



## Temperature dependence of dissociative electron attachment to 1-bromo-2-chlorobenzene and 1-bromo-3-chlorobenzene

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### ABSTRACT

Dissociative electron attachment (DEA) to 1-bromo-2-chlorobenzene (1,2-C<sub>6</sub>H<sub>4</sub>BrCl) and 1-bromo-3-chlorobenzene (1,3-C<sub>6</sub>H<sub>4</sub>BrCl) is studied in a crossed electron/ molecular beams experiment in the electron energy range between about 0 and 2 eV and in the gas temperature range from 377 to 583 K. For both molecules the two fragment anions Cl<sup>-</sup> and Br<sup>-</sup> are formed. The ion yields of both Br<sup>-</sup> and Cl<sup>-</sup> show a pronounced temperature effect when the gas temperature is raised from 377 to 583 K. These DEA processes can be well interpreted qualitatively with thermodynamics calculations within adiabatic approximation scheme, in particular, the thermally excited out-of-plane bending and C–Cl/Br bond stretching vibrations may be closely related to the Cl<sup>-</sup>/Br<sup>-</sup> branching of the temporary negative anions of 1,2- and 1,3-C<sub>6</sub>H<sub>4</sub>BrCl.

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### 1. Introduction

Dissociative electron attachment (DEA) to molecules is a reaction relevant in many fields of basic and applied science (electrical discharges, plasmas, atmospheric chemistry, interstellar chemistry, radiation chemistry, etc.). In the initial step of DEA a neutral molecule captures a free electron to form a transient negative ion (TNI) state. Subsequently this TNI can undergo dissociation (DEA) or autodetachment as competitive reaction channel. The observation of parent anions within mass spectrometric timescales occurs only in several special cases. Halogenated hydrocarbons (MX) belong to the group of molecules showing the highest DEA cross sections [1]. The reactive species produced, a halogen anion X<sup>-</sup> and a hydrocarbon radical M, play an important role in dry etching plasmas used in very large scale semiconductor manufacturing and in excimer and chemical laser plasmas. Moreover, such species are possibly also involved in the processes leading to ozone depletion in the atmosphere. There also exists a similarity between DEA to halohydrocarbons and the process of reductive dehalogenation promoted by bacteria in anaerobic sediments, sewage sludge and aquifer materials [2].

It has been shown in a number of studies in the past [3–8] and also in more recent studies [9–14] that the anion yield resulting from DEA may change considerably with temperature. This is

mainly due to the fact that the formation of the temporary negative ion (TNI) includes vibrational excitation. Thus, the occupation of the vibrational states of the neutral molecule can have strong effects on the vibrational states of the TNI and thus on its fragmentation behaviour. How this influence manifests itself in the ion yield curves of the individual fragments is a complex issue and depends largely on the relative position of the involved neutral and anionic potential energy surfaces. In addition, the temperature dependence reflects the thermodynamics of the particular dissociative attachment reaction and also gives some insight into the underlying mechanisms and dynamics. The study of temperature effects becomes particularly interesting in cases where competitive reaction channels are available.

In this contribution we study DEA to 1-bromo-2-chlorobenzene and 1-bromo-3-chlorobenzene in the electron energy range from 0 to 2 eV and in the gas temperature range from 377 to 583 K. The experiment consists of a crossed electron/molecular beam arrangement with a mass spectrometric detection for the anions formed. As shown below the temperature dependence of the DEA cross-sections in the low electron energy range shows a similar behaviour for both molecules.

