Iodine−Benzene Complex as a Candidate for a Real-Time Control of a Bimolecular Reaction. Spectroscopic Studies of the Properties of the 1:1 Complex Isolated in Solid Krypton

Tiina Kiviniemi,* Eero Hulkko, Toni Kiljunen, and Mika Pettersson

Nanoscience Center, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyväskylä, Finland

Received: March 5, 2009; Revised Manuscript Received: April 21, 2009

The properties of the 1:1 iodine−benzene complex isolated in a solid Kr matrix at low temperatures have been studied using UV−vis absorption, FTIR, resonance Raman, and femtosecond coherent anti-Stokes Raman spectroscopy (fs-CARS). The use of all these techniques on similar samples provides a wide view on the spectroscopic properties of the complex and allows comparison and combination of the results from different methods. The results for the complex cover its structure, the changes in the iodine molecule's vibrational frequencies and electronic absorption spectrum upon complexation, and the dynamics of the complexed I_2 molecule on both ground and excited electronic states. In addition, polarization beats between uncomplexed benzene and iodine molecules are detected in the fs-CARS spectra, showing an amplification of an electronically nonresonant CARS signal by the resonant iodine signal. The possibility of controlling the charge-transfer reaction of the I_2−Bz complex using the excitation of a well-defined ground-state vibrational wavepacket, according to the Tannor−Rice−Kosloff scheme, is discussed on the basis of the experimental findings.

Introduction

The study of the iodine−benzene complex can be considered to have begun in the 1940′s, with Benesi and Hildebrand finding its charge-transfer UV absorption at ∼280 nm.[1,2] Ever since, it has been a subject of numerous theoretical and experimental studies, aiming to the understanding of the properties and reactions of this interesting system, which can be considered as a prototype of a complex with a low-lying charge-transfer state. Considering the amount of work done on this complex, it is rather surprising that the agreement between electronic structure calculations and experiments on its ground-state structure was not achieved until recently by matrix isolation IR studies.[3] However, the I_2−Bz complex still continues to offer new, interesting research ideas as the research methods improve. For example, the emergence of ultrafast laser methods in the 1990′s opened up a new way to study the dynamics of this complex after the charge-transfer excitation.[4−10]

One of the most interesting properties of the iodine−benzene complex is its low-lying charge-transfer state and the processes that follow from the excitation to this state. The ultrafast processes initiated by the charge-transfer excitation have been well studied by several groups both in the liquid state and in clusters in molecular beams.[4−6] The main dissociation channels for the complex after charge-transfer excitation have been found to be the ejection of either a neutral iodine atom or an iodine molecule, and the rates of these processes have been found to depend strongly on the environment. The molecular dissociation channel proceeds via coupling to a neutral repulsive potential surface, while the atomic dissociation occurs via formation of a charge-transfer complex between iodine atom and benzene molecule, with a simultaneous elongation of the I−I bond. The direct excitation of the complex from the ground state to the charge-transfer state thus leads to a fast predissociation, due to several crossings of repulsive surfaces with the charge-transfer state. This model is also supported by the fact that, according to our knowledge, no emission from the relaxed molecular charge-transfer state to the ground state of the complex has been observed.

Recently, we have studied the vibrational dynamics on the ground state of the I_2−Xe complex isolated in a solid krypton matrix using femtosecond coherent anti-Stokes Raman scattering (fs-CARS) technique.[11] In this method, a coherent vibrational wavepacket on the ground electronic state is generated and probed using femtosecond pulses, enabling control and manipulation of vibrations of molecules or molecular complexes. This opens up interesting prospects of reaction control by exploiting the evolution of the vibrational wavepacket, as suggested originally by Tannor, Kosloff, and Rice.[12,13] When used for a molecular complex, this kind of method might allow for control of a bimolecular reaction, such as charge-transfer or dissociation reactions. The I_2−Bz complex is an interesting candidate in this perspective due to its low-lying charge-transfer state and rather well-known properties. The idea in this case is to design a three-pulse sequence, where two pulses create a vibrational wavepacket on the ground electronic state by stimulated Raman scattering. After a suitable time delay, the third pulse excites the wavepacket to the charge-transfer state, where the reaction takes place. Manipulation of the iodine vibrations on the ground electronic state using the fs-CARS method allows for the charge-transfer excitation to start from different complex conformations, corresponding to the motion of the wavepacket, making different outcomes of the photoreaction possible. Trapping the I_2−Bz complex in a solid, low-temperature rare-gas matrix allows for a well-defined, stable complex with long vibrational dephasing times, and samples that are concentrated enough to gain strong signals. However, there are no constraints for the same reaction control scheme to be realized also in solid, liquid, and possibly even gas phase.

The execution of this kind of process demands, however, detailed knowledge of the ground and excited states of the

---

* Corresponding author. E-mail: titakivi@jyu.fi.

10.1021/jp902012u CCC: $40.75

complex, as well as the dephasing times of the vibrations on the ground electronic state. The initiation of the process asks for high enough probability for the creation of a wavepacket with the desired vibrational eigenstates. Then, the lifetime of the wavepacket needs to be long enough so that the wavepacket will not dephase before reaching the conformation wanted for the excitation. In addition, the excited-state potentials have to be well-known to allow for explaining and understanding the outcome of the reaction. However, if these conditions can be fulfilled, the iodine−benzene complex might be an excellent model system for a bimolecular reaction control.

In this paper, we present results from several spectroscopic studies of the I_2−Bz complex isolated in a solid krypton matrix at low temperatures. By combining the results from UV−vis, infrared (IR), and resonance Raman measurements, MP2 calculations and fs-CARS measurements, we obtained detailed information on the properties and dynamics of the complex. The use of all these spectroscopic techniques on similar samples provides a wide view on the properties of the complex. The results for the complex cover its structure, the changes of the vibrational frequencies and electronic absorption spectrum upon complexation, and the dynamics of the complexed I_2 molecule on both ground and excited electronic states. Combining these results, the possibility of using this complex as a model system for coherent control of a bimolecular reaction, and the difficulties that are encountered, are discussed.

