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Vibrational Characterization of the 1:1 Iodine−Benzene Complex Isolated in Solid Krypton

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The structure and properties of a 1:1 iodine−benzene complex isolated in an inert krypton matrix at low temperature have been studied with infrared and resonance Raman spectroscopy and with MP2 calculations. The structure of the ground-state complex is found to be unsymmetric, and the I−I vibrational frequency is found to be red-shifted by 3.94 cm^{-1} upon complexation. The experimental data agree well with computational results, leading to the conclusion that the I_2−Bz complex structure is not axial but of above-bond type, identically with other halogen−benzene complexes.

Introduction

The I_2−benzene complex has been a subject of numerous experimental and computational studies ever since Benesi and Hildebrand assigned its charge-transfer transition band in the UV spectrum of iodine−benzene solution.[1] It can be considered as a prototype of a complex having a low-lying charge-transfer excited state, and it is still an object of wide interest for example in elucidating the dynamics of charge-transfer reactions.[2–7]

Considering the amount of research done on this complex, it is surprising that there is still no clear consensus in the literature on such fundamental subjects as the ground-state structure of the complex and the effect of the complexation on the vibrational frequency of the iodine molecule. Most of the more recent computational work predicts an unsymmetric ground-state structure, where the iodine molecule is located either above one of the C−C bond centers or above one C atom of benzene.[2,7–9] The I_2 bond axis may also be slightly tilted from the axis perpendicular to the plane of the benzene ring (oblique structure).[2,7,8] However, there are also several studies that support the axial structure instead, with the iodine molecule located above the center of the benzene ring, perpendicularly to the benzene ring plane.[10–12] Especially, the matrix isolation studies by Nelander et al. claimed that the I_2−Bz complex is axial although the other halogen complexes have an unsymmetric structure.[11–13]

Most of the spectroscopic data on the I_2−benzene complex are measured from liquid samples, where usually no distinct features of a well-defined 1:1 complex are found.[14–19] Instead, the iodine vibration frequency shifts as a function of the benzene concentration, but no separate bands are detected for the monomeric and complexed iodine.[14,15] This is due to the fact that there is no well-defined 1:1 complex in the solution but the iodine molecule rather interacts dynamically with several solvent molecules.[14] An exception is the work of Besnard et al. who observed a separate Raman band for I_2−benzene complex in benzene/*n*-heptane mixtures at low temperature (213 K).[20] However, the relatively small mole ratio of *n*-heptane/benzene (5.5) used in the experiments leaves it uncertain whether the observed band was due to a 1:1 complex. In addition, in liquids, bandwidths are rather large, making it difficult to see small shifts in the vibrational frequencies and to characterize the shifts accurately. These facts make the experimental determination of the properties of a separate 1:1 complex more challenging.

The structures of halogen−benzene complexes other than the I_2−Bz have been studied also by X-ray crystallography.[21,22]The most recent results for the bromine complex[21] support the unsymmetric structure similar to the isolated 1:1 complexes.[11,13] However, to our knowledge, no experimental crystallographic data have been reported on the iodine complex, which was predicted to be different from the other complexes.[11–13] It should also be pointed out that the environment in a solid benzene−halogen crystal is very different from the environment in the gas phase or in an inert rare gas matrix, and extending these observations to cover the 1:1 complex structure should be made with caution.

In their femtosecond studies of the reaction dynamics of the I_2−Bz complex, Zewail et al. determined the structure of the transition state for the complex as oblique from the recoil direction of the iodine atom products.[4] However, this result cannot be taken as a direct evidence of the ground-state structure of the complex, as the laser excitation of the complex is highly selective to the tilted structure due to a larger transition moment.[2–4] In addition, in any ground-state structure of the I_2−Bz complex, the iodine molecule undergoes a large amplitude torsional motion, and even for the axial structure the excitation in an oblique conformation with femtosecond pulses is possible.[4] Thus, the question of whether the ground-state I_2−Bz complex is axial or not, is still lacking a conclusive experimental answer.

In this work, we have characterized the properties of the iodine−benzene complex isolated in a solid krypton matrix at low temperature by IR and resonance Raman spectroscopy. Using this technique, we can make sure that we are studying a well-defined, isolated 1:1 complex that is only weakly perturbed by its environment. Due to the resonance condition, a long vibrational progression for both the complexed and the monomeric iodine molecule is observed in the Raman spectrum, allowing an accurate determination of the vibrational parameters

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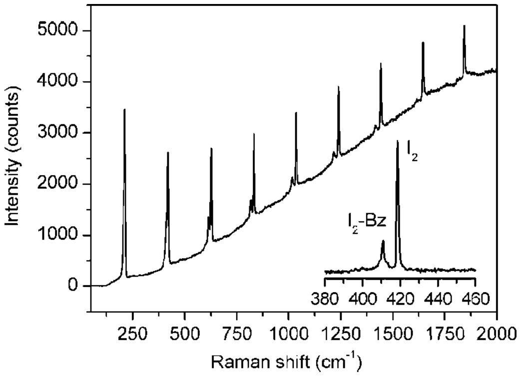

Figure 1. Resonance Raman spectrum of a Bz/I_2/Kr = 1/0.77/2000 sample at $T = 30$ K, showing the vibrational progression of both free and complexed iodine molecules. The inset shows the higher resolution spectrum of the $v = 2$ band with clearly separated bands for monomeric and complexed iodine.

