Vibrational distributions of the $\widetilde{A}\ ^2\Pi_u$ state of CO_2^+ and CS_2^+ produced by electron impact on jet-cooled CO_2 and CS_2

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Fluorescence spectra of the $\widetilde{A}\,^2\Pi_u-\widetilde{X}\,^2\Pi_g$ system of CO_2^+ and CS_2^+ ions, following electron impact on supersonic jet targets of CO_2 and CS_2, have been analyzed to determine vibrational populations. The vibrational distributions of the $\widetilde{A}\,^2\Pi_u$ state of CO_2^+ and CS_2^+ were found to be independent of the impact energy in the 30–300 eV range. The distribution of the CO_2^+ ($\widetilde{A}$) state is very similar to the result obtained by He I photoelectron spectroscopy (PES), which is a Franck–Condon-type vertical ionization, whereas that of the CS_2^+ ($\widetilde{A}$) state is significantly different from the PES data. This non-Franck–Condon behavior for formation of CS_2^+ ($\widetilde{A}$) in the electron impact is discussed.

I. INTRODUCTION

Fluorescence of the CO_2^+ ion produced by electron impact on CO_2 has been studied by several research groups.[1-4] In these studies, emission cross sections for the $\widetilde{A}\,^2\Pi_u-\widetilde{X}\,^2\Pi_g$ and $\widetilde{B}\,^2\Sigma_u^+-\widetilde{X}\,^2\Pi_g$ bands of CO_2^+ have been measured. The values thus reported are however inconsistent among them: the ratio of the emission cross section of the $\widetilde{A}-\widetilde{X}$ band to that of the $\widetilde{B}-\widetilde{X}$ band obtained at 160 eV, $\sigma_{em}(A)/\sigma_{em}(B)$, is 3.3 (Ref. 1), 1.4 (Ref. 3), and 1.7 (Ref. 4). The CO_2^+ ($\widetilde{A}-\widetilde{X}, \widetilde{B}-\widetilde{X}$) emissions have also been studied in photoionization[5,6] and Penning ionization.[7,8] In photoionization of CO_2, there is a significant difference between reported values for the branching ratio of the $\widetilde{A}-\widetilde{X}$ and $\widetilde{B}-\widetilde{X}$ transitions: $\sigma_{em}(A)/\sigma_{em}(B) = 1.5$ (Ref. 5), 2.7 (Ref. 6). On the basis of the Penning ionization optical emission spectroscopy (PIOS), Broida and co-workers[7] and Endoh *et al.*[8] have obtained the $\widetilde{A}$ and $\widetilde{B}$ states distribution. However, no consistent values have been also obtained for the branching ratio of the $\widetilde{A}$ and $\widetilde{B}$ states: $k(A)/k(B) = 1.5$ (Ref. 7), 3.7 (Ref. 8).

Endoh *et al.*[8] have also determined the vibrational populations of the $\widetilde{A}$ state in the $v_1' = 0-7$ levels. Their results were however fairly different from the Penning ionization electron spectroscopy (PIES) data.[9] Endoh *et al.* have concluded that this discrepancy is due to the interelectronic state coupling between the $\widetilde{A}$ and $\widetilde{B}$ states.[10] Photoelectron–photon coincidence data[11] suggested that the 0^0, 1^1, and 1^2 levels of the $\widetilde{B}$ state are coupled with the $\widetilde{A}$ state.

Fluorescences and decay processes of CS_2^+ ($\widetilde{A}$) have been studied by photoionization,[12] electron-impact ionization,[13,14] Penning ionization,[15,16] and the charge transfer reaction of $(CO^+$ or $Ar_2^+) + CS_2$.[17,18] Endoh *et al.*[18] have evaluated the vibrational populations of the $\widetilde{A}$ state in the $v_1' = 0-1$ levels produced in $CS_2 + Ar_2^+$ reaction. The vibrational populations thus obtained are very different from the PES data.[19] Endoh *et al.* have concluded

that the thermal energy $CS_2 + Ar_2^+$ reaction leading to CS_2^+ ($\widetilde{A}$) is not a Franck–Condon-type ionization.

