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# OPTICAL EXCITATION IN COLLISIONS OF $Ar^+$ AND $He^+$ IONS WITH $CS_2$

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By the impact of $Ar^+$ or $He^+$ ion beam of 2 - 3 keV, $CS_2$ exibits similar spectra, although the recombination energies of $Ar^+$ and $He^+$ ions are very different: the intense $\tilde{B}$-$\tilde{X}$ system of $CS_2^+$ and the weak A-X system of CS. The observed data are inconsistent with the predictions from the energy defect and Massey's adiabatic parameter. But the charge-exchange reactions can be explained by the Franck-Condon principle.

Optical studies in collisions of rare-gas ions with gaseous molecules provide direct information on the excitation process by heavy particles. In the present study, ion-molecule reactions in collisions of $Ar^+$ and $He^+$ ions with $CS_2$ were investigated by optical emission spectroscopy, and the predominant factor which governs the charge-exchange reactions was determined.

The ion-impact apparatus was constructed by reference to the experiments of Haugh and Bayes.[1,2] Ions produced in a 2450 MHz microwave discharge were accelerated between a probe and an aperture electrode. The beam was extracted through a draw-out electrode and focused into the collision chamber containing the target gas. Ion-beam current in the collision chamber ranged between 10 and 70 μA for ion energies of 2 - 3 $keV_{Lab}$. Photoemission in the 220 - 400 nm region was detected using a Nippon Jarrell Ash 1m monochromator equipped with a RCA 1P28 photomultiplier. A further experimental detail will be described elsewhere.[3]

The emission spectrum excited by the impact of 2 keV $He^+$ ion beam on $CS_2$ is shown in Fig. 1. This spectrum is in good agreement with the electron-impact spectra at 75 - 200 eV;[4,5] the intense doublet band at 282 and 286 nm and the weak bands at 287 and 291 nm are assigned to $CS_2^+(\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Pi_g)$, and a few bands around 260 nm to $CS(A^1\Pi - X^1\Sigma^+)$. A similar spectrum was found when the incident ion was replaced by

$Ar^+$ ion. In the case of $He^+$ impact, an atomic line of HeI was observed at 3889 Å ($3p^3P$-$2s^3S$). The variation in the incident ion energy between 2 and 3 keV did not induce any appreciable change in the spectra. Haugh et al.[6] have observed the identical band systems by 2 keV $Ar^+$ and $Kr^+$ impact, although photoemission from neutral $CS_2$ could not be detected in the present study. The present spectrum of $CS_2^+(\tilde{B}$-$\tilde{X})$ is almost identical with the fluorescence spectra by direct photoionization ($\lambda$555 - 827 Å);[7] the transition only from the (0,0,0) level of the $\tilde{B}$ state is observed. Meanwhile, the $CS_2^+(\tilde{B}$-$\tilde{X})$ emission was absent in the spectrum obtained in the flowing helium afterglow, even though responsible excitation species, $He(^3S)$ and thermal $He^+$, have sufficient excitation energy.[8]

