

30 January 1998

Chemical Physics Letters 283 (1998) 1-6

CHEMICAL PHYSICS LETTERS

Spin-orbit transitions $({}^{2}P_{1/2} \leftarrow {}^{2}P_{3/2})$ of iodine and bromine atoms in solid rare-gases

Mika Pettersson^{*}, Janne Nieminen¹

Laboratory of Physical Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland

Received 1 September 1997

Abstract

Infrared absorptions of iodine and bromine atoms in solid rare-gases are presented. The isolated atoms are produced by UV-photolysis of HI or HBr in solid Ar, Kr and Xe. The absorptions are characterised by sharp zero-phonon lines and broad structured phonon side bands. Some of the zero-phonon lines are resolved and split into two components, separated by a few wavenumbers. The production of the atoms follow second-order kinetics indicating that the primary hydrogen atom undergoes a secondary reaction with the hydrogen halide producing a halogen atom and a hydrogen molecule. This is supported by the observation of the infrared absorptions of hydrogen molecules in concentrated matrices after photolysis. © 1998 Elsevier Science B.V.

1. Introduction

Halogen atoms have been extensively studied in rare-gas matrices. Production of the halogen atoms can be achieved by photolysing suitable precursor molecules in the matrix or by depositing a gas mixture through a discharge or a high temperature oven [1–3]. Halogen atoms have been directly observed by using laser induced fluorescence, ESR, or Mössbauer techniques. [1,4,5]. Engdahl and Nelander indirectly observed iodine and bromine atoms complexed with different molecules, by recording the infrared absorptions of the complexed molecules [3,6–8]. many authors [9–12]. Despite the fact that matrix isolation combined with IR-absorption measurements is a common method we are not aware of infrared absorption detection of halogen atoms in rare-gas matrices. In the gas phase these transitions, which are strictly forbidden within the electric dipole selection rules, have been extensively studied and they have been found to be pure magnetic transitions [13,14]. For iodine atoms, the integrated absorption cross section was found to be $1.05(\pm 0.25) \times 10^{-23}$ cm² [13].

The spin-orbit transition of the iodine atom has been observed in emission in rare-gas matrices by

During resent years, we have conducted a series of experiments with rare-gas matrices doped with hydrogen halides [15–20]. UV-photolysis of such matrices leads to the dissociation of the precursor and subsequent trapping of the neutral atoms. Moreover, several different molecular ions have been

^{*} Corresponding author. E-mail: mika.pettersson@csc.fi.

¹ Present address: Customs Laboratory, Tekniikantie 13, P.O. Box 53, 02150 Espoo, Finland.

^{0009-2614/98/\$19.00 © 1998} Elsevier Science B.V. All rights reserved. *PII* \$0009-2614(97)01305-5

observed as a consequence of the excitation of charge-transfer and trapping of the positive and negative charges [21,22]. In these experiments our mainv detection scheme has been FTIR-spectroscopy and in the course of these experiments we have frequently found absorptions, which can be directly assigned to halogen atoms.

In this Letter, the infrared absorptions of iodine and bromine atoms in Ar, Kr, and Xe matrices are presented. The bromine absorptions and the absorptions of iodine atom in Ar and Kr are reported. Iodine atom absorption in Xe was reported earlier in connection with our studies of the mechanism of formation of HXel [20].

2. Experimental

Hydrogen iodide was synthesized from iodine, red phosporous and water [23] and purified by low temperature distillation. HBr of 99% purity (Matheson) was used without further purification. The purities of the rare-gases were Ar (99.999%), Kr (99.997%, CF₄ free) and Xe (99.997%, CF₄ free) and they were not further purified. The gas mixtures were deposited onto a CsI window through a 1/16 in stainless steel capillar. Closed cycle helium cryostats (AirProducts, DE-202, HS-4) were used in the experiments.

The FTIR spectra were recorded with a Nicolet 60 SX FTIR spectrometer with a resolution of 1.0 cm^{-1} . In the mid infrared region a KBr beamsplitter and MCT detector were used and in the near-infrared region a Quartz beamsplitter and InSb detector were used. The samples were photolysed with an excimer laser (ELI-76, Estonian Academy of Sciences), operating at 193 or at 248 nm, pulse energy varying between 1-50 mJ.