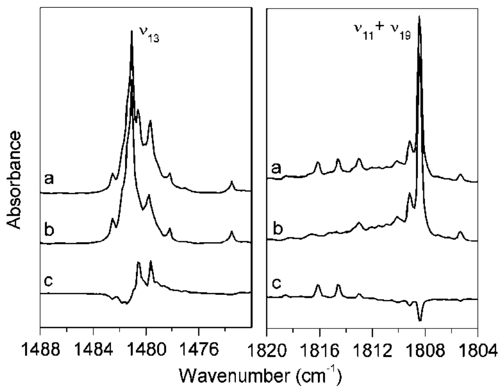

Figure 2. IR spectra for two benzene vibrations at $T = 40$ K: (a) Bz/I_2/Kr = 1/0.77/2000; (b) Bz/Kr = 1/2000; (c) the difference spectrum. The splitting in the I_2−Bz complex vibrations shows that the symmetry of the benzene molecule is broken.

for the complexed I_2. The IR spectrum of an identically prepared sample confirms that the structure of the complex is unsymmetric, which is also supported by our MP2 calculations.

Experimental and Computational Methods

The Bz/I_2/Kr = 1/0.77/2000 samples were prepared at $T = 40$ K in a liquid helium flow cryostat. As described earlier, this method produces matrices of very high optical quality.[23] The presence of a 1:1 complex was confirmed by studying the dependence of the IR spectrum on the benzene concentration. The resonance Raman spectra were measured at $T = 30$ K, using a single-mode, frequency doubled CW Nd:YAG laser (Alphalas, 532 nm), resonant with the B ← X transition of the iodine molecule, with two resolutions; 5 and 1 cm^{-1}. The frequency scale of the Raman spectra was calibrated using the vibrational frequencies of monomeric iodine in krypton determined earlier with high accuracy by femtosecond coherent anti-Stokes Raman spectroscopy from a similarly prepared sample.[23] The FTIR spectra were measured with a 0.25 cm^{-1} resolution at $T = 40$ K.

The computational evaluation of the complex geometries and harmonic vibrational frequencies was based on the MP2 level of theory as implemented in MOLPRO.[24] We used the contracted avdz basis set for the Bz atoms and the effective core potential ECP46MWB combined with the corresponding uncontracted vtz basis for the I_2. The computed displacement vector of the normal mode localized at the I−I vibration was further used in the calculation of the corresponding potential energy curve, which was then used to solve for the anharmonic vibrational energies taking into account the diagonal anharmonicity. The basis set superposition error was corrected throughout (structures, spectra) by the counterpoise procedure.

Results and Discussion

In the resonance Raman spectrum (Figure 1), the vibrational progressions for both complexed and monomeric iodine are clearly visible. The frequency shift of the complex is so small that the lowest frequency bands are only resolved in the higher resolution spectra. The complex bands are narrow (instrument limited, <1 cm^{-1}) single lines, indicating a well-defined structure of the complex and a highly homogeneous matrix.

The vibrational progression of the complexed iodine allows us to determine accurate spectroscopic parameters for the I−I vibration. The Birge−Sponer analysis of the high resolution data yields the values $\omega_e = 207.22 \pm 0.07$ cm^{-1} and $\omega_e x_e = 0.612 \pm 0.015$ cm^{-1} for the complex. Upon complexation, the harmonic vibrational frequency (ω_e) of the iodine molecule is thus red-shifted by 3.94 cm^{-1} from the monomeric iodine vibration in solid Kr ($\omega_e = 211.16 \pm 0.01$ cm^{-1}). This result agrees well with our anharmonic computational result of a 6.8 cm^{-1} red shift. It also corresponds to the red shift of 3.5 cm^{-1} found by Besnard et al.[20] Interestingly, the anharmonicity constant is reduced 0.02 cm^{-1}, showing a perturbation of the vibrational potential upon complexation.