Experimental Methods

The solid matrix samples were prepared by depositing I_2/Bz/Kr gas mixture on a window held at $T = 40$ K, which produces optically excellent matrices with good reproducibility of structure and concentration.[14] A CaF_2 window in a closed cycle helium cryostat was used for the IR measurements, and a ~100 μm thin sapphire window in a liquid helium flow cryostat for the other measurements. The I_2/Kr = 1/2600 ratio was kept constant for all the samples, while the benzene/krypton ratio in the matrix was varied between 1/2000 and 1/500. The presence of the 1:1 I_2−Bz complex was verified by studying the dependence of the IR spectrum on the benzene concentration. The FTIR spectra were measured using a Nicolet Magna-IR 760 ESP spectrometer with a 0.25 cm^{-1} resolution at several temperatures in the range of $T = 11$−40 K.

The Stokes branch spontaneous resonance Raman spectra were measured using a 532 nm single-mode frequency-doubled CW Nd:YAG laser (Alphalas), resonant with the B ← X transition of iodine. The spectra were collected in a backscattering configuration using a 50 cm focal length spectrograph (Acton SpectraPro 2500i) with 600 and 2400 grooves/mm gratings to obtain resolutions of 5 and 1 cm^{-1}, respectively. The frequency scale of the Raman spectra was calibrated using the vibrational frequencies of monomeric iodine in solid krypton determined earlier with high accuracy by fs-CARS measurements from a similarly prepared sample.[14]

The UV−vis spectra were measured using a deuterium discharge lamp (Cathodeon Deuterium C710) as a light source and an Ocean Optics USB2000 spectrometer with an optical fiber for detection. Quartz lenses were used for focusing and collimating the light beam. The spectra for different concentrations were measured at $T = 40$ K at a wavelength range of 237−650 nm.

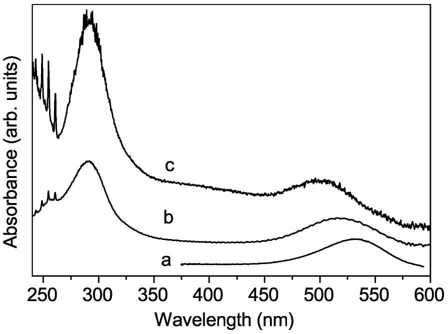

Figure 1. UV−vis spectrum of Bz/I_2/Kr samples at $T = 40$ K: (a) I_2/Kr = 1/2600 (no benzene); (b) Bz/I_2/Kr = 1/0.77/2000; (c) Bz/I_2/Kr = 1/0.19/500. The spectra are normalized to the B ← X absorption maxima at the visible region (~500−530 nm). The B ← X transition shifts as benzene is added to the sample, while the charge-transfer absorption (~290 nm) only becomes more intensive. Sharp bands at $\lambda \sim 250$ nm are due to the uncomplexed benzene A ← X absorption.[25]

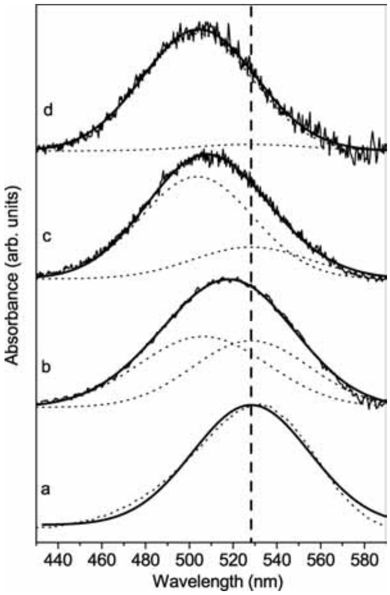

Figure 2. Spectrum of the iodine B ← X absorption for samples with different benzene concentrations: (a) I_2/Kr = 1/2600; (b) Bz/I_2/Kr = 1/0.77/2000; (c) Bz/I_2/Kr = 1/0.30/780; (d) Bz/I_2/Kr = 1/0.19/500. Key: solid line = measurement; dotted line = Gaussian fits. The absorption shifts as a function of benzene concentration and can be fitted with two bands with band maxima at $\lambda = 529$ and 504 nm, corresponding to monomeric and complexed iodine, respectively. The spectra are baseline corrected.

The setup used for the fs-CARS measurements has been described in detail in our previous publication.[11] In the present experiments, the parameters for the pulses were (wavelength/bandwidth in nanometers): pump (580/13), dump (621/14), and probe (580/13). The CARS signal was collected with a photomultiplier tube, averaging 100 pulses per measurement with a 20 fs step size of the probe delay line. The time delay between the pump and dump pulses was adjusted so that the CARS signal was maximized.

Results and Discussion

UV−Vis Absorption Measurements. The UV−vis absorption spectra of I_2/Bz/Kr samples with different benzene concentrations are shown in Figures 1 and 2. The B ← X absorption of iodine molecule is blue-shifted as a function of the benzene concentration, and the band can be fitted with two Gaussian functions with maxima at $\lambda = 529$ and 504 nm, corresponding to the uncomplexed iodine and the I_2−Bz complex, respectively. The UV band at $\lambda = 291$ nm (Figure 1), due to the charge-transfer absorption of the iodine−benzene complex only grows

TABLE 1: Complex to Iodine Concentration Ratio and Integrated Absorption Coefficient for the B ← X Absorption in the Iodine−Benzene Complex, Calculated for Different Sample Concentrations

Bz/I_2/Kr	[complex]/[iodine]	ε_C(int) [10^5 nmM^{-1} cm^{-1}]
1/3.72/9300	0.022 ± 0.004	6.6 ± 1.3
1/0.77/2000	0.09 ± 0.02	6.8 ± 2.0
1/0.29/780	0.54 ± 0.09	4.4 ± 0.9
1/0.19/500	2.3 ± 0.5	4.4 ± 1.2
		5.6 ± 1.3[a]

[a] Averaged value.

but does not shift as a function of benzene concentration, supporting the interpretation that the "shift" of the band in the visible region is indeed due to two different, overlapping bands that change intensities as a function of benzene concentration, as assumed in the fit. This kind of environmentally induced blue shift of the iodine B ← X absorption, due to the stabilization of the iodine ground state, has been detected earlier in several different environments, from different solvents[2] to clathrate hydrate cages.[15] Interestingly, the absorption maximum of the 1:1 I_2−Bz complex isolated in solid krypton (504 nm) is very close to the absorption maximum of the iodine molecule solvated in liquid benzene (500 nm),[2] whereas the absorption of the uncomplexed iodine in Kr matrix (529 nm) is located, expectedly, at almost the same wavelength as the absorption in the gas phase (530 nm).[16] Thus, it seems that only one benzene molecule complexed with the iodine molecule is enough to induce a blue-shift in the B ← X absorption that corresponds almost completely to the shift in liquid benzene, and that the addition of more benzene molecules has a much smaller effect. It also suggests that, in liquid benzene, iodine molecule is on average mainly complexed with one benzene molecule.