In recent years considerable data on ionization of CO_2 and CS_2 have been thus accumulated because of the interest in fluorescence spectroscopy of gas-phase positive ions. Despite this, we have not enough of the consistent data and the knowledge about ionization and decay processes of these molecules. This has been caused by two problems: (1) the ion of interest often decay electronically or rovibrationally before photoemission is possible owing to large quenching cross section and then it is difficult to determine the emission cross section and the nascent internal distribution; (2) vibronic energy levels of the ions are complicated on account of several types of interaction such as Renner–Teller effect and Fermi resonance[13,20] and then it is difficult to analyze the emission spectrum.

In this study, ionization processes of linear triatomic molecules CO_2 and CS_2 have been investigated by analyzing vibrational populations of $\widetilde{A}$ ion state produced by electron impact. In contrast to photoionization, when a molecule is ionized by electron impact, various types of excitation contribute to formation of the interest ion. This is because several states of the target molecule below the impact energy can be excited via the optically allowed or forbidden transition. Moreover, the internal distribution of the produced ion can be affected by post-collision interactions with the scattered and ejected electrons. Thus, energy dependence of the rovibrational populations of the produced ion is thought to reflect the nature of excitation mechanism and ionization dynamics involved. Neutral CO_2 and CS_2 molecules subjected to the electron impact are obtained from a supersonic free jet expansion. Since the ions thus produced retain low rotational temperature of parent molecules,[21] the fluorescence spectra should be simplified. This enables us to analyze the intensities of the vibronic bands accurately.
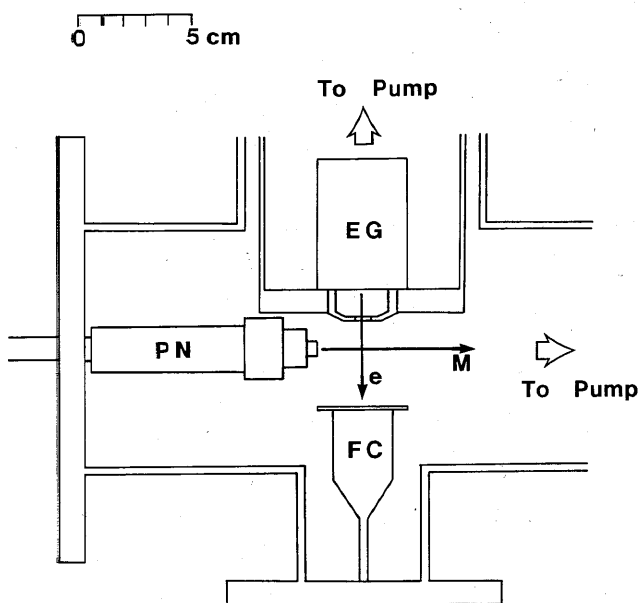
FIG. 1. A schematic diagram of the apparatus: (EG) electron gun, (FC) Faraday cup, (PN) pulsed nozzle. A supersonic free jet (M) of neat CO_2 or CS_2 in He crosses an electron beam (e) perpendicularly.

II. EXPERIMENTAL

The apparatus consists of two differentially pumped chambers as shown in Fig. 1: a collision chamber and an electron beam source. Supersonic free jet was produced by expanding target gas into a collision chamber through a pulsed nozzle with a 0.8 mm diameter orifice. A neat CO_2 gas at a stagnation pressure of 1–3.5 atm was expanded into the collision chamber through the nozzle, while the CS_2 vapor was sent to the nozzle after being bubbled with helium carrier gas at 1.5 atm (CS_2:He = 1:6). In the measurement the nozzle was pulsed at a repetition frequency of 20 Hz and each pulse lasting 4 ms. The ambient pressure at the collision chamber was kept below 4×10^{-4} Torr and the electron beam source was evacuated to 2×10^{-5} Torr under the operating condition of a stagnation pressure of one atom and a 20 Hz repetition rate. The free jet crossed an electron beam perpendicularly about 1.5 cm (19 nozzle diameters) down stream from the nozzle.

