Electron energy loss spectra of alkali metal halides in the vapour phase†
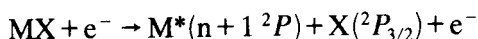
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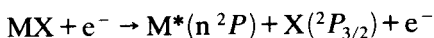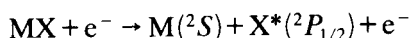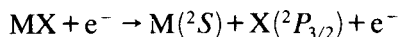
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Electronic transitions of alkali metal halides in the vapour phase have been studied for the first time by low energy electron energy loss spectroscopy. All the observed transitions correspond to dissociation processes. The study has established similarities in the alkali metal halide spectra.

Although the electronic spectra in the visible (Vis) and ultraviolet (UV) regions of several high-temperature vapours have been investigated extensively in the past few decades, electron energy loss spectroscopic studies of such species have been limited. Vapour phase spectra of alkali metal halides up to ~ 6 eV have been studied by UV spectroscopy[1]. Electron impact spectroscopic studies using high energy electrons (~ 25 keV) have also been carried out on these systems[2,3]. The objective of these studies was primarily to understand the inner electron excitations and also to obtain structural parameters. The similarity in the electronic spectra of alkali metal halides and the corresponding alkali metals[4] has also been reported. Available experimental information suggests that the electronic excitation processes of these molecules are dissociative in nature. Though the UV/Vis spectroscopic investigations[1] show the presence of excitations at low energies, electron impact spectra do not show any clear bands below ~ 5 eV, possibly due to the small electron impact cross-sections of these processes. Cross-sections for the photoabsorption processes are known to be small at these energies[5].

Geiger and Pfeiffer[2] suggested the dissociation of alkali metal halides into the following four products as the cause of the energy losses in the 5-11 eV region:

$$MX + e^- \rightarrow M(^2S) + X(^2P_{3/2}) + e^-$$

$$MX + e^- \rightarrow M(^2S) + X^*(^2P_{1/2}) + e^-$$

$$MX + e^- \rightarrow M^*(n\,^2P) + X(^2P_{3/2}) + e^-$$

$$MX + e^- \rightarrow M^*(n+1\,^2P) + X(^2P_{3/2}) + e^-$$

MX, M, and X refer to the alkali metal halide, the alkali metal and the halogen respectively. The asterisk

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indicates that the atom is in an excited state. Most of the intense transitions in the spectra occur in the region around 10 eV and the energy losses start at low energies and show broad maxima.

The present investigation was undertaken to examine the similarities in the excitation processes of various alkali metal halides. It was also of interest to obtain possible electronic transitions of the dimers, since it is known that alkali metal halide vapours contain significant proportion of dimers[6]. Our study does not reveal the presence of any dimer bands, but it has helped to establish similarities in the excitation processes in the alkali metal halide spectra.

Materials and Methods

Commercial samples of the halides were used without further purification. Electron energy loss spectra were recorded with a home built instrument described in detail elsewhere[7]. Minor modifications were done to carry out high temperature experiments. A resistively heated stainless steel furnace was incorporated to generate the alkali halide vapours. The powdered solid sample was taken in a quartz tube sealed at one end and inserted into the furnace directly. Heating up to 850°C was necessary to obtain reproducible spectra. The temperature was monitored by a thermocouple spot-welded on the furnace. The resolution of the instrument was around 300 meV at 50 eV primary beam. The spectra were calibrated with air. All the spectra were recorded after heating the sample under vacuum for a prolonged period of time to remove moisture, since it is known that the presence of water causes a small fraction of the halides to hydrolyse[8]. Over a period of time, the spectrometer performance deteriorated due to the deposition of halide vapours on the sensitive surfaces of the spectrometer. Resistive heating of the sample did not cause any decrease in the spectrometer resolution.

Results and Discussion

In Figs 1 to 3 are shown the electron energy loss spectra of several alkali metal halides. The spectra show well resolved maxima. The region up to 6 eV is flat showing no energy loss, probably due to the small impact cross sections of the low energy processes.