The absorption bands at 529 and 291 nm can be fitted by using the absorption coefficients by Tellinghuisen[16] and Weng et al.,[9] respectively, to yield an estimate for the complex to iodine concentration ratio ([complex]/[uncomplexed iodine]) for different concentrations (Table 1). In the calculation, integrated absorption coefficients were estimated from the absorption coefficients at the absorption maxima, assuming a Gaussian band shape, yielding $\varepsilon_{CT} = (1.04 \pm 0.13) \times 10^6$, and $\varepsilon_{I_2} = (9.3 \pm 0.9) \times 10^4$ nmM^{-1} cm^{-1} for the complex charge-transfer absorption and the uncomplexed iodine B ← X absorption, respectively. Using the determined complexation ratio, the integrated absorption coefficient for the B ← X transition of iodine in the I_2−Bz complex can be estimated from the area under the fitted band at $\lambda = 504$ nm, yielding an average value of $\varepsilon_C = (5.6 \pm 1.3) \times 10^5$ nmM^{-1} cm^{-1}, which is about 6 times higher than the integrated absorption coefficient for the uncomplexed iodine. This distinct change of the absorption coefficient upon complexation might be due to mixing of the relevant electronic states with the low-lying charge-transfer state.

FTIR Absorption Measurements. The FTIR spectra for selected wavenumber regions are shown in Figures 3 and 4. When iodine is added to a Bz/Kr sample, several new bands appear. In Figure 3, two transitions of the complex are shown, corresponding to the ν_2 and ν_{11} vibrations, which are symmetry forbidden for the uncomplexed benzene (numbering according to Herzberg[17]). Also, other bands, corresponding to degenerate vibrations of pure benzene, such as ν_{13} and $\nu_{11} + \nu_{19}$ (Figure 4) are found to be shifted and split upon complexation. The characterization of the observed IR bands, their wavenumbers, and relative absorption intensities are presented in Table 2, with comparison to earlier experimental[18] and computational[3] results. The observation of new and split bands confirm the fact that upon complexation the C_6 symmetry of the benzene molecule is broken and thus the I_2−Bz complex structure has to be unsymmetric. The temperature dependence of the IR spectrum shows no significant changes in the relative intensities of the split bands, which would be typical for a site-effect, i.e., for different sites of molecules in the matrix, thus validating our conclusion that the splitting is in fact due to the removal of degeneracy in the system upon complexation. The results also agree well with the calculations, which predict that the lowest energy form of the complex is the unsymmetric structure, where the iodine molecule is located above either one of the C−C bond centers or one of the C atoms of benzene molecule, almost perpendicularly to the benzene ring plane.[3,9,19,20] These two structures lie very close in energy and the experiments can not distinguish between them, but most of the calculations suggest that the above-bond structure is the more stable one.[3,19−21] The observed splitting of the ν_{13} band, 0.96 cm^{-1}, agrees reasonably well with the calculations that vary between 1−4 cm^{-1} depending on the reference.[3,9,19] The observed relative IR intensities also follow the trend of the calculations rather well, except for two induced bands (ν_{11} and ν_{16}) that show lower intensities than predicted. Thus, the agreement of the experimental and computational data indicates that the I_2−Bz structure is in fact of above-bond type, as found earlier for the other halogen−benzene complexes as well.[3,10,18,21]

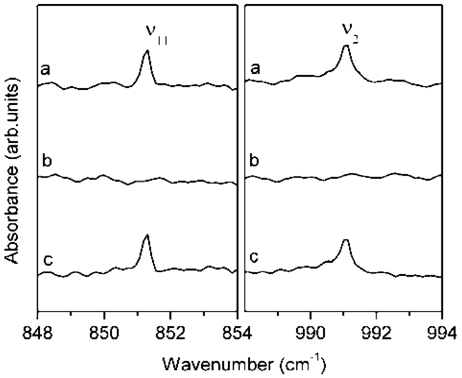

Figure 3. IR spectra for two benzene vibrations at $T = 40$ K: (a) Bz/I_2/Kr = 1/0.77/2000; (b) Bz/Kr = 1/2000. (c) Difference spectrum. The bands are induced upon complexation with iodine. For monomeric benzene molecule, the transitions are forbidden in the IR due to symmetry and thus are not visible.

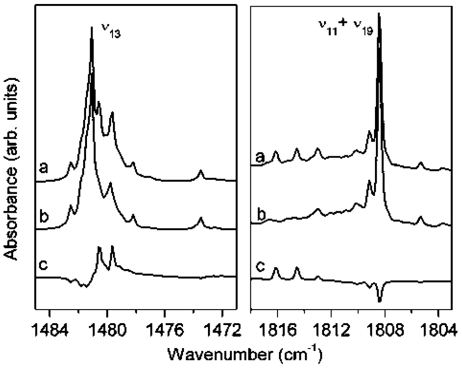

Figure 4. IR spectra for two benzene vibrations at $T = 40$ K: (a) Bz/I_2/Kr = 1/0.77/2000; (b) Bz/Kr = 1/2000. (c) Difference spectrum. The splitting of the complex vibrations shows that the C_6 symmetry of the benzene molecule is broken upon complexation.