The electron beam was produced by a gun equipped with a thoria coated tungsten filament. The gun consists of a repeller and an einzel lens used to focus the electron beam onto the free jet. Moreover, a coaxial magnetic field of 30 gauss was used for additional collimation at low impact energy. The electron energy was controlled in the 18–300 eV range and the beam current was typically 80 μA at 30 eV. The energy of the impinging electrons was calibrated against the appearance potential of the CO_2^+ ($\widetilde{A}-\widetilde{X}$) emission (17.6 eV) or the CS_2^+ ($\widetilde{A}-\widetilde{X}$) emission (12.7 eV);[22] the energy spread of the beam was estimated to be about 1 eV (FWHM).

The fluorescence resulting from the electron-impact ionization of CO_2 or CS_2 was observed in a direction perpendicular to both the molecular beam and the electron beam. The fluorescence dispersed with a 90 cm monochro-
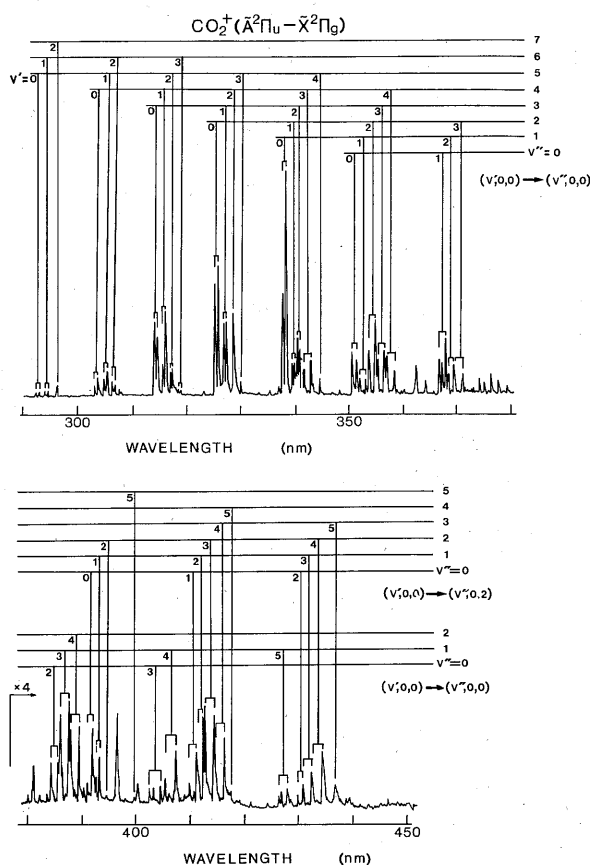

FIG. 2. Fluorescence spectrum of the CO_2^+ ($\widetilde{A}\,^2\Pi_u-\widetilde{X}\,^2\Pi_g$) system obtained by electron-impact ionization of neat CO_2 at 50 eV with the 0.3 nm FWHM resolution. The intensity of (b) is multiplied by four of that for (a). Two dominant progressions, $(v_1',0,0)\rightarrow(v_1'',0,0)$ and $(v_1',0,0)\rightarrow(v_1'',0,2)$ are indicated.

mator (Spex 1702) was detected by a Hamamatsu R585 photomultiplier, whose output pulse is monitored by a single photon counting electronics. The monochromator slits were parallel to the electron beam. The optical path was carefully baffled in order to detect only the central portion of the collision zone. In the fluorescence measurement, however, emissions produced by electron impact on ambient thermal molecules was also detected. In order to eliminate the emission from thermalized ions, the emission intensity obtained at the nozzle-off period was subtracted from that obtained at the nozzle-on period. The relative intensity response of the monochromator and the detection system was calibrated with a standard halogen lamp (Ushio Electric Corp.). The data acquisition was controlled by a QC-10 (Epson) microcomputer.