### 2. Experiment

The present experiments are performed in the Bratislava laboratory with a crossed electron/molecular beam apparatus. The experimental setup has been described previously in detail [7,15] and thus only a brief description will be given here. The electron

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beam is formed by means of a trochoidal electron monochromator. In the present experiments the instrument is operated at an electron energy resolution of about 90 meV (Full-width-at-half-maximum FWHM). Calibration of the electron energy scale and estimation of the electron energy resolution is carried out using the well known electron attachment process  $SF_6^-/SF_6$ . The molecular beam is produced in an effusive molecular beam source (MBS) which is temperature controlled. The beam is formed by effusing the gas from the source through a channel (0.5 mm diameter and 4 mm long) into vacuum. The vapor of the sample is introduced into the MBS via a precision leak valve which is connected to a (unheated) flask containing the liquid. The 1-bromo-2-chlorobenzene and 1-bromo-3-chlorobenzene samples were obtained from Sigma Aldrich with a stated purity of  $\geq 99\%$  and are used without further purification. The pressure inside the MBS (typically 1 Pa) is measured by a capacitance manometer providing absolute pressure values. For such a molecular beam source it is well known that the gas density  $n_0$  in the beam varies with the gas temperature  $T$ ,

$$n_0 \propto T^{-0.5} \quad (1)$$

The negative ions formed by the intersecting electron and molecular beams are extracted by a weak electric field ( $1 \text{ V m}^{-1}$ ) and focused into a quadrupole mass spectrometer. The mass analyzed negative ion signal is then detected as a function of the electron energy at different target gas temperatures. Due to the large mass difference (44 u) between the  $Cl^-$  and  $Br^-$  negative ions and due to the detection of no other fragment anions within the sensitivity range of the apparatus (see below) the quadrupole mass spectrometer may be tuned to rather low resolution and thus high transmission efficiency. Under these conditions, there are negligible differences in the transmission of the different ions through the mass spectrometer. The mass selected negative ions are detected as a function of the electron energy in a single ion counting mode using a secondary electron multiplier. We note that the lowest temperature studied was 377 K because at lower temperatures the performance of the monochromator, which was heated additionally by two bulbs mounted in the chamber, deteriorated strongly.

### 3. Results and discussion

In the energy range from about 0 to 2 eV the fragment ions  $Br^-$  and  $Cl^-$  are the only negative ions observable in DEA to 1,2- $C_6H_4BrCl$  and 1,3- $C_6H_4BrCl$ . No molecular anion can be observed within the time frame of the measurement and the sensitivity range of the apparatus. Fig. 1 shows the anion efficiency curves of both fragment anions for 1,2- $C_6H_4BrCl$  recorded at different gas temperatures. The anion efficiency curves are measured in the gas temperature range between 377 and 583 K for  $Cl^-$  and between 377 and 500 K for  $Br^-$ , respectively. The electron energy resolution for all measurements is about 90 meV. The ion yields for  $Br^-$  and  $Cl^-$  at 377 K are the bottom curves, while the yields at higher temperature are shifted upwards for better visibility. We observe that at 377 K the  $Br^-$  yield is a factor of about 40 higher than that of  $Cl^-$ . At 377 K  $Br^-$  (Fig. 1a) shows a threshold peak close to  $\approx 0$  eV, a resonance at 0.26 eV, and weak peaks at 0.75 and 1.13 eV. When increasing the gas temperature to 500 K we can see an obvious change of the ion yield: the threshold peak grows relative to the 0.26 feature. Even more pronounced is the temperature effect for  $Cl^-$  (Fig. 1b) where the measurements are extended also to higher gas temperatures. While at 377 K only one resonance at 0.54 eV can be observed, a threshold peak and further peaks at 0.85 and 1.2 eV appear when the gas temperature is raised to 583 K. We may assign these additional peaks or shoulders on the high energy tail of the 0.54 eV peak to a true physical effect, i.e., excitation of vibra-