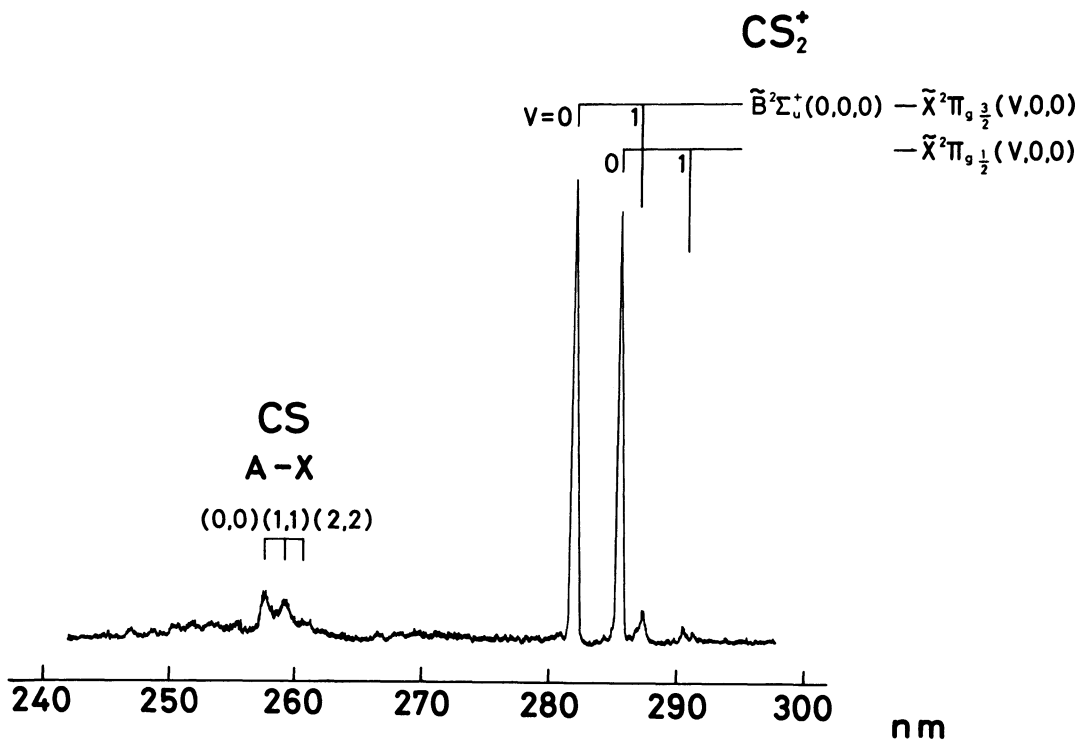


Fig. 1. Emission spectrum obtained by $He^+$ impact on $CS_2$ at 2 keV.

Figure 2 shows the dependence of the band intensities of $CS_2^+$ and CS on the incident ion-beam current and the target-gas pressure in the case of $Ar^+$ impact. The gas pressure was measured in the gas reservoir, where the pressure was assumed to be proportional to that in the collision region. A McLeod gauge attached to the collision chamber indicated that the pressure of 80 Torr in the gas reservoir corresponded to about 0.6 mTorr in the collision region. The band intensities of $CS_2^+$ and CS are proportional both to the ion-beam current and to the gas pressure, and

the same results were obtained in the case of $He^+$ impact. These results suggest that the excited species are produced by a direct, one-step excitation mechanism under these experimental conditions, and that the secondary reaction as has been found in the formation of the excited parent ion by $He^+$ and $Ne^+$ impact on $CO_2$[9,10] is negligible. Since Smith[4,11] has found that the $CS_2^+$ $\tilde{B}$-$\tilde{X}$ transition and the CS A-X transition are cascade free in the lifetime measurements under the electron-impact excitation, we can expect that $CS_2^+(\tilde{B})$ and CS(A) are produced through direct excitation under the present ion-impact excitation.