Carbon dioxide (Nihonsanso, stated purity of 99.9%) and Helium (Teisan, stated purity of 99.995%) were used without further purification, while carbon disulfide (Wako, $\geqslant$99%) was used after several pump–thaw cycles.

III. RESULTS

A. Emission spectra of the $\widetilde{A}-\widetilde{X}$ transition

Fluorescence spectrum of the CO_2^+ ($\widetilde{A}\,^2\Pi_u-\widetilde{X}\,^2\Pi_g$) transition in the 290–450 nm region measured at 50 eV is displayed in Fig. 2. Each vibronic band in the present re-
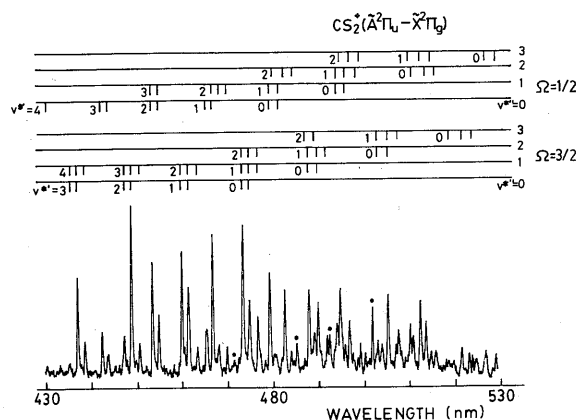
FIG. 3. Fluorescence spectrum of the CS_2^+ ($\tilde{A}^2\Pi_u$–$\tilde{X}^2\Pi_g$) system obtained by electron-impact ionization of CS_2 in He at 100 eV with the 0.3 nm FWHM resolution: the quantum number v^* means $v_1 + v_2/2$. The symbol (●) shows He I lines.

TABLE I. Relative vibrational populations of the CO_2^+ ($\tilde{A}$) state.

Method	Impact energy (eV)	Vibrational level v'_1								Reference
		0	1	2	3	4	5	6	7	
EI[a]	30	12	26	21	19	13	6	2	1	This work
	50	13	23	22	20	13	6	2	1	
	100	13	23	21	19	14	6	2	1	
	300	14	23	23	20	14	5	2	1	
PES[b]		8	18	28	18	12	9	4	2	Ref. 22
PIES[c]		10	22	27	24	16				Ref. 9
PIOS[d]		12	19	20	24	16	7	1	1	Ref. 8

[a]Electron impact ionization.
[b]Photoelectron spectroscopy.
[c]Penning ionization electron spectroscopy.
[d]Penning ionization optical spectroscopy.

sult is resolved better than the spectra displayed in previous studies.[6,8] This is mainly due to the rotational cooling of parent molecules in the supersonic free jet. The assignment of these bands was made with aid of previous data.[3,8,23,24] The vibrational bands are grouped into two series: the $(v'_1,0,0) \to (v''_1,0,0)$ bands for $\Delta v_1 = v'_1 - v''_1 = -$ 4–5, and the $(v'_1,0,0) \to (v''_1,0,2)$ bands for $\Delta v_1 = 0$–2.

Fluorescence spectrum of the CO_2^+ ($\tilde{A}^2\Pi_u$–$\tilde{X}^2\Pi_g$) transition in the 430–530 nm region measured at 100 eV is displayed in Fig. 3. The rotational distributions in this spectrum clearly display the cooling effect in supersonic free jet; a number of vibronic bands appeared by Fermi resonance in the $\tilde{A}$ or $\tilde{X}$ state are well resolved. These vibrational bands are assigned on comparing with the data reported by Balfour[13] and Endoh *et al.*[18] Main progressions are attributed to the $(v'_1,v'_2,0)$–$(v''_1,v''_2,0)$ bands with $v^{*'} = v'_1 + v'_2/2 \leqslant 4$ and $v^{*''} = v''_1 + v''_2/2 \leqslant 4$. This coincides with the result of $Ar_2^+ + CS_2$ reaction.[18] Each vibronic band consists of two components caused by the Λ-type doubling. Their splittings are larger than those of the CO_2^+ ($\tilde{A}$–$\tilde{X}$) band owing to a large coupling constant (432 cm^{-1}) for the $\tilde{X}^2\Pi_g$ state[13] and then can be easily assigned. Some additional bands observed in the 530–600 nm region can be assigned to the $(0,0,0)$–$(0,v''_2,2)$ progression with $v''_2 \geqslant 2$.