In the infrared spectrum of Bz/I_2/Kr sample, several new bands appear when compared to a Bz/Kr sample, corresponding to forbidden transitions of monomeric benzene such as ν_2 (a_{1g}) and ν_{11} (e_{1g}) (numbering according to Herzberg[25]). The activation of these bands was also detected in matrix isolation experiments by Nelander et al.,[11,12] who assigned the I_2−Bz structure as axial. This assignment was mainly based on the absence of other induced transitions that they observed for other halogen−benzene complexes. However, as a new observation, we have additionally found a splitting in several vibrational bands of the complexed benzene, corresponding to degenerate vibrations of pure benzene. Two of these bands (ν_{13} (e_{1u}) and $\nu_{11} + \nu_{19}$ (e_{1u})) are shown in Figure 2 for both I_2/Bz/Kr and Bz/Kr samples.

The splitting of the IR bands shows that the C_6 symmetry of the benzene molecule is broken upon complexation. The same effect has been observed for other halogen−benzene complexes like Br_2−Bz and Cl_2−Bz.[13] The C_6 symmetry is broken in the above−bond structure (C_s) but not in the axial structure (C_{6v}), leading to the conclusion that the ground-state structure of the isolated complex is indeed not axial, contradictory to Fredin and Nelander's conclusion.[11] The value of the splitting of the ν_{13} band, 0.96 cm^{-1}, also agrees with several computational values that vary between 1−4 cm^{-1} depending on the reference.[2,8,26] In this work, the splitting is calculated as 3.7 cm^{-1}.

The observation of only two induced fundamental absorptions for the complex is in agreement with the computed intensities, which predict that all the other induced bands should be much weaker.[26] The above−bond structure is also predicted to be lower in energy than the axial structure by ab initio calculations.[2,7–9] One more argument in favor of the above−bond structure is that we observed the strong charge-transfer absorption of the complex at 291 nm and this transition is forbidden for the axial structure.[2,3,8,9]

We have also calculated the structure and vibrational properties for the Br_2−Bz complex, and the results are very similar to the I_2−Bz complex. Recently, the structure of the Br_2−Bz complex was experimentally determined to be of above−bond type by X-ray diffraction.[21] The observed structure is in agreement with the calculations as well as with the matrix isolation studies of Fredin and Nelander.[13] Our new experimental findings bring the iodine complex to the same point where the calculations and experiments agree on the ground-state structure. Thus the most recent results, both experimental and computational, now support the above−bond structure consistently for all halogen−benzene complexes.

Conclusions

The experimental and computational data presented here give new information about the nature of the isolated 1:1 ground-state iodine−benzene complex. Using resonance Raman spectroscopy, and by isolating the complex in an inert krypton matrix, we have been able to measure the vibrational progression of the I−I vibration in the complex and to extract its spectroscopic parameters with high accuracy. The shift of the I−I vibration upon complexation also agrees well with the computational data. The above−bond structure of I_2−Bz complex is supported by both computational and experimental results, which agree well with each other. Thus, our results support a consistent structure for all halogen−benzene complexes.

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Supporting Information Available: Computed cartesian coordinates for the I_2−benzene complex structure and vibrational frequencies with corresponding intensities (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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

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

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

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

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

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

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

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

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

(10) Ferguson, E. F. *J. Chem. Phys.* **1956**, *25*, 577–578.

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

(12) Engdahl, A.; Nelander, B. *J. Chem. Phys.* **1983**, *78*, 6563–6568.

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

(14) Rosen, H.; Shen, Y. R.; Stenman, F. *Mol. Phys.* **1971**, *22*, 33–47.

(15) Shen, Y. R.; Rosen, H.; Stenman, F. *Chem. Phys. Lett.* **1968**, *1*, 671–674.

(16) Yarwood, J.; Person, W. B. *J. Am. Chem. Soc.* **1968**, *90*, 594–600.

(17) Klaboe, P. *J. Am. Chem. Soc.* **1967**, *89*, 3667–3676.

(18) Stammreich, H.; Forneris, R.; Tavares, Y. *Spectrochim. Acta* **1961**, *17*, 1173–1184.

(19) Lascombe, J.; Besnard, M. *Mol. Phys.* **1986**, *58*, 573–592.

(20) Besnard, M.; Del Campo, N.; Cavagnat, R. M.; Lascombe, J. *Chem. Phys. Lett.* **1989**, *162*, 132–136.

(21) Vasilyev, A. V.; Lindeman, S. V.; Kochi, J. K. *Chem. Commun.* **2001**, 909–910.

(22) Hassel, O.; Rømming, Chr. *Q. Rev. Chem. Soc.* **1962**, *16*, 1–18.

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

(24) MOLPRO, version 2006.1, a package of *ab initio* programs, Werner, H. J., et al., see http://www.molpro.net.

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

(26) This work, see Supporting Information.

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