3. Results and discussion

The infrared absorptions resulting from the photolysis of HI-doped Ar, Kr and Xe matrices at 7 K are presented in Fig. 1. The main features consist of the sharp peak and the broad structured side band on the blue side of the sharp absorption. The absorptions shift to higher energy and the difference between the sharp peak and the side band increases on



Fig. 1. Iodine atom absorptions appearing after UV-photolysis of HI doped rare-gas matrices.

going from Xe to Ar. Also, the width of the side band increases from Xe to Ar. The corresponding absorptions of the bromine atom recorded at 15 K are presented in Fig. 2 and they resemble the iodine absorptions. Especially, comparison of the spectra of different halogen atoms in the same rare-gas environment recorded at the same temperature look strikingly similar. The positions of the absorptions are collected in Table 1.

The observed absorptions can be assigned to isolated atoms by following arguments. The absorptions are produced in matrices with a wide range of doping (1:150–1:3000 were studied). They are only halogen dependent, since deuterated hydrogen halides produce the same absorption as hydrogen forms. There are no hydrogen halide absorptions, which would correspond to the atomic absorptions, which excludes the possibility of absorptions being due to a hydrogen halide–halogen atom-complex. One more



Fig. 2. Bromine atom absorptions appearing after UV-photolysis of HBr doped rare-gas matrices. An absorption belonging to a water molecule is marked with an asterix.

possibility is a complex between a molecular halogen and a halogen atom but this can be excluded, since the absorptions appear in diluted matrices,

Table 1

Observed wavenumbers of iodine and bromine atoms in Ar, Kr and Xe. ZPL = zero-phonon line, PSB = phonon side band. The wavenumbers of the phonon side bands are the resolved maxima of the broad bands. Iodine atom absorptions are recorded at 7 K and bromine atom absorptions at 15 K

	Ar (cm ^{-1})	$\operatorname{Kr}(\operatorname{cm}^{-1})$	$Xe (cm^{-1})$	Gas phase (cm ⁻¹)
I (ZPL)	7620.1	7551.5	7456.6	7603 ^a
	7615	7548		
I (PSB)	7670	7585	7483	
		7598	7497	
Br (ZPL)	3699.3	3662.7	3623.1	3685 ^b
	3694.5			
Br (PSB)	3743	3696	3648	

^aRef. [13].^bRef. [14].

where mostly monomers and some dimers of the hydrogen halides are visible. The heavy halogen atoms do not diffuse at the temperatures used, which means that the formation of such a complex would require total photolysis of a trimer.

The thermal behaviour of the iodine atom absorption in xenon is presented in Fig. 3. The main effect is the broadening and a blue shift on going to higher temperatures, the effect being reversible. Also, at higher temperatures, there is intensity growth on the red side of the sharp peak. This thermal behaviour applies to both halogen atoms in different matrices. All the spectral features can be explained if the sharp peak is assigned to an inhomogeniously broadened zero-phonon line (ZPL) and the broad features to phonon side bands (PSB). The positions of the ZPLs are red-shifted from the gas phase positions, except in argon where the ZPL exceeds the gas-phase value by a few wavenumbers. The relatively large intensity in the PSB indicates substantial electron-phonon coupling.



Fig. 3. Temperature dependence of the iodine atom absorptions in Xe. The changes are reversible.

The growth curves of the iodine and bromine absorptions as a function of the number of photolysis pulses are presented in Fig. 4. It is to be noted that the curves cannot be fitted by first-order expression but rather by a second-order expression. The same observation was made by LaBrake et al. when they studied the photogeneration of bromine atoms in solid xenon by observing the fluorescence from the Xe-Br charge-transfer states [24]. They suggested that the primary hydrogen atoms formed in the photolysis migrate extensive distances in the lattice due to their excess kinetic energy and react subsequently with HBr molecules producing H_2 and Br atoms. More evidence from this reaction is obtained from this study, because in some concentrated matrices (1/300-1/500) the formation of hydrogen molecules was observed during photolysis.

The IR and Raman spectra of hydrogen molecules in rare-gases are known [25–27]. We observed after



Fig. 4. Kinetics of the photoproduction of bromine and iodine atoms in Xe. Bromine data is from a HBr/Xe = 1/150 matrix photolysed by 248 nm irradiation. Iodine data is from a HI/XE = 1/500 matrix photolysed by 193 nm irradiation.