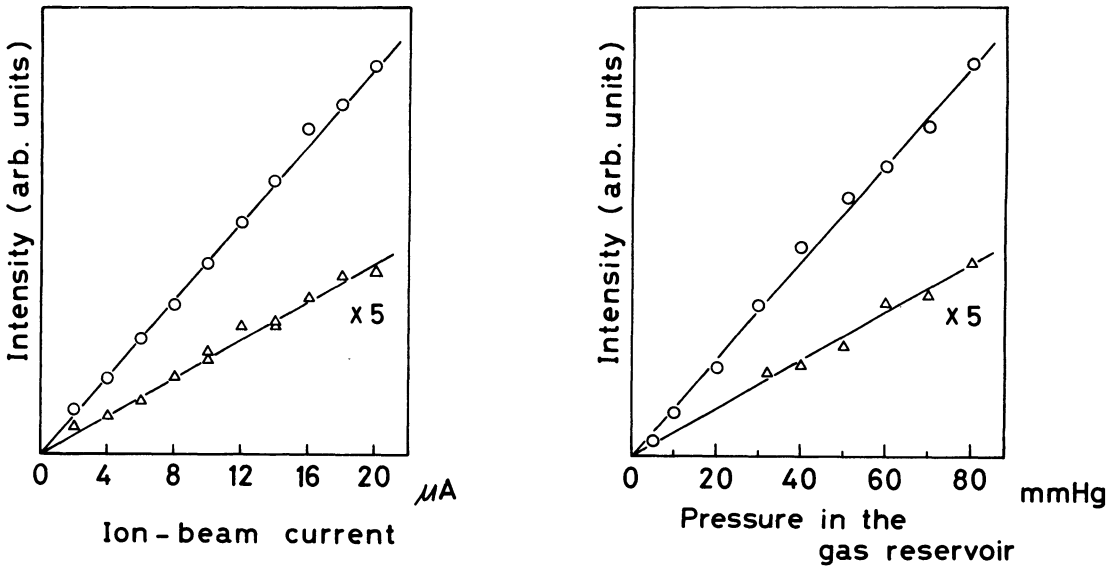


Fig. 2. Dependence of photoemission intensities of $CS_2^+$(○) and CS(△) on the ion-beam current and the pressure in the gas reservoir. The energy of $Ar^+$ ion was 2 keV.

The most striking characteristics of inelastic positive ion scattering at energies of a few keV is that in most cases charge-exchange reaction dominates the excitation process, and the relative importance of the different charge-exchange channels has been predicted by a simple resonance model and an adiabatic parameter derived from Massey criterion. A particular excitation cross-section is large, when the absolute value of the energy defect $|\Delta E|$ is small in the former model, on the other hand when the adiabatic parameter p is nearly 1 or less according to the latter concept.

Possible collision processes of $Ar^+$ and $He^+$ with $CS_2$ mainly leading to $CS_2^+$ and CS species are given in Table 1 along with the calculated values of $\Delta E$ and p at 2 keV;

the average value of the ionization potentials of the $^2P_{3/2}$ and $^2P_{1/2}$ states of $Ar^+$ is used for the calculation, assuming no vibrational, rotational, and kinetic energies in the products. The observation of the HeI line shows that not only exothermic reactions producing the ground state of He, such as the processes (1) - (11), but also very endothermic reactions terminating $He(^3P)$, such as the processes (12) - (14), occur. The simultaneous conversion of ion kinetic energy to internal energy makes

Table 1. The collision processes of $CS_2$ with $Ar^+$ and $He^+$ ions

| Collision processes $Ar^+(^2P_{3/2,1/2}), He^+(^2S_{1/2}) + CS_2 \longrightarrow$ | | Energy defect[a] ΔE (eV) | | Adiabatic parameter[b] $p_{2keV}$ | |
|---|---|---|---|---|---|
| | | $Ar^+$ | $He^+$ | $Ar^+$ | $He^+$ |
| $Ar(^1S), He(^1S) + CS_2^+(\tilde{X}^2\Pi_g)$ | (1) | -5.8 | -14.5 | 10.0 | 7.9 |
| $CS_2^+(\tilde{A}^2\Pi_u)$ | (2) | -3.2 | -11.9 | 5.4 | 6.5 |
| $CS_2^+(\tilde{B}^2\Sigma_u^+)$ | (3) | -1.4 | -10.1 | 2.4 | 5.5 |
| $CS_2^+(\tilde{C}^2\Sigma_g^+)$ | (4) | 0.3 | -8.4 | 0.6 | 4.6 |
| $CS_2^+(\tilde{D}^2\Sigma_u^+)$ | (5) | 0.8 | -8.0 | 1.3 | 4.4 |
| $+ CS(X^1\Sigma^+) + S^+(^4S)$ | (6) | -2.2 | -11.0 | 3.9 | 6.0 |
| $CS(X^1\Sigma^+) + S^+(^2D)$ | (7) | -0.4 | -9.1 | 0.7 | 5.0 |
| $CS(A^1\Pi) + S^+(^4S)$ | (8) | 2.6 | -6.2 | 4.4 | 3.4 |
| $CS(A^1\Pi) + S^+(^2D)$ | (9) | 4.4 | -4.3 | 7.6 | 2.4 |
| $+ C(^3P) + S^+(^4S) + S(^3P)$ | (10) | 5.6 | -3.2 | 9.6 | 1.7 |
| $C^+(^2P) + 2S(^3P)$ | (11) | 6.5 | -2.3 | 11.1 | 1.2 |
| $He(^3P) + CS_2^+(\tilde{B}^2\Sigma_u^+)$ | (12) | | 12.9 | | |
| $CS(A^1\Pi) + S^+(^4S)$ | (13) | | 16.9 | | |
| $CS(A^1\Pi) + S^+(^2D)$ | (14) | | 18.7 | | |
| $Ar^+(^2P_{3/2,1/2}), He^+(^2S_{1/2}) + CS(A^1\Pi) + S(^3P)$ | (15) | 8.1 | 8.1 | | |