Assignments of the energy loss features were made on the basis of *ab-initio* molecular orbital (MO) calculations. Earlier calculations[9] on alkali metal halides have shown the highest occupied molecular orbital (HOMO) to be π and the lowest unoccupied molecular orbital (LUMO) to be σ^*. The HOMO is mainly centred on the halogen and the LUMO has the major contribution from the alkali metal *s* orbital. Ordering of the HOMOs was confirmed by photoelectron spectroscopy[10]. The molecular orbital calculations on LiCl and NaCl were carried out at the MP4/6-31G*[11] level. The 6-31G* optimized geometries were used in the MP4/6-31G* calculations. The essential results are summarized in Table 1. The calculations show that the first excitation energy is 4.80 eV for LiCl and 4.55 eV for NaCl. The spectra obtained in the present study do not show any transition at this energy. Moreover, absorption spectroscopic results show that no stable excited molecular state exists for these halides[5].

The only meaningful assignment that can be made of the energy loss spectra is in terms of the various dissociation processes. Dissociation energies[1,12] of alkali metal halides to corresponding neutral atoms are available in the literature. The values for NaBr, KBr, RbBr and CsBr are 4.96, 4.88, 4.81 and 4.87 eV respectively (for the $M\ ^2S + X\ ^2P_{3/2}$ dissociation). The excitation energies of alkali metal at-
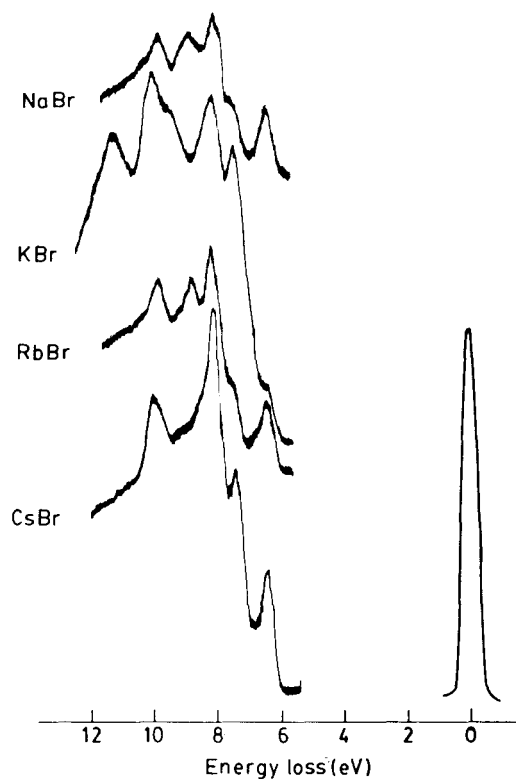

Fig. 2—Electron energy loss spectra of NaBr, KBr, RbBr and CsBr.
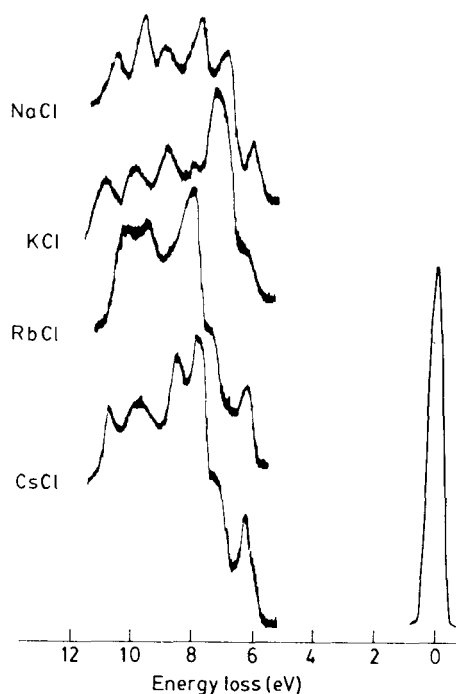

