1494	1454
ν_8	1551	1545	1513	1528	1545	1591	1504	1509

[a] The notation corresponds to the normal modes of D0-*trans*-stilbene, while D2, D10, and D12 frequencies are ordered with respect to the character of the equivalent D0 normal mode motion.

The *trans*-stilbene enigma of an order of magnitude discrepancy between thermally averaged gas-phase rate constants k_∞

and low viscosity liquid-phase rate constants k_{nr} remains unresolved. The problem is even aggravated by the present analysis, because it is shown that k_∞ and k_{nr} are identical for the photoisomerizations of diphenylbutadiene, dimethylaminocyanostilbene, and benzocyclobutenyliden-benzocyclobuten[29] (in low viscosity solvents) in striking contrast to *trans*-stilbene. We have followed experimentally the transition from low-pressure gas phase to high density solvents for *trans*-stilbene and attributed the effect to a modification of E_0 by increasing extent of solvation, formally expressed by a density-dependent E_0.[24] While this allows for a satisfactory representation of the experimental observations, it does not provide an answer to the question, why k_∞ and k_{nr} differ so much for *trans*-stilbene while they agree for diphenylbutadiene, dimethylaminocyanostilbene and benzocyclobutenyliden-benzocyclobutene.

Acknowledgment. The authors thank Ch.Müller for many helpful discussions and assistance. We are also thankful for the help of Rainer Oswald in computational questions. Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB 357 “Molekulare Mechanismen unimolekularer Prozesse”) is gratefully acknowledged.

References and Notes

(1) Lewis, G.; Magel, T. T.; Lipkin, D. *J. Am. Chem. Soc.* **1940**, *62*, 2973.

(2) Dyck, R.; McClure, D. *J. Chem. Phys.* **1962**, *36*, 2326.

(3) Hammond, G.; Saltiel, J.; Lamola, A. A.; Turro, N.; Bradshaw, J.; Cowan, D.; Counsell, R.; Vogt, V.; Dalton, C. *J. Am. Chem. Soc.* **1964**, *86*, 3197.

(4) Gegiou, G.; Muszkat, K.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 12.

(5) Saltiel, J.; D’Agostino, J.; Megarity, E.; Metts, L.; Neuberger, K.; Wrighton, M.; Zafirion, O. *Org. Photochem.* **1971**, *3*, 1.

(6) Beveridge, D.; Jaffé, H. *J. Am. Chem. Soc.* **1965**, *87*, 5340.

(7) Orlandi, G.; Siebrand, W. *Chem. Phys. Lett.* **1975**, *30*, 352.

(8) Orlandi, G.; Palmieri, P.; Poggi, G. *J. Am. Chem. Soc.* **1979**, *101*, 3492.

(9) Olbrich, G. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 209.

(10) Troe, J.; Weitzel, K.-M. *J. Chem. Phys.* **1988**, *88*, 7030.

(11) Molina, V.; Merchán, M.; Roos, B. O. *J. Phys. Chem. A* **1997**, *101*, 3478.

(12) Syage, J.; Lambert, W.; Felker, P.; Zewail, A.; Hochstrasser, R. *Chem. Phys.* **1982**, *88*, 266.

(13) Khundkar, L.; Marcus, R.; Zewail, A. *J. Phys. Chem.* **1983**, *89*, 5402.

(14) Troe, J. *Chem. Phys. Lett.* **1985**, *114*, 241.

(15) Troe, J.; Amirav, A.; Jortner, J. *Chem. Phys. Lett.* **1985**, *115*, 245.

(16) Amirav, A.; Sonnenschein, M.; Jortner, J. *Chem. Phys.* **1986**, *102*, 305.

(17) Schroeder, J.; Schwarzer, D.; Troe, J.; Voβ, F. *J. Chem. Phys.* **1990**, *93*, 2393.

(18) Felker, P.; Zewail, A. *J. Phys. Chem.* **1985**, *89*, 5402.

(19) Schroeder, J.; Troe, J. *J. Phys. Chem.* **1986**, *90*, 4215.

(20) Nordholm, S. *Chem. Phys.* **1989**, *137*, 109.

(21) Troe, J. *Pure Appl. Chem.* **1997**, *69*, 841.

(22) Schroeder, J. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 643.

(23) Gershinsky, G.; Pollak, E. *J. Chem. Phys.* **1997**, *107*, 812.

(24) Meyer, A.; Schroeder, J.; Troe, J. *J. Phys. Chem. A* **1999**, *103*, 10528.

(25) Amirav, A.; Jortner, J. *Chem. Phys. Lett.* **1983**, *95*, 295.

(26) Warshel, A. *J. Chem. Phys.* **1975**, *62*, 214.

(27) Leitner, D.; Wolynes, P. *Chem. Phys. Lett.* **1997**, *280*, 411.

(28) Negri, F.; Orlandi, G. *J. Phys. Chem.* **1991**, *95*, 748.

(29) Ernst, D.; Rupp, L.; Frank, R.; Kühnle, W.; Lemmen, P.; Lenoir, D.; Schroeder, J.; Grimm, C.; Steinel, T. *Z. Phys. Chem.* **2002**, *216*, 555.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. J.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(31) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian Inc.: Pittsburgh, PA, 1996.

(32) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(33) Mulliken, R. *J. Chem. Phys.* **1955**, *23*, 1997.

(34) Herzberg, G., Ed. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1966; Vol. 2.

(35) Syage, J.; Felker, P.; Zewail, A. *J. Chem. Phys.* **1984**, *81*, 4685.

(36) Spangler, L.; Zee, R.; Zwier, T. *J. Phys. Chem.* **1987**, *91*, 2782.

(37) Urano, T.; Maegawa, M.; Yamanouchi, K.; Tsuchiya, S. *J. Phys. Chem.* **1989**, *89*, 3459.

(38) Chiang, W.; Laane, J. *J. Chem. Phys.* **1995**, *100*, 8755.

(39) Urano, T.; Hamaguchi, H.; Tasumi, M.; Yamanouchi, K.; Tsuchiya, S.; Gustafson, T. *J. Chem. Phys.* **1989**, *91*, 3884.

(40) Beyer, T.; Swinehart, D. *Chem. Phys.* **1973**, *16*, 379.

(41) Semichem. *GaussView 2.0*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(42) Lienau, C. PhD thesis, Georg-August-Universität Göttingen, Göttingen, 1991.

(43) Courtney, S.; Balk, M.; Philips, L.; Webb, S.; Yang, D.; Levy, D.; Fleming, G. *J. Chem. Phys.* **1988**, *89*, 6697.

(44) Felker, P.; Lambert, W.; Zewail, A. *J. Chem. Phys.* **1985**, *82*, 3003.

(45) Daum, R.; Hansson, T.; Nörenberg, R.; Schwarzer, D.; Schroeder, J. *Chem. Phys. Lett.* **1995**, *246*, 607.

(46) Majors, T.; Even, U.; Jortner, J. *J. Chem. Phys.* **1984**, *81*, 2330.

(47) Greene, B.; Hochstrasser, R.; Weisman, R. *J. Chem. Phys.* **1979**, *71*, 544.

(48) Greene, B.; Hochstrasser, R.; Weisman, R. *Chem. Phys.* **1980**, *48*, 289.

(49) Perry, J.; Scherer, N.; Zewail, A. *Chem. Phys. Lett.* **1983**, *103*, 1.

(50) Rettig, W.; Majenz, W. *Chem. Phys. Lett.* **1989**, *154*, 335.

(51) Balk, M.; Fleming, G. *J. Phys. Chem.* **1986**, *90*, 3975.