Resonance Raman Measurements. In the resonance Raman spectra (Figure 5), the vibrational progression is clearly visible

TABLE 2: Characterization of the Strongest IR Absorption Bands of I_2−Bz Complex, the Frequency Shifts upon Complexation (in cm^{-1}), and the Relative Intensities of the Bands, Compared with Earlier Experimental Results on the I_2−Bz Complex and with MP2 Calculations

vibrational mode	I_2−Bz in Kr frequency[a] (shift) [rel int]	I_2−Bz in N_2 frequency[b]	I_2−Bz, MP2 calc frequency[c] (shift) [rel int]
$\nu_{13} + \nu_{16}$	3093.31 (−1.09) [0.41]		
$\nu_{13} + \nu_2 + \nu_{18}$	3072.46 (−1.96) [0.24]		
$\nu_7 + \nu_{19}$	1958.39 (+6.39) [0.36]		
$\nu_{11} + \nu_{19}$	1816.16 (+7.95) [0.31]		
	1814.60 (+6.39) [0.28]		
$\nu_{16}{}^d$			1618.76 (−3.90) [0.00]
	1585.35 (−2.53)[e] [0.03]		1615.89 (−6.75) [0.23]
$\nu_4 + \nu_{11}$	1530.02 (+12.89) [0.19]		
	1527.01 (+9.88) [0.18]		
ν_{13}	1480.60 (−0.61) [1.00]		1468.53 (−1.68) [0.99]
	1479.64 (−1.57) [0.81]		1464.88 (−5.28) [1.00]
$\nu_{17}{}^d$			1182.95 (−0.19) [0.01]
	1177.35 (−0.60)[e] [0.16]		1181.97 (−1.12) [0.05]
ν_{14}	1036.37 (−2.37) [0.19]		1049.64 (−1.28) [0.41]
	1035.60 (−3.14) [0.37]		1047.66 (−3.23) [0.78]
$\nu_2{}^d$	991.13 (−3)[f] [0.27]	990.9	1001.54 (−3.06) [0.37]
$\nu_{11}{}^d$	851.31 [0.17]	855.6	855.03 (+9.77) [0.81]
			848.47 (+3.21) [0.06]

[a] From this work, Bz/I_2/Kr = 1/0.77/2000, T = 20 K. [b] From ref 18, T = 20 K. [c] From Supporting Information in ref 3, relative intensities with respect to the absorption coefficient of 8.37 km/mol. [d] IR inactive in gaseous, uncomplexed benzene. [e] Although inactive in gas phase, the vibration of the uncomplexed benzene is induced in the matrix environment, resulting in weak bands.[10] [f] Shift determined from the fs-CARS measurements; the vibration of uncomplexed benzene is IR inactive.

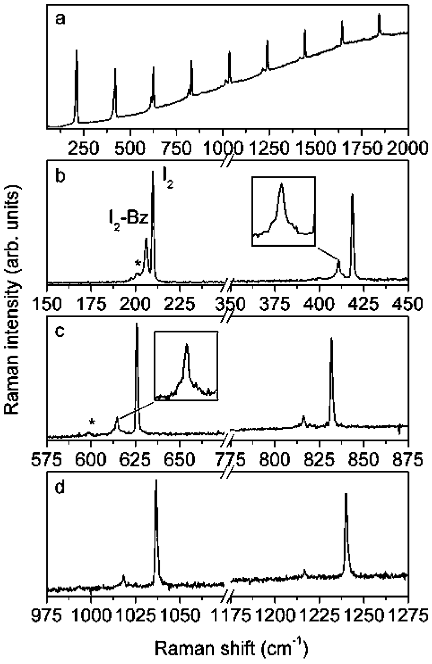

Figure 5. Resonance Raman spectrum of a Bz/I_2/Kr = 1/0.77/2000 sample at T = 30 K, showing the vibrational progression for both monomeric iodine and I_2−Bz complex (a). The higher resolution spectra of the v = 1−6 bands in panels (b)−(d) show clearly separated, sharp bands for monomeric and complexed iodine with the complex band at the lower frequencies. The complex bands for v = 2 and 3 (see insets) show two overlapping bands with different widths, indicating two different time scales for dephasing. The intensities are not comparable between the panels because each graph is scaled to the highest intensity to show the features of the weaker bands. The shoulder in the lowest frequency band in (b) and the weak band at ~590 cm^{-1} in (c), marked with *, are due to iodine clusters.[22]

for both uncomplexed and complexed iodine. The complexation induced frequency shift of the vibration is so small that the lowest frequency bands are only resolved in the higher resolution spectra (b−d in Figure 5). The bands are narrow and instrument limited (<1 cm^{-1}) single lines, indicating a well-defined complex and a highly homogeneous matrix environment. In the lowest frequency band, the shoulder marked with an asterisk at ~202 cm^{-1} is not due to the complex but to iodine dimers that are sometimes present in the sample in small concentrations.[22] Weak, corresponding bands are also visible in higher frequency regions. From the resonance Raman spectrum, accurate spectroscopic parameters for the I−I vibration in the benzene complex were determined, as reported before.[3] The harmonic vibrational frequency of the iodine molecule, found to be ω_e = 207.22 ± 0.07 cm^{-1}, is red-shifted by 3.94 cm^{-1} upon complexation, and the anharmonicity constant, $\omega_e x_e$ = 0.612 ± 0.015 cm^{-1}, is slightly reduced as compared to the uncomplexed iodine in solid krypton ($\omega_e x_e$ = 0.642 ± 0.001 cm^{-1}).[14]

From the resonance Raman spectra in Figure 5 it is also evident that the intensities of the I_2−Bz complex Raman bands decay faster as a function of the vibrational quantum number v than the intensities of the uncomplexed iodine bands. This effect is shown in Figure 6 as a decay of the normalized resonance Raman intensities for both the uncomplexed and the complexed iodine molecule. The faster decay of the band intensities for the complex indicates a faster electronic dephasing on the excited state of the complex than for the uncomplexed iodine. This can be understood by considering the dynamics on the excited state right after excitation.[23] As the I−I coordinate starts to stretch, the electronic-state coherence is lost faster in the strongly bound complex, since the electronic energy is expected to depend more sensitively on small changes in the geometry than in the isolated I_2 molecule, which interacts with the cage atoms dominantly via long-range dispersion interaction. Due to the faster dephasing on the B state, the higher vibrational states on the ground electronic state of the complex are much more difficult to reach using a resonance Raman process than those of the uncomplexed iodine. A more detailed description of this complex process involving a multitude of degrees of freedom of both the system and its bath, would require an in-depth simulation of the time-dependent correlation function of the system,[23] and is thus out of the scope of this article.