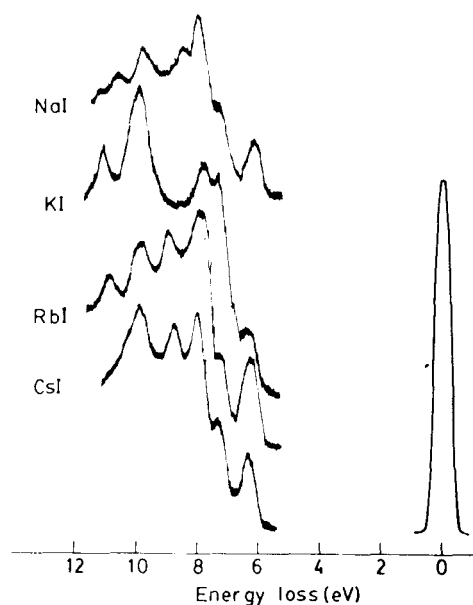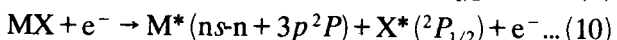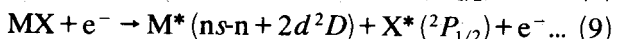Fig. 1—Electron energy loss spectra of NaCl, KCl, RbCl and CsCl.
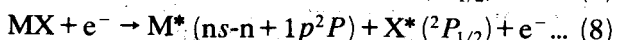

Fig. 3—Electron energy loss spectra of NaI, KI, RbI and CsI

oms are also well known[13]. We can see that the differences between the two consecutive energy losses are close to the alkali metal atom excitation energy, within the range of experimental error. The observed energy losses are assigned to the following dissociation processes:

$$MX + e^- \rightarrow M^*(ns\text{-}np\ ^2P) + X\ (^2P_{3/2}) + e^- \quad \ldots (1)$$

$$MX + e^- \rightarrow M^*(ns\text{-}np\ ^2P) + X^*\ (^2P_{1/2}) + e^- \quad \ldots (2)$$

$$MX + e^- \rightarrow M^*(ns\text{-}nd\ ^2D) + X^*\ (^2P_{1/2}) + e^- \quad \ldots (3)$$

$$MX + e^- \rightarrow M^*(ns\text{-}nd\ ^2D) + X\ (^2P_{3/2}) + e^- \quad \ldots (4)$$

$$MX + e^- \rightarrow M^*(ns\text{-}n+1p\ ^2P) + X^*\ (^2P_{1/2}) + e^- \ldots (5)$$

$$MX + e^- \rightarrow M^*(ns\text{-}n+1p\ ^2P) + X\ (^2P_{3/2}) + e^- \ldots (6)$$

$$MX + e^- \rightarrow M^*(ns\text{-}n+1d\ ^2D) + X^*(^2P_{1/2}) + e^- \ldots (7)$$
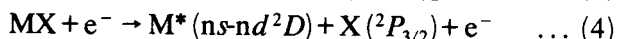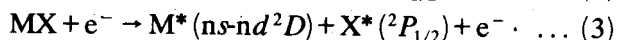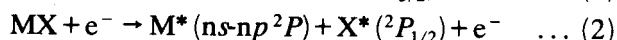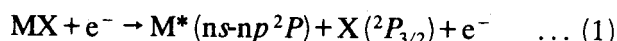
$$MX + e^- \rightarrow M^*(ns\text{-}n+1p\ ^2P) + X^*\ (^2P_{1/2}) + e^- \ldots (8)$$

$$MX + e^- \rightarrow M^*(ns\text{-}n+2d\ ^2D) + X^*\ (^2P_{1/2}) + e^- \ldots (9)$$

$$MX + e^- \rightarrow M^*(ns\text{-}n+3p\ ^2P) + X^*(^2P_{1/2}) + e^- \ldots (10)$$
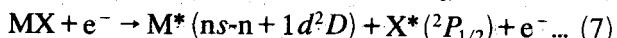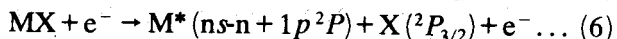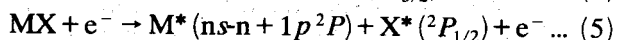
The assignments of the observed bands are listed in Table 2. The width of the bands can be appreciated considering the changes in the vibrational population distribution at the high temperatures. The transitions observed above 9 eV arise from the dissociation processes in which the alkali metal atom excitations originate from the inner levels.