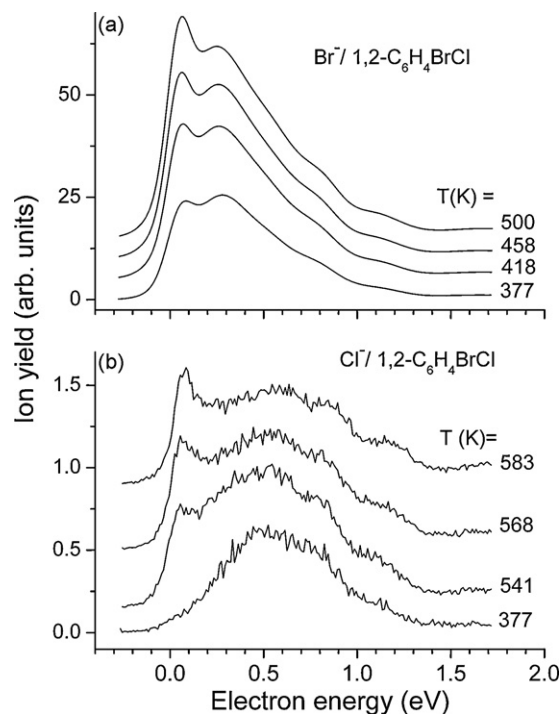


Fig. 1. (a)  $Br^-$  and (b)  $Cl^-$  ion yields for DEA to 1,2- $C_6H_4BrCl$  measured at different gas temperatures, respectively.

tions in the molecules. However, these peaks could also arise as an artifact of the utilized trochoidal electron monochromator (see discussion in [16]) which seems to be more pronounced at increased temperatures. A check of the  $Br^-$  ion yield with a hemispherical monochromator does not show any structure on the high energy tail and thus we rather ascribe these peaks to an artifact.

Qualitative very similar anion efficiency curves are obtained for  $Cl^-$  and  $Br^-$  in DEA to 1,3- $C_6H_4BrCl$  investigated in the temperature range between 380 and 583 K. The corresponding ion yields are shown in Fig. 2. For 380 K the  $Br^-$  yield peaks at 0.19 eV and the peak position is slightly shifted to the red at higher gas temperature. Moreover, at elevated temperatures a threshold peak close to zero eV and further peaks at 0.55, 0.75 and 1.08 eV become apparent. For  $Cl^-$  at 380 K only one dominant resonance exists at 0.48 eV, however, at elevated gas temperatures peaks appear at about zero, 0.8 and 1.1 eV. At the gas temperature of 380 K the formation of  $Br^-$  is about 50 times higher than that of  $Cl^-$ .

Thus one general feature in DEA to 1,2/1,3- $C_6H_4BrCl$  is the strong dominance of  $Br^-$  over  $Cl^-$ . The present results are in qualitative accordance with previous DEA measurements by Nakagawa [17] and Illenberger and co-workers [18]. Nakagawa studied DEA of thermalized electrons to  $C_6H_4XY$  ( $X, Y = \text{halogen}$ ) in combination with negative chemical ionization mass spectrometry. In this study the production of  $Br^-$  turned out to be much stronger than  $Cl^-$  production (e.g.,  $Br^-/Cl^- = 33$  for 1,2  $C_6H_4ClBr$ ). Illenberger and coworkers [18] studied the temperature dependence in DEA to 1,4- $C_6H_4ClBr$  and observed at room temperature the ratio  $Br^-/Cl^- = 70$ . This strong predominance of  $Br^-$  over  $Cl^-$  may be due to energetic reasons (see below) and in addition, the higher polarizability of Br may lead to a preferential localization of the excess charge towards the Br site already at the incident of electron attachment.

In order to gain deeper insight into the DEA process we perform DFT calculations. The structures of 1,2- $C_6H_4BrCl$  and 1,3- $C_6H_4BrCl$ , together with two neutral radicals,  $C_6H_4Br$  and  $C_6H_4Cl$ , that may be the possible fragments produced in the DEA process, are optimized at the B3LYP/6-311G(d) level of theory. The harmonic vibrational frequencies and the zero point vibrational energies (ZPVE) of all