No emission band including odd quantum numbers of v'_3 (asymmetric stretching) has appeared in the spectra from both molecules. This is caused by the fact that formation of these vibrational levels of the $\tilde{A}^2\Pi_u$ ion state from the parent is symmetry-forbidden. In the same symmetry consideration, the vibrational bands for $\Delta v_3 =$ odd are forbidden in the $\tilde{A}^2\Pi_u$–$\tilde{X}^2\Pi_g$ transition.

In order to determine the rotational temperature of the $\tilde{A}$ state of CO_2^+ and CS_2^+ ions, emission spectra were observed with a higher-resolution (0.019 nm FWHM). Since the spectral resolution is not enough to resolve each rotational line, the observed spectra were compared with the synthetic spectrum produced by a band envelope analysis.

The best-fitted spectrum was obtained with a rotational temperature of 30 K.[25] This indicates that the rotational relaxation of the emitting species is insignificant at the observing region.

B. Vibrational populations of the $\tilde{A}$ state

The corrected emission intensity $I_{v'v''}$ in photon(s) can be expressed by the r-centroid approximation as follows:[26]

$$I_{v'v''} = K \cdot N_{v'} \cdot v^3_{v'v''} \cdot \mathrm{Re}(\overline{r}_{v'v''})^2 \cdot q_{v'v''}, \tag{1}$$

where $N_{v'}$ is the vibrational population for the v'_1 level of the $\tilde{A}$ state, and $q_{v'v''}$ and $v_{v'v''}$ are the Franck–Condon factor and the wave number, respectively, for the v'–v'' band. The electronic transition moment $\mathrm{Re}(\overline{r}_{v'v''})$ generally depends on the internuclear distance. A constant K is not adjusted in this study.

To our knowledge, there is no reliable value of Franck–Condon factors for the $\tilde{A}$–$\tilde{X}$ system of CO_2^+ and CS_2^+ obtained experimentally and theoretically. In order to determine vibrational distributions of the $\tilde{A}^2\Pi_u$ state of CO_2^+ and CS_2^+, we used the method employed by Endoh *et al.*[8] Since the summation of $q_{v'v''}$ over all v'' values is equal to one, Eq. (1) reduces to

$$N_{v'} = K \sum_{v''} \frac{I_{v'v''}}{v^3_{v'v''} \mathrm{Re}(\overline{r}_{v'v''})^2}. \tag{2}$$

If all of the vibrational bands are isolated, Eq. (2) is applicable to the population analysis. The electronic transition moment for the CO_2^+ ($\tilde{A}$–$\tilde{X}$) system can be assumed constant on the basis of the data presented by McCallum and Nicholls[27] and Judge and Lee.[28] The relative vibrational populations in the $v'_1 = $ 0–7 levels of the CO_2^+ ($\tilde{A}$) state are estimated from emission intensities of the 72 bands of the $\tilde{A}$–$\tilde{X}$ transition in the 290–450 nm region. Table I summarizes the relative vibrational populations of the CO_2^+ ($\tilde{A}$) state in the impact energy of 30–300 eV comparing with the data obtained from Penning ionization optical spectroscopy (PIOS),[6,8] Penning ionization electron spectroscopy (PIES) by He(2^3S) impact[9] and PES by He I resonance line.[19] The uncertainty for

TABLE II. Relative vibrational populations of the CS_2^+ ($\tilde{A}$) state.

Method	Impact energy (eV)	Vibrational level v_1'								Reference
		0	1	2	3	4	5	6	7	
EI[a]	30	34	32	20	12	2				This work
	50	34	32	20	11	2				
	100	35	32	20	11	2				
	300	35	32	20	11	2				
PES[b]		10	20	24	19	13	9	5	2	Ref. 19
CT[c]		90	10							Ref. 18

[a]Electron impact ionization.
[b]Photoelectron spectroscopy.
[c]Charge transfer reaction of $Ar_2^+ + CS_2$.

