Site effects in the VUV-spectroscopy of chlorine atoms in neon matrices

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Excitation and emission spectra of chlorine atoms isolated in neon matrices were studied in the VUV spectral range using synchrotron radiation. Spectra of the electronic transitions between the ${}^{2}P$ ground state and the first ${}^{2}P$ and ${}^{2}D$ excited states clearly show the existence of three different possible sites for the chlorine atom in a neon surrounding. By annealing, a rearrangement takes place so that only one site is left. The fine structure of the excitation and emission peaks shows the spin-orbit splittings of the electronic states with values very close to the gas phase.

1. Introduction

A large amount of studies, both experimental and theoretical have been reported on the spectroscopy of atoms isolated in rare gas matrices. Most of them concern rare gas and metal atoms [1]. Instead of the expected twofold ²P spin-orbit splitting, a splitting into three components of the ²P_{3/2}, ²P_{1/2} \leftarrow ²S_{1/2} transitions was observed for alkali and noble metal atoms. Several proposals have been made to account for this observed triplet structure of the ²P \leftarrow ²S transition: the static distorted lattice effect [2–5], exciplex formation between the excited atom and a host atom [6,7] and more, recently, the dynamic Jahn-Teller effect [8–17].

In many of these experimental publications, it was shown, that the samples have to be carefully prepared because otherwise multiple trapping sites occur, which make the assignment difficult [18,19].

The present investigation of chlorine atoms in neon matrices is an additional contribution to this field.

The ground state has ²P character and the spin-orbit splitting is so large that only the lower $(3s^2, 3p^5)$ ²P_{3/2} state is occupied in the cold matrix. From this ground state, we have excited the $(3s^2, 3p^4, 4s)$ ²P_{1/2,3/2} and $(3s^2, 3p^4, 4s)$ ²D_{3/2,5/2} doublet components which have a spin-orbit splitting in the gas phase of 80 and 0.2 meV, respectively [20]. After a fast relaxation to the respective lower component, we could observe the fluorescence down to the ²P ground state with a gas-phase spin-orbit splitting of 109 meV.

Our results show that the chlorine atom occupies three different sites in the neon matrix, so that three sets of spectra were obtained. Each set shows spinorbit splitting and intensity ratios very similar to the gas-phase values. No additional splitting of the ²P states was observed, in contrast to the alkali and noble metal atoms in rare gas matrices.

2. Experiment

The measurements were carried out with synchrotron radiation at the experimental station HIGITI of the Synchrotron Radiation Laboratory HASYLAB at DESY/Hamburg. The apparatus and the preparation technique are described elsewhere [21]. In order to extend the fluorescence detection to 110 nm, an EMI 9426B Photomultiplier in an argon atmosphere was used.

For the spectroscopy of chlorine atoms in neon matrices, samples of a mixture of Cl_2 and neon were prepared and the chlorine was photolysed afterwards. The photolysis was done by shining the sample with undispersed light from the primary monochromator. The atomic chlorine emission increased during photolysis reaching a plateau after some minutes. Highest intensity was achieved with a mixture of 0.02% Cl_2 in neon. After this photolysis, the amount of chlorine atoms was constant for the time of investigation (≈ 5 h).

3. Results and discussion

Fig. 1 shows excitation and emission spectra of the transition $3p^4$, $4s^2P_{3/2,1/2} \leftrightarrow 3p^{5\,2}P_{3/2,1/2}$ of the chlorine atom in neon matrix. For a better comparison, all features are normalized to the same height. Due to the large Stokes shift, excitation and emission spectra are well separated. The mean-energy blue-shift with respect to the gas phase [20] is 810 meV in excitation and 150 meV in emission. By a careful



Fig. 1. Emission and excitation spectra of the transition $(3p^4, 4s)$ ${}^2P_{3/2,1/2} \leftrightarrow (3p^5) {}^2P_{3/2,1/2}$ of atomic chlorine in neon matrix for the three different sites.

choice of the excitation and emission energy, it was possible to separate three emission and three excitation spectra which have the same spectral shape except some features due to spectral overlap, but are situated at different energies. In this way, three pairs of excitation/emission spectra could be observed and were assigned to three different sites numbered 1, 2 and 3.

The assignment of these pairs of excitation/emission spectra to three different sites is proved by an annealing experiment. Fig. 2 shows the excitation spectrum of the total fluorescence between 9.1 and 9.6 eV for different temperatures. The spectrum at 5 K shows a convolution of the three sites. With increasing temperature, site 1 and 3 disappear irreversibly, so that for well annealed samples only site 2 is left. Also lifetime measurements corroborate this interpretation since all three emissions have the same lifetime of 1.8 ns. This value, corrected for the refractive index of the solid neon [22] gives a lifetime in vacuum of 2.5 ns, which is equal to the gas-phase lifetime (2.5 ns [23]). Wiggenhauser et al. have shown, that the Jahn-Teller components of an atomic level have different lifetimes [24].

As mentioned above, the spectral shape of all emissions and all excitations is very similar. It can be well fitted by the sum of two Gaussian curves for the emission as well as for the excitation as shown in fig. 3a for site 2. From these fits, the energetic positions, halfwidths and intensity ratios of the two components are derived and collected in table 1,



Fig. 2. Excitation spectra of the total emission of the ${}^{2}P$ state in atomic chlorine for different temperatures of the matrix.