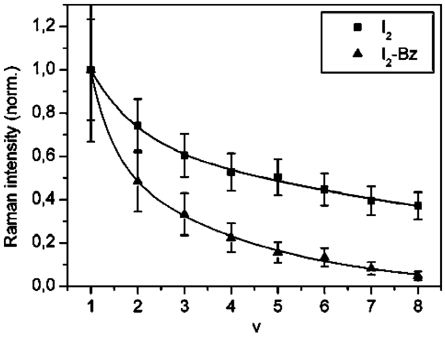

Figure 6. Normalized intensities of the resonance Raman bands for both monomeric and complexed iodine molecules as a function of the vibrational quantum number υ. The intensity of the I_2-Bz complex bands decays faster than the intensity of the monomeric iodine bands, indicating faster electronic dephasing and a perturbation on the properties of the excited electronic state upon complexation. The lines are for guiding the eye only.

The widths of the Raman bands, on the other hand, are proportional to the dephasing rates of the vibrations on the ground electronic state. Unfortunately, the resolution of our Raman equipment is not good enough to resolve the true bandwidths of any of the detected Raman bands. As a result, we can only deduce an instrument limited lower value for the dephasing time, giving a value longer than ~10 ps for the states with $\upsilon = 1-8$, which are observed in our measurements. Comparing the highest visible υ-states, where the real dephasing time is expected to be closest to the instrument limited bandwidth, the dephasing in the complex is found to be at most about 5 times faster than measured for the uncomplexed iodine.[14] This indicates that the dephasing rate of the ground-state vibrations is not radically increased upon complexation, although the perturbation on the iodine properties by benzene is stronger than for example in the I_2-Xe complex. The slow dephasing thus suggests that the coupling of the iodine vibrations to the benzene molecule is relatively weak. In any case, the lifetime of the wavepacket is, at least at the lower vibrational eigenstates, long enough for the wavepacket to make tens to hundreds of round-trips on the ground-state potential before dephasing.

A careful inspection of the low-frequency complex bands reveals that there is a weak and broad band superimposed with the sharp main band (see insets in Figure 5), which might be evidence of interesting dynamics of the complex. Because both bands are centered at the same frequency, it seems unlikely that they would belong to two different forms of the complex. This kind of structure could indicate two time scales for vibrational dephasing, leading to corresponding features in the spectrum. For example, the broad band might be due to a fast, but slight, rearrangement of the intermolecular coordinates after impulsive excitation of iodine and the sharp band would then give the dephasing time of the relaxed complex. Further investigations are, however, needed to get more insight into this issue.

fs-CARS Measurements. In the fs-CARS process, three femtosecond laser pulses are used to study the vibrations of the iodine molecule in its ground electronic state. The two first pulses, "pump" and "dump", are used to create a vibrational wavepacket on the ground electronic state of iodine. The third pulse, "probe", is then used to investigate the properties of the wavepacket by creating a third-order polarization in the sample. The intensity of light emitted by this polarization is then measured as a function of the delay between the dump and probe pulses. If the sample contains only monomeric iodine, the signal will oscillate as the wavepacket evolves on the ground state, at difference frequencies of the vibrational eigenstates that are included in the vibrational wavepacket.[14] These oscillations are called quantum beats. The signal is relatively strong, because the wavelength of the pump pulse is selected to be in resonance with the $B \leftarrow X$ transition of iodine.

However, if the sample contains another species that can contribute to the CARS signal, such as complexed iodine molecules that have slightly different vibrational frequencies than the uncomplexed I_2, there will be an additional modulation to the signal due to the interference of the CARS signals from the two different species, called polarization beating, that consists of difference frequencies of the vibrations of the two different species. This phenomenon has been characterized in several experimental and theoretical studies, for example, in our previous study of the I_2-Xe complex,[11] and for the gas-phase iodine by Faeder et al.[24] If the amount of the other species, here the complexed iodine, is much less than the amount of the uncomplexed iodine molecule, the polarization beating proves very useful as the strong iodine signal serves as an "amplifier" for the weaker signal, of which the quantum beating may not be detectable at all in itself.[11] So, in the $Bz/I_2/Kr$ samples, we would expect to detect at least the quantum beating of the uncomplexed iodine molecules, which are plenty in the sample, and the polarization beating between the signals of the uncomplexed and complexed iodine molecules. The quantum beating of the I_2-Bz complex may not be detected, if its concentration is notably smaller than the amount of uncomplexed iodine, or if its vibrational frequencies are too similar to the uncomplexed I_2 frequencies so that the quantum beat signals overlap each other in the frequency domain.

The fs-CARS results for a $Bz/I_2/Kr$ sample are shown in Figure 7. The frequency domain spectrum (right side, panels d−f) is obtained simply by Fourier transforming the time domain signal (left side, panels a−c). The time-domain signal as a whole is long-lived and shows oscillations up to more than 100 ps. However, as can be seen from panels b and c in Figure 7, the modulation pattern due to polarization beating is much more short-lived, disappearing already at a delay of ~15 ps. This means that the vibrational coherence of the other species contributing to the signal is short-lived, when compared to the vibrational coherence of the uncomplexed iodine. In the frequency domain, panels d−f in Figure 7, the different beat frequencies in the signal can be seen. The lowest frequency shown in panel d is a polarization beat, a difference frequency of two vibrations of two different species in the sample, because the beat frequency is much lower than the separation of any two internal vibrational levels in the sample molecules. In panel e, four different frequencies are detected, with two strong and two weak bands. The strong bands are the quantum beats of the uncomplexed iodine molecule with the wavepacket consisting of vibrational eigenstates $\upsilon = 4-7$, and the frequencies detected are the difference frequencies between two successive vibrational eigenstates of uncomplexed iodine, such as $\upsilon = 4$ and 5. This can be confirmed by comparing the detected frequencies to previous results on uncomplexed iodine in solid krypton.[11,14] The bands with lower intensities on both sides of the quantum beats are again polarization beats between the two different species in the sample. Then, at the highest frequencies (panel f in Figure 7), more quantum beats of the uncomplexed iodine molecule are detected, with the interfering vibrations being now two levels apart, such as $\upsilon = 4$ and 6.