Chlorides and iodides show similar energy loss features (Table 3). Many of the high energy features are not assigned in Table 3. We presume that these arise from the dissociation processes in which the excitations of the alkali atoms originate from the core levels as in the case of bromides. Since the energy difference between the $P_{3/2}$ and $P_{1/2}$ states is very small (0.1 eV) for chlorides, we have not been able to observe processes leading to these states separately. Except the 6.3 eV band for CsCl, no other band observed here has been reported in the optical studies[1].

When we compare the spectra of chlorides, bromides and iodides, we see that the bands observed in each group are almost at the same energies. The band maxima for the various chlorides, bromides and iodides in the absorption spectroscopic measurements were also found at similar energies[1]. For example, NaCl, KCl, RbCl and CsCl show the first maxima at 5.29, 5.09, 4.99 and 5.02 eV respectively. NaBr, KBr, RbBr and CsBr show the corresponding bands at 4.46, 4.47, 4.43 and 4.50 eV respectively. The bands observed in the iodides are at similar energies as well. The same is true of the results obtained from electron impact studies also[2,3].

Although the dimer: monomer ratio of the alkali metal halide vapours varies from 0.02 to unity[6], we have not been able to observe transitions due to the

Table 1—Important parameters obtained from the MP4/6-31G* calculations on LiCl and NaCl

	Total energy (Hartree)	
	HF/6-31G*	MP4/6-31G*
	LiCl	
$^1\Sigma_g$[b]	467.0092	467.1610
$^3\pi$	466.8551	466.9843
$^1\pi$	466.8543	466.9833
Excitation energy (eV)		
Triplet	4.19	4.80
Singlet	4.21	4.83
	NaCl	
$^1\Sigma_g$	621.3996	621.5492
$^3\pi$	621.2543	621.3815
Excitation energy (eV)		
Triplet*	3.95	4.55

*Singlet state could not be optimized.

Table 2—Electronic excitation energies (in eV) of alkali bromides obtained from EELS. The dissociation process corresponding to each energy loss is indicated in the bracket. For K, Rb and Cs, in the processes leading to the ^2D states, the terminating orbitals are $(n\text{-}1)d$, nd and $(n+1)d$, instead iof nd, $(n+1)d$ and $(n+2)d$

NaBr	KBr	RbBr	CsBr
6.4	6.3	6.3	6.3
(1)	(2)	(2)	(2)
7.6	7.3	7.3	7.3
(3)	(3)	(3)	(5)
8.8	8.0	8.0	8.0
(5)	(5)	(7)	(7)
—	—	8.7	—
		(9)	
9.8	9.6	9.8	9.8

Table 3—Electronic excitation energies (in eV) of alkali metal chlorides and iodides obtained from EELS. See caption for Table 2.

NaCl	NaI	KCl	KI	RbCl	RbI	CsCl	CsI
6.3[a]	6.3	6.4	6.3	6.3	6.3	6.2	6.4
	(1)	(1)	(1)	(1)	(1)	(1)	(4)
7.2[b]	7.4	7.2	7.3	7.2	7.4	7.5	7.1
	(2)	(3)	(2)	(3)	(2)	(8)	(3)
7.9	8.1	—	7.7	—	7.9	—	7.8
(1)	(4)		(4)		(4)		(5)
9.2	8.6	8.9	—	—	8.8	8.6	8.7
(3)	(6)	(8)					
9.9	9.8	9.9	9.7	9.7	9.8	9.9	9.8
(7)	(5)						
10.8	—	10.8	10.9	—	10.9	10.8	—

[a]Probably due to $M(^2S) + X\ (^2P_{3/2})$ dissociation.
[b]Geiger and Pfeiffer (Ref. 2) find a band at 7.1 eV which is assigned to the process (1).

dimers. This could be possibly due to the fact that in the present experimental set up, the vapour had to go through a long quartz tube, which could have reduced the dimer: monomer ratio.

Acknowledgement

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