$N_{v'}$ in the present experiment was estimated to be within 10% of the given value.

The electronic transition moment in the CS_2^+ ($\tilde{A}-\tilde{X}$) system was assumed to be constant.[18] The vibrational distribution of the $\tilde{A}$ state of CS_2^+ has been obtained by summing up emission intensities from each upper vibrational level in the 430–530 nm region (60 bands). Table II summarizes the relative vibrational populations of the CS_2^+ ($\tilde{A}$) state in the impact energy of 30–300 eV together with the results obtained from PES by He I resonance line[19] and charge transfer reaction of $Ar_2^+ + CS_2$.[18] The uncertainty for $N_{v'}$ in the present experiment was estimated to be within 15% of the given values.

IV. DISCUSSION

Ionization of a molecule by electron impact occurs in two different channels: direct ionization and autoionization.[29] In direct ionization, the ejected and scattered electrons leave the ion simultaneously or within 10^{-16} s and then the Franck–Condon approximation is applied. When an ion is formed via the direct process, the vibrational branching ratio of the product ion is equal to the ratio of the corresponding Franck–Condon factors between the neutral ground state and the ion state produced, and is independent of the impact energy.[30]

On the other hand, autoionization proceeds by a two-step mechanism: first, a molecule is excited to a superexcited bound state, and then in a finite time the excited neutral decays into an ion–electron pair by radiationless transition. In this case the vibrational distribution of the product ion is determined by Franck–Condon factors between the autoionizing state and the final ion state.[30] Hence the resulting vibrational distribution is generally different from that for the direct ionization and probably depends on the impact energy.

The branching ratios obtained in the present experiment represent the nascent vibrational distribution of the $\tilde{A}$ state if collisional relaxation, interelectronic coupling with the other states, and cascading from upper states can be ignored. The frequencies of collisions that CO_2^+ ($\tilde{A}$) and CS_2^+ ($\tilde{A}$) suffer under our experimental conditions are estimated on the basis of the theoretical data obtained by

Lubmann *et al.*[31] using a hard sphere collision cross sections of 1 Å^2. The collisional probabilities of CO_2^+ ($\tilde{A}$) and CS_2^+ ($\tilde{A}$) during the lifetime are estimated to be 5×10^{-4}–2×10^{-3} and ~ 0.03, respectively, on comparing with the fluorescence lifetime of CO_2^+ ($\tilde{A}$) 124 ns,[11] and that of CS_2^+ ($\tilde{A}$) 4.09 μs.[32] Hence, the vibrational relaxation of the emitting species is negligible.

A. Carbon dioxide (CO_2)

It becomes evident from Table I that the vibrational distribution of CO_2^+ ($\tilde{A}$) is independent of the impact energy within the experimental error. This fact leads to the result that the process leading to formation of CO_2^+ is the same in the 30–300 eV range. We did not measure emission spectra at impact energies below 30 eV because of weak intensity. The distribution in the present experiment is very similar to that obtained by PES,[22] which corresponds to a Franck–Condon-type vertical ionization. It is concluded that, in the electron impact in the 30–300 eV range, an excitation of Franck–Condon type mainly contributes to formation of CO_2^+ ($\tilde{A}$). Nevertheless, the vibrational distribution produced by electron impact has the highest population at the $v_1' = 1$–2 levels, which is slightly shifted to lower vibrational levels than those obtained by PES[22] and PIES.[9]