Interestingly, a more detailed analysis of the polarization beat spectrum shows that there is only one vibrational frequency interfering with the uncomplexed iodine vibrations. This should not be the case if the signal is due to the I_2-Bz complex,

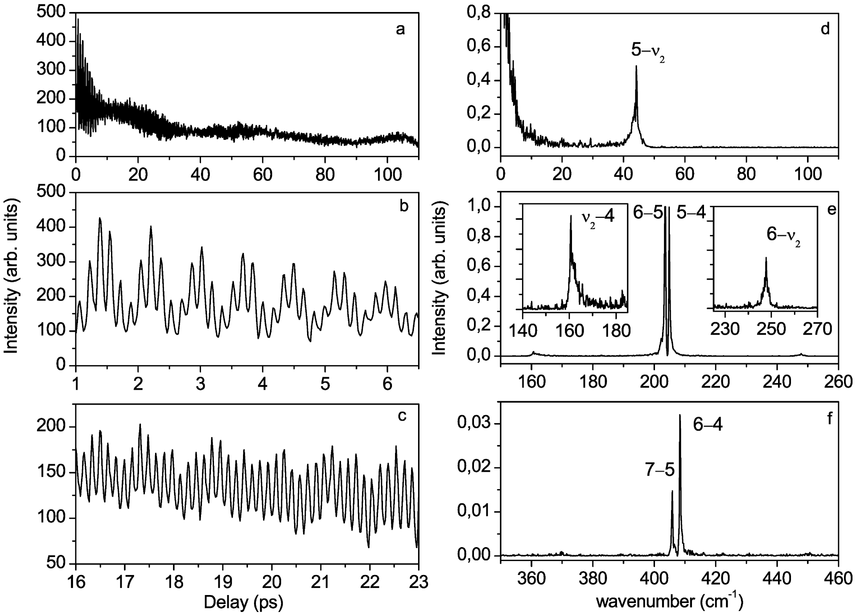

Figure 7. fs-CARS spectra of the Bz/I_2/Kr = 1/0.19/500 sample at T = 10 K (a)−(c) and its Fourier transform (d)−(f). The short-lived (∼10 ps) polarization beating between uncomplexed iodine (υ = 4−7) and the benzene ring stretch (ν_2) vibrations is seen in both frequency and time domains, together with the long-lived (>100 ps) quantum beats of uncomplexed iodine. The numbers in the band labels in frequency domain spectra (d)−(f) refer to the vibrational eigenstates of iodine, while ν_2 refers to the ring stretch vibration of benzene. No signal from I_2−Bz complex is visible in the spectra.

because the vibrational eigenstates of iodine are separated by only ∼200 cm^{-1}, and thus the vibrational wavepacket of the complexed iodine, excited by our broad-band fs-CARS cycle with a fwhm of the convolution of pump and dump pulses ∼730 cm^{-1}, would consist of several vibrational eigenstates, similarly to the uncomplexed iodine. Thus, another explanation for the polarization beats is needed, and this is offered by the uncomplexed benzene molecules in the sample, which are clearly detected in the IR and UV−vis measurements (Figures 1 and 4).[10,25] Although the excitation wavelengths are not resonant with any electronic transitions of benzene, the CARS process can still be initiated nonresonantly, however, with lower probability. This weak signal will then be "amplified" by the strong uncomplexed iodine signal exactly like in the iodine−xenon system,[11] the only difference being the reason for the weakness of the signal, which is now due to the electronically nonresonant process instead of the small concentration. The analysis of the polarization beat frequencies yields a value of 994 cm^{-1} for the interfering frequency, which matches the frequency of the strongly Raman active benzene ring stretch (ν_2) vibration (gas-phase Raman value 992 cm^{-1}),[26] easily reached by the fs-CARS wavelengths used here (the difference between the pump and dump pulse maxima is ∼1100 cm^{-1}). From the FTIR measurements, the frequency of the corresponding vibration in the complex is found to be 991.13 cm^{-1}, yielding a red shift of ∼3 cm^{-1} upon complexation, which corresponds fully with the MP2 calculations (see Table 2). Measurements with different wavelengths, where the difference of the pump and dump frequencies moved further away from the benzene ν_2 frequency, showed only the quantum beats of the uncomplexed iodine molecule, further confirming the assignment of the polarization beats being due to uncomplexed benzene. The dephasing time for the benzene ν_2 vibration is found from the polarization beat bandwidths to be ∼6 ps, which is, as expected, fast compared to the dephasing time of ∼50 ps for the uncomplexed iodine. This is also clearly visible in the time domain spectrum (left side of Figure 7), where the polarization beating pattern disappears in about 15 ps while the quantum beating of iodine molecule is still visible at delay times longer than 100 ps.

Unfortunately, no signal from the complexed iodine is visible in the fs-CARS signal. In addition to the measurement in Figure 7, several different pump and dump wavelengths were used to create different vibrational wavepackets, but none of the measurements showed signals from the I_2−Bz complex. This is somewhat surprising, as the resonance condition should be present for the complex, too, even though the B ← X transition is slightly shifted, as shown in Figure 2. Additionally, the IR, UV−vis, and the resonance Raman measurements confirm that the complex is present in the sample. The smaller concentration of the complex should not be a problem in detecting the complex due to the "amplification" in the polarization beats, which works even for a nonresonant process, as shown above. In addition, as can be seen from Table 1, the concentration ratio of the I_2−Bz complex to uncomplexed iodine in these experiments was higher than the concentration ratio of the I_2−Xe complex in our earlier experiments (∼0.33),[11] further confirming that the concentration of the complex should not be a limiting factor in detecting the polarization beats. Thus, the most plausible explanation for not detecting the CARS signal for the complex is another process competing with the CARS process, thus weakening the CARS signal of the complex below detection limit. One possible explanation is a two-photon absorption to the charge-transfer state of the complex, which is situated at about double energy when compared to the B ← X absorption (see Figure 1). As the oscillator strength for the CT absorption is large, the two-photon absorption can indeed be strong enough to diminish the intensity of the CARS process and damp it below detection limit. This situation is unfortunate, because the obvious idea of changing the fs-CARS wavelengths so that they would not match the CT two-photon absorption will also move us away from the B ← X resonance condition, weakening the uncomplexed iodine CARS signal too, thus making the detection of even weaker polarization beats much more challenging.