a) The energy defect was calculated using the data in Refs. 12 - 14.

b) $p = a|\Delta E|/hv$; a: characteristic interaction length 7 Å,[15] h: Planck's constant, v: relative collision velocity.

these reactions possible. However, the weakness of the atomic line comparing with the band intensity of the parent ion indicates relative inefficiency of such reactions. A similar result has been obtained in $He^+$ impact on $CO_2$,[9] although secondary process participates in the reaction. The spin conservation rule[14] requires prior excitation of $CS_2^+$ to a quartet state in the processes (6) and (8), while to a triplet state in the process (15). The process (15) has been observed in the photodissociation,[16] and how rigorously this rule holds has not yet been clear in the dissociation of polyatomic molecules; therefore, spin forbidden channels cannot be removed from the possible process.

The simple resonance model and the adiabatic hypothesis predict that the most likely charge-exchange process of $CS_2$ by $Ar^+$ and $He^+$ impact is significantly different with each other due to the large difference in the recombination energy between $Ar^+$(15.759, 15.937 eV) and $He^+$(24.581 eV); the processes (4) and (7) will have large cross section in $Ar^+$ impact, while such processes as one or a few atomic fragments in the processes (10) and (11) are excited are favorable in $He^+$ impact. The similarity of the observed spectra in $Ar^+$ and $He^+$ impact contradicts these predictions. However, the coincidence of the present spectra with the fluorescence spectra by photoionization suggests that the level population is interpreted on the basis of the Franck-Condon transition between the ground state of $CS_2$ and the molecular ion. According to the Franck-Condon factors obtained by photoelectron spectroscopy,[12] the (0,0,0) levels of the $\tilde{X}^2\Pi_g$ (the FC factor 1.0), $\tilde{C}^2\Sigma_g^+$ (0.92), and $\tilde{B}^2\Sigma_u^+$ (0.89) states are preferentially populated. The observation of intense photoemission from the last level leads us to conclude that the level population in the charge-exchange reactions of $Ar^+$ and $He^+$ ions with $CS_2$ is mainly determined by the Franck-Condon principle. This finding is consistent with the previous work of Haugh and Bayes[1] for triatomic molecules in $Ar^+$ and $Kr^+$ impact. The location of the (0,0,0) band from the $\tilde{C}$ state is predicted to be 202 nm for the $\tilde{C}$-$\tilde{X}$ transition and 721 nm for the $\tilde{C}$-$\tilde{B}$ transition. Although they are outside range of the present observation, such radiation has not been detected; it has been attributed to the predissociation into $CS(^1\Sigma^+) + S^+(^4S)$ and $CS^+(X^2\Sigma^+) + S(^3P)$.[17]

As to the formation of CS(A), both the processes (8) and (9) which proceed through dissociative charge exchange and the process (15) through direct collisional dissociative-excitation are possible. Haugh et al.[6] concluded that CS(A) was probably formed through the latter process in $Ar^+$ and $Kr^+$ impact, partly because

there are no energy resonant processes leading to it. However, the possibility of the contribution from the former processes cannot be ruled out, since the charge-exchange reactions between rare-gas ions and $CS_2$ mainly follow the Franck-Condon prediction, being independent of the energy resonance. Further investigations are required to determine their relative importance to the direct collisional excitation process.

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