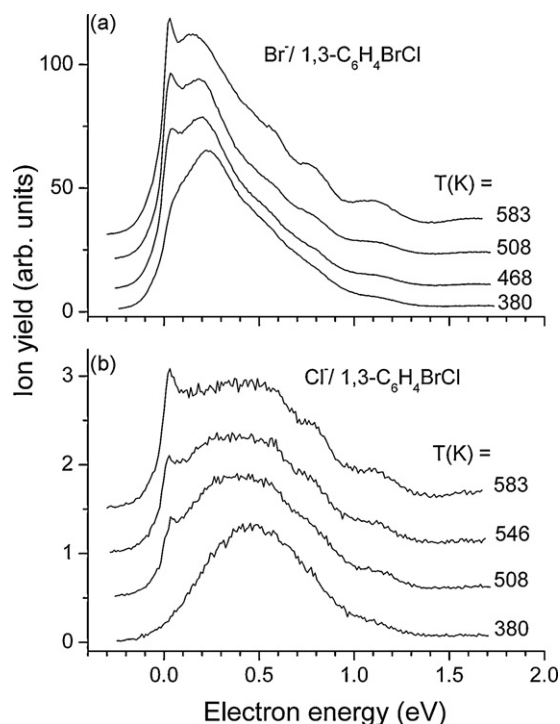
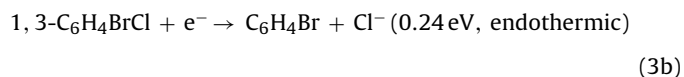
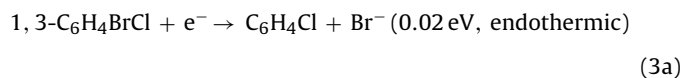
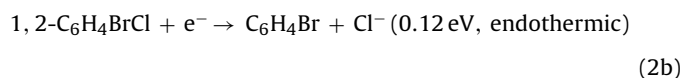
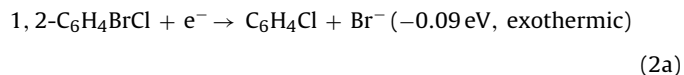


Fig. 2. (a) Br<sup>-</sup> and (b) Cl<sup>-</sup> ion yields for DEA to 1,3-C<sub>6</sub>H<sub>4</sub>BrCl measured at different gas temperatures, respectively.

mentioned species are also determined at the same level of theory. All of these calculations are performed with GAUSSIAN 03 program [19].

We calculate the threshold energies of the following reactions,



These threshold values are obtained from the calculated bond dissociation energies  $D(\text{Cl}-\text{C}_6\text{H}_4\text{Br})=3.73 \text{ eV}$ ,  $D(\text{Br}-\text{C}_6\text{H}_4\text{Cl})=3.27 \text{ eV}$  for 1-bromo-2-chlorobenzene and the bond dissociation energies  $D(\text{Cl}-\text{C}_6\text{H}_4\text{Br})=3.85 \text{ eV}$ ,  $D(\text{Br}-\text{C}_6\text{H}_4\text{Cl})=3.38 \text{ eV}$  for 1-bromo-3-chlorobenzene and the well known electron affinities  $\text{EA}(\text{Cl})=3.61 \text{ eV}$  and  $\text{EA}(\text{Br})=3.36 \text{ eV}$  [20]. In the present experiments (electron energy resolution is about 90 meV), both Cl<sup>-</sup> and Br<sup>-</sup> anions produced via reactions (2) and (3) can be observed at electron energy close to 0 eV. Although the reaction (3b),  $1,3\text{-C}_6\text{H}_4\text{BrCl} + e^- \rightarrow \text{C}_6\text{H}_4\text{Br} + \text{Cl}^-$ , is predicted to occur at a little higher energy, the present low-level DFT calculations are still in good agreement with the experimental observations (see Figs. 1 and 2). The observation of an ion yield for endothermic channels at about 0 eV is possible not only due to the finite resolution of the electron beam, but also due to internal rotational and vibrational energy of the molecules, which for molecules of this size and at the temperatures used in the present experiment could achieve values of several 100 meV.