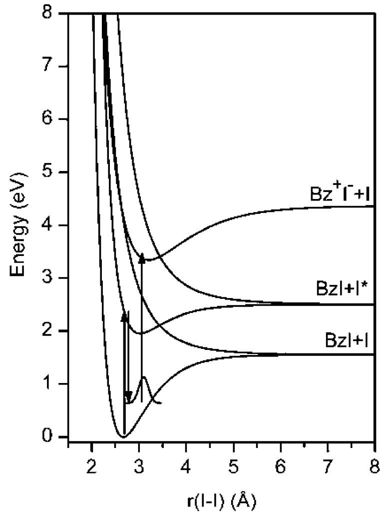

Figure 8. Potential curves of the I_2−Bz complex as a function of the I−I distance. The arrows represent the proposed control scheme for the bimolecular charge-transfer reaction exploiting the evolution of the ground-state vibrational wavepacket. The potential curves are adapted using parameters from refs 27−30).

Reaction Control of the I_2−Bz Complex. The possibility to manipulate vibrations of a molecule or a molecular complex by using a designed femtosecond pulse sequence opens up interesting possibilities for controlling the reactions of molecules or their complexes, as was shown theoretically by Tannor, Kosloff, and Rice.[12,13] The fs-CARS method offers a good starting point for this kind of experiment, as the process involves generating a vibrational wavepacket on the ground electronic state with a controlled sequence of two coherent femtosecond laser pulses. As the ground electronic state has no crossing repulsive states, the vibrational wavepacket will be long-lived and predissociation is not a problem, as often is the case with the excited electronic states.

The iodine−benzene complex isolated in solid krypton might be a good prototype for controlling a bimolecular reaction, due to its low-lying charge-transfer state and rather well-known properties. Isolating the complex in a rare gas matrix allows for a well-defined structure with only weak interactions with the environment, thus making the planning and explaining the experiment easier. The proposed scheme for controlling the charge-transfer reaction of the I_2−Bz complex is shown in Figure 8, where the potential curves are adapted using parameters from refs 27−30. The pump and dump pulses of the fs-CARS process are used as in the measurements in this paper, to generate a vibrational wavepacket of the selected vibrational eigenstates on the ground electronic state of the iodine molecule in the complex. Then, the wavepacket is allowed to evolve, so that it reaches a desired position and shape on the ground-state potential surface. At the right moment, the third pulse is used to excite the wavepacket to the charge-transfer state. Depending on the composition of the wavepacket and the delay between the dump and excitation pulses, it is possible to choose the position (here, in practice, the bond length of iodine molecule) where the wavepacket reaches the charge-transfer state. As can be seen from Figure 8, the direct Franck−Condon excitation to the CT state will lead to fast predissociation.[4−6] However, should the excitation happen after the evolution of a wavepacket on higher vibrational states of the ground electronic state, the outcome of the excitation, and thus the charge-transfer reaction, can be controlled by choosing the right excitation time. More specifically, the bottom of the potential well of the charge-transfer state might be reachable in such a way that the crossings with the repulsive states could be avoided and the complex would be "trapped" in the potential well with no obvious relaxation channel other than emission of a photon. This emission could then be used as an indication of the process being controlled in a desired way.

Our study, although the fs-CARS experiments did not fully reach the goal, implies that there should not be any general constraints against realizing this control scheme. The structure and properties of the I_2−Bz complex are now well known, allowing a rather detailed tailoring of the femtosecond laser pulses needed to design the wavepacket desired. From the resonance Raman measurements, the iodine vibrational energy levels in the ground-state complex are accurately known, and with the IR measurements, the structure has been experimentally confirmed to be of above-bond type, allowing a more detailed modeling or simulation of the process, if desired.

The vibrational eigenstates with v up to 8 are shown to be reachable using a resonance Raman process, however, with a smaller probability than for the uncomplexed iodine, presumably due to the faster electronic dephasing on the B state. This may present a problem in case the reaction control needs a vibrational wavepacket with much higher-lying vibrational eigenstates. A rough estimate for the vibrational eigenstate from which the potential minimum of the CT state at I−I bond length of 3.2 Å could be reached gives a value of $v \geq 20$, but even a smaller bond length may suffice, depending on the exact position of the crossings of the repulsive and bound states. In any case, judging from the resonance Raman bandwidths, the lifetime of the wavepacket on the ground electronic state allows for more than tens of round-trips before dephasing, indicating that there is plenty of time to wait for the right conformation to be reached before the excitation to the charge-transfer state.

The outcome of the fs-CARS experiments with no signal from the I_2−Bz complex seems rather discouraging but does not altogether rule out the possibility of using the CARS scheme for the reaction control. Even though the CARS signal was not detected here, the resonance Raman spectrum shows that it should in principle be possible. Possibly, it is necessary to change the pump and dump wavelengths outside the B ← X resonance, thus weakening the probability of the two-photon excitation to the charge-transfer state, which we now believe is diminishing the intensity of the CARS signal. This change, however, will weaken the CARS signal, and rather good sensitivity is required of the measurement.

At this moment, the coherent control of the bimolecular reaction between iodine and benzene molecules by using a predesigned fs-CARS sequence is still not a reality, but the work presented here brings the realization one step closer and outlines a general recipe for accomplishing it. Should the coherent control work with the I_2−Bz complex isolated in solid krypton, the same scheme might be applicable also to solid, liquid, and gas phase, bringing the coherent control of bimolecular reactions ever closer to real-life applications.