The vibrational populations of the $\tilde{A}$ state in the PIOS result[8] shift to higher vibrational levels compared with the PIES result.[9] This discrepancy is attributed to the inter-electronic state coupling between the $\tilde{A}$ and $\tilde{B}$ states. Leach *et al.*[10] suggested that the (3,6,0), (4,4,0), and (0,2,2) levels are possible states perturbing with the (0,0,0) level of the $\tilde{B}$ state. In order to interpret the population enhancement of the $v_1' = 3$–5 levels, Endoh *et al.*[8] pointed that the emissions from these perturbing states are probably overlapped with the emissions from the $v_1' = 3$–5 levels. Although several vibrational bands appears in the 360–410 nm region (Fig. 2), we failed to identify the transitions from these perturbing levels. In the present experiment the transitions from the $v_1' = 3$–5 levels are clearly isolated. This indicates that the present results is not affected by the interelectronic coupling between the $\tilde{A}$ and $\tilde{B}$ states. This is consistent with the fact that the vibrational distribution in the present result rather shifts to lower vibrational levels compared with the other data.

B. Carbon disulfide (CS_2)

In the CS_2^+ ($\tilde{A}-\tilde{X}$) emission, the $(v_1' - 1,2,0)$–$(v_1',0,0)$ bands are observed in addition to the principal $(v_1',0,0)$–$(v_1'',0,0)$ bands owing to Fermi resonance.[13] Thus, there is little regularity in intensity variation of vibrational bands compared with the CO_2^+ ($\tilde{A}-\tilde{X}$) emission.

On the basis of the Franck–Condon principle and the selection rules for linear–linear transitions, the progression of the symmetric stretching mode v_1 is strongly allowed, whereas the progression of the bending mode v_2 should be weak.[33] Nevertheless, the transitions involving two quanta of v_2 can borrow intensity from the allowed transitions through Fermi resonance[13] between the levels $(v_1',v_2',0)$ and $(v_1' - 1,v_2' + 2,0)$, which are of the same symmetry species;

in the $\widetilde{A}$ state the frequency of v_1' 610 cm^{-1} are almost equal to that of $2v_2''$ 550 cm^{-1}. Hence, we evaluated the nascent populations of the $(v_1',0,0)$ levels with including the populations of the $(v_1' - 1,2,0)$ levels. The present result for $N_{v'}$, which is constant in the impact energy of 30–300 eV, is significantly different from the PES data.[19] This indicates that the electron-impact ionization of CS_2 leading to the $\widetilde{A}$ ion state is not a Franck–Condon-type.

In the 30–300 eV range, the CS_2^+ ions can be produced in the $\widetilde{B}^2\Sigma_u^+$ and $\widetilde{C}^2\Sigma_g^+$ states as well as in the $\widetilde{A}^2\Pi_u$ state. If the $\widetilde{A}$ state ions are formed by cascading from the $\widetilde{B}$ and $\widetilde{C}$ states, the vibrational population of the $\widetilde{A}$ state may be different from the $\widetilde{A}$ state produced directly by the excitation of the Franck–Condon type. Nevertheless, the $\widetilde{C}$ state fully predissociates,[33] and no $\widetilde{B}$–$\widetilde{A}$ emission has been identified yet since the $\widetilde{B}$–$\widetilde{A}$ transition is symmetry forbidden. Thus, cascading from upper states can be neglected.

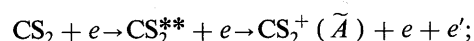The electronic configuration of the ground state of CS_2 except core electrons is[34]

$$(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4$$

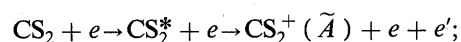and that of the produced $\widetilde{A}$ ion state is

$$(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^3(2\pi_g)^4.$$

In the electron impact there can be three types of ionization as non-Franck–Condon excitation:
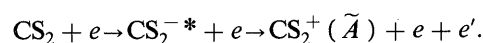
(1) Autoionization of Rydberg states converging to the $\widetilde{B}^2\Sigma_u^+$ state:

$$CS_2 + e \rightarrow CS_2^{**} + e \rightarrow CS_2^+ (\widetilde{A}) + e + e';$$

(2) Shape resonance:

$$CS_2 + e \rightarrow CS_2^* + e \rightarrow CS_2^+ (\widetilde{A}) + e + e';$$

(3) Negative ion formation:

$$CS_2 + e \rightarrow CS_2^{-*} + e \rightarrow CS_2^+ (\widetilde{A}) + e + e'.$$