As proposed by several theoretical studies on DEA [21–24], the neutral aromatic molecule can capture the excess electron forming

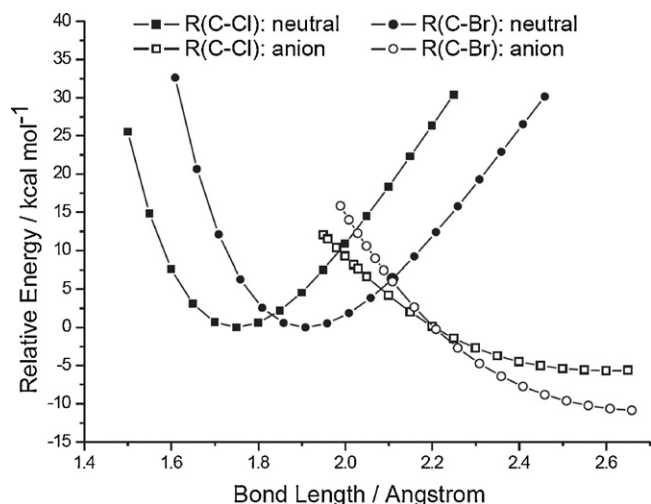


Fig. 3. Adiabatic potential energy curves as function of the C–X (X = Br or Cl) distance of the neutral and anionic 1,2-C<sub>6</sub>H<sub>4</sub>BrCl.

an electron-molecule resonance state. In the (unstable) TNI state the attached electron frequently occupies the lowest empty molecular orbital ( $\pi^*$  for the aromatic molecule) of the neutral, namely, the vertical (or adiabatic) attachment leads to a valence-bound state of TNI which has the equilibrium structure of the neutral. If the TNI structure is deformed along any vibrational motions, in particular the C–X bond stretching discussed in the following text, the anti-bonding  $\sigma_{\text{C-X}}^*$  is formed due to the intramolecular charge-transfer  $\pi^* \rightarrow \sigma^*$ . Such vibrational excitations accompanying with the electron transfer  $\pi^* \rightarrow \sigma^*$  are the diabatic processes, namely, beyond the Born-Oppenheimer approximation which is the base of quantum chemistry calculations. However, to elucidate the activation energies for the DEA reaction, the adiabatic potential energy profiles both of the neutral and TNI around the equilibrium configuration still can qualitatively mimic the dissociation dynamics [24–27].

Here we explored the different  $\pi^* \rightarrow \sigma^*$  channels taking into account the various molecular vibrations such as the in-plane (ip) and out-of-plane (oop) bending, and bond stretching modes. 1,2-C<sub>6</sub>H<sub>4</sub>BrCl is selected as an example and the potential energy as a function of the C–Cl or C–Br distance (the rest of the molecule being kept at the equilibrium geometry and not reoptimized) is calculated for the  $\pi^*$  resonance-state and the dissociative  $\sigma^*$  state. The calculations are performed at the B3LYP/6-311G(d) level of theory and the potential energy curves are plotted in Fig. 3. The exact metastable anionic energy curves are even more difficult to obtain here than in [24] for cyanochlorobenzene and the two-dimensional conical intersection with its avoided crossing can probably not be treated quantitatively at all. According to the energy profiles shown in Fig. 3, we can estimate the activation energies to be 10 kcal/mol (434 meV) and 6 kcal/mol (260 meV) for  $[1,2\text{-C}_6\text{H}_4\text{BrCl}]^{*-} \rightarrow \text{C}_6\text{H}_4\text{Br} + \text{Cl}^-$  and  $\rightarrow \text{C}_6\text{H}_4\text{Cl} + \text{Br}^-$ , respectively. Here the thresholds for the DEA are assumed as the energies that are obtained from the attached electron and equal to the energy difference between the equilibrium point of the neutral and the cross point of the neutral-anionic profiles. On the other hand, in Fig. 3 one may notice that above two dissociations are exothermic, but  $1,2\text{-C}_6\text{H}_4\text{BrCl} + e^- \rightarrow \text{C}_6\text{H}_4\text{Br} + \text{Cl}^-$  is predicted to be endothermic according to Eq. (2b). It is noted that the energetic values derived with the profiles far from the equilibrium distance C–Br/Cl in Fig. 3 are unreliable because the rigid molecular structures are adopted in the potential energy scanning.