Conclusions

In this work, the 1:1 iodine−benzene complex was studied with several different spectroscopic methods in a solid krypton matrix with a prospect of using it as a model system in a coherently controlled bimolecular reaction. The UV−vis spectrum of the iodine molecule is shifted ~25 nm upon complexation with benzene, which is very close to the absorption shift upon dissolving iodine in liquid benzene. The absorption coefficient of the B ← X transition is estimated to be about 6 times larger for the complex than for the uncomplexed iodine. Several IR bands for the I_2−Bz complex are found and characterized, and the structure of the ground-state complex is experimentally confirmed to be of above-bond type. The electronic dephasing on the B state is found to be faster in the complex than for the uncomplexed iodine. The dephasing times of the iodine vibrations on the ground electronic state are estimated from the instrument limited bandwidths of the resonance Raman spectra to be longer than ∼10 ps, which is at most about 5 times faster than in the uncomplexed iodine molecule in krypton, indicating only a weak coupling of iodine with the benzene molecule in the complex. A fs-CARS signal from the complex was not detected at the wavelengths used here, possibly due to a competing two-photon excitation to the charge-transfer state of the complex. However, a polarization beating between uncomplexed iodine and uncomplexed benzene molecules was found, showing that the strong, electronically resonant signal of the iodine molecule can be used as an "amplifier" for an electronically nonresonant CARS signal of benzene. The prospects of controlling the charge-transfer reaction of the I_2−Bz complex using a fs-CARS scheme is discussed. The reaction control is found to be possible, but difficult to realize, due to the fast electronic dephasing on the B state and to the high sensitivity needed for the measurements.

Acknowledgment. This work was supported by the Academy of Finland (Decision Nos 122620 and 124974).

References and Notes

(1) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1948**, *70*, 2832–2833.

(2) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.

(3) Kiviniemi, T.; Hulkko, E.; Kiljunen, T.; Pettersson, M. *J. Phys. Chem. A* **2008**, *112*, 5025–5027.

(4) DeBoer, G.; Burnett, J. W.; Young, M. A. *Chem. Phys. Lett.* **1996**, *259*, 368–374.

(5) Cheng, P. Y.; Zhong, D.; Zewail, A. H. *J. Chem. Phys.* **1996**, *105*, 6216–6248.

(6) Zhong, D.; Zewail, A. H. *J. Phys. Chem. A* **1998**, *102*, 4031–4058.

(7) Lenderink, E.; Duppen, K.; Everdij, F. P. X.; Mavri, J.; Torre, R.; Wiersma, D. A. *J. Phys. Chem.* **1996**, *100*, 7822–7831.

(8) DeBoer, G.; Burnett, J. W.; Fujimoto, A.; Young, M. A. *J. Phys. Chem.* **1996**, *100*, 14882–14891.

(9) Weng, K.-F.; Shi, Y.; Zheng, X.; Phillips, D. L. *J. Phys. Chem. A* **2006**, *110*, 851–860.

(10) Fredin, L.; Nelander, B. *Mol. Phys.* **1974**, *27*, 885–898.

(11) Kiviniemi, T.; Kiljunen, T.; Pettersson, M. *J. Chem. Phys.* **2006**, *125*, 164302.

(12) Tannor, D. J.; Rice, S. A. *J. Chem. Phys.* **1985**, *83*, 5013–5018.

(13) Tannor, D. J.; Kosloff, R.; Rice, S. A. *J. Chem. Phys.* **1986**, *85*, 5805–5820.

(14) Kiviniemi, T.; Aumanen, J.; Myllyperkiö, P.; Apkarian, V. A.; Pettersson, M. *J. Chem. Phys.* **2005**, *123*, 064509.

(15) Kerenskaya, G.; Goldschleger, I. U.; Apkarian, V. A.; Fleischer, E.; Janda, K. C. *J. Phys. Chem. A* **2007**, *111*, 10969–10976.

(16) Tellinghuisen, J. *J. Chem. Phys.* **1982**, *76*, 4736–4744.

(17) Herzberg, G. *Infrared and Raman Spectra*; Van Nostrand Reinhold: New York, 1945; pp 363−365.

(18) Fredin, L.; Nelander, B. *J. Am. Chem. Soc.* **1974**, *96*, 1672–1673.

(19) Mebel, A. M.; Lin, H. L.; Lin, S. H. *Int. J. Quantum Chem.* **1999**, *72*, 307–318.

(20) Grozema, F. C.; Zijlstra, R. W. J.; Swart, M.; Duijnen, P. T. v. *Int. J. Quantum Chem.* **1999**, *75*, 709–723.

(21) Ammal, S. S. C.; Ananthavel, S. P.; Venuvanalingam, P.; Hedge, M. S. *J. Phys. Chem. A* **1998**, *102*, 532–536.

(22) Hulkko, E.; Kiljunen, T.; Kiviniemi, T.; Pettersson, M. *J. Am. Chem. Soc.* **2009**, *131*, 1050–1056.

(23) Almy, J.; Kizer, K.; Zadoyan, R.; Apkarian, V. A. *J. Phys. Chem. A* **2000**, *104*, 3508–3520.

(24) Faeder, J.; Pinkas, I.; Knopp, G.; Prior, Y.; Tannor, D. J. *J. Chem. Phys.* **2001**, *115*, 8440–8454.

(25) Merrithew, R. B.; Marusak, G. V.; Blount, C. E. *J. Mol. Spectrosc.* **1968**, *25*, 269–271.

(26) Shimanouchi, T. Molecular Vibrational Frequencies. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, http://webbook.nist.gov (retrieved November 25, 2008).

(27) Herzberg, G. *Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950.

(28) Mulliken, R. S. *J. Chem. Phys.* **1971**, *55*, 288–309.

(29) de Jong, W. A.; Visscher, L.; Nieuwpoort, W. C. *J. Chem. Phys.* **1997**, *107*, 9046–9058.

(30) Zanni, M. T.; Davis, A. V.; Frischkorn, C.; Elhanine, M.; Neumark, D. M. *J. Chem. Phys.* **2000**, *112*, 8847−8854; *J. Chem. Phys.* **2000**, *113*, 8854.

JP902012U