Fig. 3. (a) The two spin-orbit components of the transitions ${}^{2}P \leftrightarrow {}^{2}P$ in emission and in excitation. (b) The emission and excitation spectra of the ${}^{2}D \leftrightarrow {}^{2}P$ transition of site 2.

where also the gas-phase values are included for comparison [23]. For a better understanding of the transitions, an energy-level diagram of the chlorine atom is drawn in fig. 4. The $3s^2$, $3p^5$ ground state is split into the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ levels with a separation of 109 meV. Due to this splitting, only the lower ${}^2P_{3/2}$ state is occupied at a temperature of 5 K. From this level, excitation takes place to the two components of the $3s^2$, $3p^4$, $4s {}^2P_{1/2,3/2}$ states at ≈ 9.2 eV, which are split by 80 meV. The intensity ratio of these two transitions is measured to be 0.29 [23]. After excitation, the ${}^2P_{1/2}$ state will relax to the lower ${}^2P_{3/2}$ level and this state will decay to the two components of the ground state with an intensity ratio of 5.3 [23]. Our values in neon matrix show a close



Fig. 4. Energy level diagram of atomic chlorine for the electronic states discussed.

correspondence to these gas-phase data. There is no evidence for a Jahn-Teller splitting of the levels as for metal atoms, and no change of the spin-orbit splitting of a chlorine atom in neon matrix is observed.

The same observation can be made when studying the next-higher electronic excitation to the ${}^{2}D_{5/2,3/2}$ states. As shown in the energy-level diagram in fig. 4 the spin-orbit splitting of the ${}^{2}D$ state is negligibly small (0.21 meV [20]), so that we expect only one excitation peak. If we assume a relaxation to the lower ${}^{2}D_{5/2}$ state, we would expect only one emission line to the ${}^{2}P_{3/2}$ component of the ground state, because the ${}^{2}D_{5/2} \rightarrow {}^{2}P_{1/2}$ transition is forbidden. But the energy splitting of ${}^{2}D_{5/2} \rightarrow {}^{2}D_{3/2}$ is so small, that both states are occupied and, therefore, we observe two

Table 1		
Spectroscopic data of the transition (3p ⁴ , 4s)	${}^{2}P_{3/2,1/2} \leftrightarrow (3p^{5}) {}^{2}P_{3/2,1/2}$ in gas-phase [23] and in the three sites of the neon matrix

		Energy (eV)	fwhm (meV)	Energy (eV)	fwhm (meV)	Splitting (meV)	I_1/I_2
emission	gas-phase	9.202	-	9.093	-	109	5.3
	site 1	9.413	75	9.305	85	1 08	3.5
	site 2	9.366	90	9.256	80	110	5.3
	site 3	9.288	85	9.176	85	112	6.9
excitation	gas-phase	9.282	-	9.202	-	80	0.29
	site l	9.95 7	120	9.891	120	66	0.4
	site 2	10.256	130	10.176	124	80	0.21
	site 3	10.074	166	9.987	153	87	0.34

		Energy 1 (eV)	fw hm (meV)	Energy 2 (eV)	fwhm (meV)	Splitting (meV)	I_{1}/I_{2}
emission	gas-phase	10.429	_	10.320	-	109	1.9
	site 1	10.646	73	10.526	82	120	1.3
	site 2	10.675	63	10.563	65	112	1.5
excitation	gas-phase	10.429	_				
	site 1	11.083	161				
	site 2	11.362	144				

Table 2

Spectroscopic data of the transition $(3p^4, 4s) {}^2D_{5/2,3/2} \leftrightarrow (3p^5) {}^2P_{3/2,1/2}$ in gas-phase [23] and in the three sites of the neon matrix

emission lines to the ground-state components with an energy splitting and intensity ratio close to the gasphase values. Fig. 3b shows the emission and excitation spectrum of the site 2 as an example. Because of the smaller halfwidth of the emission lines, the splitting is much more pronounced. As expected, the excitation consists of only one single line with a symmetric Gaussian shape. The energies and intensities are shown in table 2 for the sites 1 and 2. The site 3 can also be excited, but has a completely different deexcitation channel, which will be the subject of a forthcoming paper [25]. From this table, one can conclude that, as for the ²P state, no Jahn-Teller splitting and no change of the spin-orbit splitting are observed.

An interesting result is obtained when the gas-tomatrix shifts of the ²P and ²D excitations in the different sites are compared. Fig. 5 shows the spectra of



Fig. 5. Comparison of the excitation spectra of the ${}^{2}D$ and ${}^{2}P$ state of atomic chlorine in neon matrix for all three sites with a relative energy scale.

²P and ²D excitations with a relative energy scale. It is seen that the gas-to-matrix shifts of all sites are similar for the ²P and ²D states. This illustrates the fact that in both cases a 3p electron is excited into a 4s orbital which is interacting with the crystal environment around the different sites. Because the environment is not changed during excitation, the interaction is nearly the same for the ²P and ²D states so that similar splittings occur. But after excitation, the neon environment around the excited chlorine atom will rearrange in a different manner for every site and electronic state. Therefore, the emission energies and Stokes shifts are quite different.

4. Conclusion

We have measured excitation and emission spectra of the electronic transitions between the ²P ground state and the first ²P and ²D excited states of chlorine atoms in neon matrix. Three sites of the chlorine atom in neon surrounding could be distinguished. For every site, a splitting was observed, which could be assigned to the spin-orbit splitting of the chlorine atomic states with values close to the gas phase. Also the lifetime, corrected for the refractive index of solid neon, is equal to the gas-phase lifetime.

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