Interestingly, for 1,4-C<sub>6</sub>H<sub>4</sub>ClBr an unusual temperature effect was observed previously, i.e., raising the gas temperature led first

to an increase of the  $\text{Br}^-/\text{Cl}^-$  ion yields and after passing a maximum (400 K for  $\text{Br}^-$  and 460 K for  $\text{Cl}^-$ ) to a decrease [18]. Thus we observe a pronounced isomeric effect on the temperature dependence of the DEA reaction for this molecule. We note that we recently observed such an effect also for dichlorobenzene isomers where  $\text{Cl}^-/1,3\text{-C}_6\text{H}_4\text{Cl}_2$  did not show a temperature dependence at all while for  $1,2\text{-C}_6\text{H}_4\text{Cl}_2$  and  $1,4\text{-C}_6\text{H}_4\text{Cl}_2$  the growth of a threshold peak was observed [25].

In general the activation energy for a DEA reaction can be derived from the temperature dependence of the threshold peak value close to zero eV since the dependence of the ion signal on the temperature  $T$  can be described by an Arrhenius type equation. However, due to problems in measuring the absolute ion yield for the different temperatures in the present experiment the error involved for the corresponding data points would be too large. Thus we have refrained from determining these activation energies.

As pointed out in our previous work [25], in the present temperature range, most molecules are thermally excited to the low-frequency vibrational states. For the two isomers of bromochlorobenzene, six vibrational modes, asymmetric and symmetric oop bendings, two ip waggings, and two bond stretchings, may be involved in thermal excitations. However, it is still an open question which one is responsible for the electron transfer  $\pi^* \rightarrow \sigma^*$  and the subsequent dissociations. In Fig. 4, the electron density maps for the different vibration modes are depicted for the  $1,2\text{-C}_6\text{H}_4\text{BrCl}$  case in order to elucidate the nature of the vibration-coupled electron transfers. The top map shows the temporary valence-bound state, then the intramolecular  $\pi^* \rightarrow \sigma^*$  electron transfer may occur along the respective vibrational modes (shown in the below maps). In fact, except for the C–Br/Cl bond ip wagging, the other vibrations can lead to the  $\pi^* \rightarrow \sigma^*$  electron transfer. As

shown in Fig. 4, the corresponding frequencies are ranging from 124 to  $448\text{ cm}^{-1}$  ( $100\text{ cm}^{-1}$  corresponds to 12.4 meV). Only less than  $40\text{ cm}^{-1}$  frequency difference of the low-frequency vibrations between 1,2- and 1,3- $\text{C}_6\text{H}_4\text{BrCl}$  are obtained. Thus the thermal vibrational effects on the  $\text{Br}^-/\text{Cl}^-$  fragmentations are similar for these two isomers. In Figs. 1 and 2, we find indeed very similar behaviour for the  $\text{Br}^-$  and  $\text{Cl}^-$  ion yields. The activation energies for these two isomers are different, which is in accordance with the threshold energies predicted in Eqs. (2) and (3). This is also in line with the stronger intramolecular interactions (e.g., hyperconjugations) between C–Cl and C–Br bonds for  $1,2\text{-C}_6\text{H}_4\text{BrCl}$  as compared to that for  $1,3\text{-C}_6\text{H}_4\text{BrCl}$ . In these two aromatic molecules, the hyperconjugation interactions between  $\sigma_{\text{C-Cl(Br)}}$  and  $\sigma_{\text{C-Br(Cl)}}^*$  are different due to the different spatial distance between C–Cl and C–Br bonds. The different hyperconjugation interactions not only lead to the slightly different bond lengths,  $r(\text{C-Cl}) = 1.749\text{ \AA}$  and  $r(\text{C-Br}) = 2.209\text{ \AA}$  in  $1,2\text{-C}_6\text{H}_4\text{BrCl}$ , while  $r(\text{C-Cl}) = 1.758\text{ \AA}$  and  $r(\text{C-Br}) = 1.917\text{ \AA}$  in  $1,3\text{-C}_6\text{H}_4\text{BrCl}$  (predicted at the same level of theory), but also may affect the competitive electron transfers  $\pi^* \rightarrow \sigma_{\text{C-Cl}}^*$  or  $\sigma_{\text{C-Br}}^*$ .