In process (1), the target molecule is first excited to certain Rydberg state, which ionizes via autoionization. The vibrational distribution of the $\widetilde{A}$ state thus produced should be determined by Franck–Condon factors connecting the Rydberg state and the $\widetilde{A}$ ion state, which is generally different from that obtained via direct ionization. Lee *et al.*[12] observed the CS_2^+ ($\widetilde{A}$–$\widetilde{X}$) emission by photolysis at the photon energy of 12.4–24.8 eV. They reported that the emission cross section for the $\widetilde{A}$–$\widetilde{X}$ band is exceptionally high, 65 Mb, at 95.5 nm (13.0 eV), which is assigned to the 5s Rydberg member converging to the $\widetilde{B}^2\Sigma_u^+$ ion state in the absorption spectrum:[35,36] the fluorescence quantum yield for the $\widetilde{A}$–$\widetilde{X}$ band is 54% at 95.5 nm. Thus, more than a half of CS_2 excited in the 5s Rydberg state must finally decay into the $\widetilde{A}$ state.

The configuration of the ns Rydberg states converging to the $\widetilde{B}$ ion state is

$$(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^1(2\pi_u)^4(2\pi_g)^4(ns\sigma)^1.$$

One of the most probable mechanism for autoionization is Auger process,[26] in which an electron excited to the $ns\sigma$ Rydberg orbital is ejected by the energy released in the transition of an electron from the $2\pi_u$ orbital to the unfilled

$5\sigma_u$ orbital. In the electron energy-loss spectrum of CS_2, the ns Rydberg series is well developed and a large peak appears at 13 eV.[37] Hence, in electron impact, this autoionization process of the $(5\sigma_u)^{-1}ns\sigma$ Rydberg states should play a dominant role in formation of CS_2^+ ($\widetilde{A}$).

Next, we would like to discuss process (2), which corresponds to a shape resonance commonly observed in photoionization of several molecules.[38,39] One of the significant dynamical features in ionization arising from such a resonance is that the vibrational distribution of the final ion is no longer given simply by Franck–Condon factors.[38] In the case of CS_2, an electron escaping from the $2\pi_u$ orbital is temporally trapped in some unoccupied valence orbital (probably π^*) by the potential barrier, through which it may eventually tunnel and escape. Unfortunately, the cross section for process (2) is not known even qualitatively. Nevertheless, process (2) cannot be ruled out.

Finally, we will examine process (3). At certain energy, the incident electron excites CS_2 to the same Rydberg states as process (1) and then the scattered electron is simultaneously trapped in the field of the Rydberg excited state (core excited shape resonance).[38] The excited negative ion thus produced decays into neutral Rydberg states by one-electron process and eventually the CS_2^+ ($\widetilde{A}$) state can be produced via sequential autoionization. If process (3) is dominant, a relatively narrow structure should be exhibited in the emission cross section of CS_2^+ ($\widetilde{A}$–$\widetilde{X}$) transition. However, there are no such peaks in the cross section reported by Ajello and Srivastava.[14] Therefore, the contribution of process (3) is likely to be small.

V. SUMMARY

The CO_2^+ ($\widetilde{A}$–$\widetilde{X}$) and CS_2^+ ($\widetilde{A}$–$\widetilde{X}$) emissions produced by electron impact on jet cooled CO_2 and CS_2 were subjected to evaluate the vibrational populations of the $\widetilde{A}$ state. The vibrational distribution of CO_2^+ ($\widetilde{A}$) obtained in our careful study is similar to the PES data suggesting that the electron-impact ionization of CO_2 is an ionization of Franck–Condon type. On the other hand, the vibrational branching ratio of CS_2^+ ($\widetilde{A}$) obtained is very different from the PES data. This non-Franck–Condon behavior is mainly attributable to the autoionization of the ns Rydberg states converging to the $\widetilde{B}$ ion state.

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