_				
Ľ	`a	h	A	1
r	a	U.	LU.	- 4

UV-photolysis-induced absorptions of hydrogen molecule in concentrated hydrogen halide doped rare-gas matrices

Matrix	This work (cm^{-1})	Previous work (cm^{-1})		
Ar	4124.4	4130 ^a		
	4131.6	4137 ^a		
	4135.8	4138 ^b		
Kr	4113.0	4130 ^b		
	4119.4			
Xe	4096.0	4121 ^b		
	4098.2			
	4102.6			
	4104.9			

^aRef. [25].^bRef. [26].

photolysis of HBr/Ar three bands at 4315.8, 4131.6 and 4124.4 cm^{-1} . The first two correspond with the 4137 and 4130 cm^{-1} bands observed by Smith et al. [25]. They assigned these bands to the O-branches of para and ortho hydrogen, respectively. However, we would expect to observe mainly the para-form because of the presence of a paramagnetic halogen atom, which should enhance the ortho-para conversion as was observed in the presence of oxygen [26,27]. The third band was not seen by Smith et al. [25] and it possibly belongs to complexed hydrogen molecules. In heavier rare-gases our results differ somewhat from the previously reported Raman values as can be seen from Table 2. If the Kr and Xe bands reported by Prochaska and Andrews [26] belong to isolated H_2 , then our hydrogen molecules must be perturbed by complexation. Careful comparison of a large numbers of spectra have shown that H₂-absorptions a re not correlated with the halogen atom absorptions. Thus, it seems that molecular halogens are the best candidates for the complexing partners, because they should be formed in concentrated matrices from multimers. It is not possible to say, whether the production of hydrogen molecules is due to the reaction between two hydrogen atoms, or reaction between a hydrogen atom and hydrogen halide. Most probably, both contribute, but further experiments are needed in order to solve this problem with confidence. An interesting observation concerning the hydrogen molecules was made. In annealing experiments, they were stable up to 40 K in argon, which is a surprisingly high temperature compared to the boiling point of hydrogen. Clearly, the interactions between the argon lattice and hydrogen molecules are significant.

Splitting of the zero-phonon lines in I/Kr, I/Ar and Br/Ar matrices was observed. It is possible that the other zero-phonon lines are also split but they are not resolved. The observed splittings were only visible at the lowest recorded temperatures and at higher temperatures the lines broadened and coalesced into one band. There are three possible explanations for the splitting. One component could be due to complexation of the halogen atom with, for example, a hydrogen molecule, but this alternative was rejected above. Another possiblity is the splitting of the fourfold degenerate ground-state due to lattice vibrations. In the perfect octahedral substitutional site the ground state belongs to the fourfold degenerate G species and the excited state to the doubly degenerate E species [28]. Asymmetric motion breaks the degeneracy of the ground state into two states [12]. Quite recently, Krylov et al. investigated the nonadiabatic dynamics of chlorine atom in solid Ar by computer simulations [29]. They found that the IRabsorption spectrum of the chlorine atom consists of a doublet because of the splitting of the ground state. However, our splittings are only a couple of wavenumbers, while the simulations of Krylov et al. on chlorine give 32 cm^{-1} for the splitting. Even more importantly, the intensity ratios of the two components did not obey the Boltzman populations of two levels separated by an energy difference between the two components. Unless the two levels have different absorption coefficients this possibility has to be rejected. The third possibility is the trapping of the atoms in slightly different, but well defined environments. This is supported by the observation that especially the higher energy component became substantially narrower after an annealing cycle, indicating strong thermal relaxation of the lattice around the halogen atom in this site. The changes, however were not so large indicating a more relaxed site even before annealing.

As a continuation of this work, we are studying the complexes of halogen atoms. The simplest starting point is a complex between a halogen atom and a rare-gas atom. Preliminary experiments have yielded the spin–orbit transitions of Xel in krypton and argon [30].