In conclusion, we have measured the anion efficiency curves at different temperatures in the temperature range from 377 to 583 K for DEA to 1-bromo-2-chlorobenzene and 1-bromo-3-chlorobenzene leading exclusively to the formation of  $\text{Cl}^-$  and  $\text{Br}^-$ . For these molecules the attached electron occupies initially the lowest empty molecular orbital ( $\pi^*$ ) at equilibrium structure of the neutral. In a second step the excess electron is transferred to the anti-bonding  $\sigma_{\text{C-Cl(Br)}}^*$  orbital due to some certain vibrations (asymmetric and symmetric oop bendings, and the Cl (Br) bond stretchings), and finally the  $\sigma_{\text{C-Cl}}$  or  $\sigma_{\text{C-Br}}$  bond of the valence-bound anion is broken. While the thermal vibrational effects on the

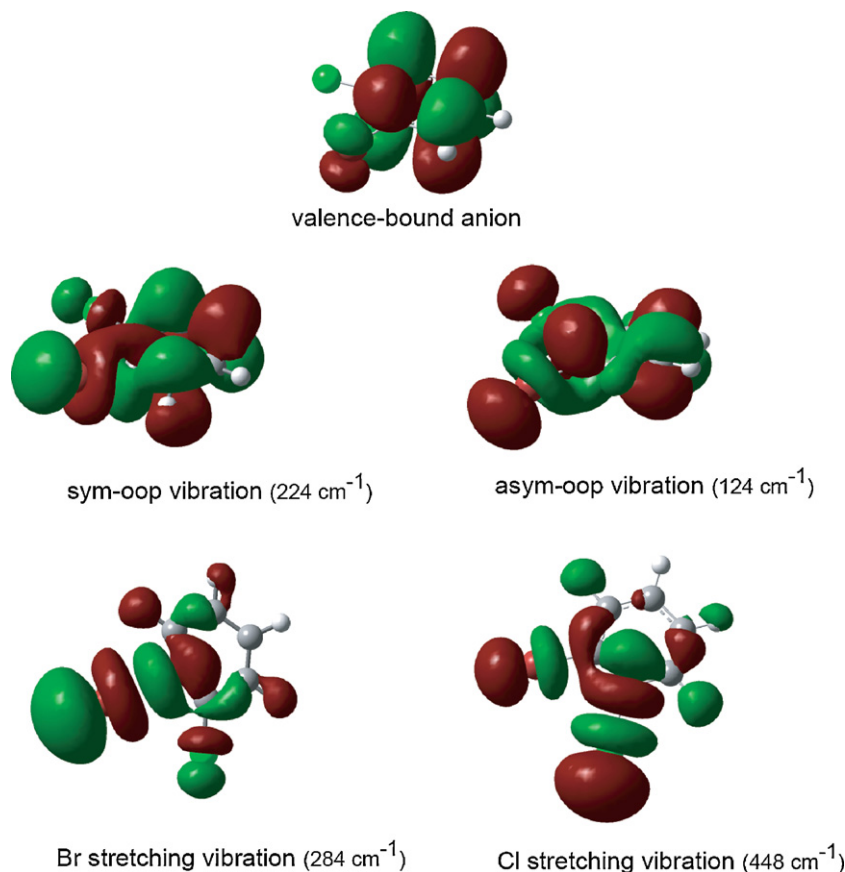


Fig. 4. Electron density maps of the various vibrational excitation modes (below) of the valence-bound (top)  $1,2\text{-C}_6\text{H}_4\text{BrCl}$  anion.

Br<sup>-</sup>/Cl<sup>-</sup> fragmentations are similar for both isomers, differences in energetics and intramolecular interactions will lead to a slightly different behaviour upon (thermally activated) DEA.

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