4. Conclusions

The spin-orbit transitions of iodine and bromine atoms in Ar, Kr and Xe matrices have been observed in absorption. These absorptions, which lie in the near infrared and mid-infrared regions consist of inhomogeniously broadened zero-phonon lines and of phonon side-bands. Some of the zero-phonon lines are split and the phonon side bands show structures at the lowest temperatures used (7 K). The splitting is attributed to the atoms being in slightly different environments. The atoms are generated by UVirradiation of hydrogen halide doped rare-gas matrices. In concentrated matrices hydrogen also molecule absorptions were observed.

Acknowledgements

M. Räsänen is thanked for the careful reading of the manuscript and for valuable comments. R. Timonen is thanked for the lone of the excimer laser.

References

- W. Lawrence, F. Okada, V.A. Apkarian, Chem. Phys. Lett. 150 (1988) 339.
- [2] V. Bondybey, G. Pimentel, P. Noble, J. Chem. Phys. 55 (1971) 540.
- [3] A. Engdahl, B. Nelander, J. Chem. Phys. 77 (1982) 1649.
- [4] M. Iwasaki, K. Toriyama, H. Muto, J. Chem. Phys. 71 (1979) 2853.
- [5] M. Van Der Heyden, M. Pasternak, G. Langouche, J. Phys. Chem. Solids 46 (1985) 1221.
- [6] A. Engdahl, B. Nelander, J. Chem. Phys. 78 (1983) 6563.
- [7] A. Engdahl, B. Nelander, Chem. Phys. Lett. 106 (1984) 527.
- [8] A. Engdahl, B. Nelander, Chem. Phys. 100 (1985) 273.
- [9] A.C. Becker, J. Langen, H.M. Oberhoffer, U. Schurath, J. Chem. Phys. 84 (1986) 2907.
- [10] R. Böhling, J. Langen, U. Schurath, Chem. Phys. 130 (1989) 419.
- [11] M. Macler, J.-P. Nicolai, M.C. Heaven, J. Chem. Phys. 91 (1989) 674.
- [12] W.G. Lawrence, V.A. Apkarian, J. Chem. Phys. 101 (1994) 1820.
- [13] T.-K. Ha, Y. He, J. Pochert, M. Quack, R. Ranz, G. Seyfang, I Thanopoulos, Ber. Bunsenges. Physik. Chem. 99 (1995) 384.
- [14] J.D. Capbell, J.V.V. Casper, Chem. Phys. Lett. 10 (1971) 436.

- [15] H. Kunttu, J. Seetula, M. Räsänen, V.A. Apkarian, J. Chem. Phys. 96 (1992) 5630.
- [16] M. Räsänen, J. Seetula, H. Kunttu, J. Chem. Phys. 98 (1993) 3914.
- [17] H. Kunttu, J. Seetula, Chem. Phys. 189 (1994) 273.
- [18] M. Pettersson, J. Lundell, M. Räsänen, J. Chem. Phys. 102 (1995) 6423.
- [19] M. Pettersson, J. Lundell, M. Räsänen, J. Chem. Phys. 103 (1995) 205.
- [20] M. Pettersson, J. Nieminen, L. Khriachtchev, M. Räsänen, J. Chem. Phys., accepted for publication.
- [21] M.E. Fajardo, V.A. Apkarian, J. Chem. Phys. 89 (1988) 4102.
- [22] M.E. Fajardo, V.A. Apkarian, J. Chem. Phys. 89 (1988) 4124.

- [23] J.R. Partington, General and Inorganic Chemistry, Macmillan, London, 1946.
- [24] D. LaBrake, E.T. Ryan, E. Weitz, J. Chem. Phys. 102 (1995) 4112.
- [25] G.R. Smith, J.A. Warren, W.A. Guillory, J. Chem. Phys. 65 (1976) 1591.
- [26] F.T. Prochaska, L. Andrews, J. Chem. Phys. 67 (1977) 1139.
- [27] J.A. Warren, G.R. Smith, W.A. Guillory, J. Chem. Phys. 72 (1980) 4901.
- [28] F.A. Cotton, Chemical Applications of Group Theory, 2nd ed., Wiley, New York, 1971.
- [29] A.I. Krylov, R.B. Gerber, R.D. Coalson, J. Chem. Phys. 105 (1996) 4626.
- [30] M. Pettersson, E. Isoniemi, V. Hänninen, M. Räsänen, work in progress.