

Vacuum ultraviolet absorption spectra of thiirane and thietane

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Photoabsorption cross sections of thiirane and thietane vapors have been studied in the 110–240 nm region using synchrotron radiation. A number of peaks from thiirane and thietane are arranged into four and five Rydberg series, respectively, converging to the first ionization potential. Many Rydberg peaks from both molecules are observed to possess vibronic structures. The vibrational progressions from thiirane are assigned to the CH₂ wagging (ν_4) and CS symmetry stretching (ν_5) modes. For thietane, the CH₂ wagging (ν_5) and CS symmetry stretching (ν_7) modes of the excited states are found to be active. Molecular geometries and vibrational frequencies for the excited states are discussed on the basis of *ab initio* calculations.

I. INTRODUCTION

The vacuum ultraviolet (VUV) absorption spectra of cyclic sulfides have appeared in the literature^{1–3} with a number of spectral properties and similarities with other sulfides and cyclic oxides. Although Clark and Simpson¹ reported the VUV spectra of thiirane and thietane, they did not offer a detailed analysis of the absorption spectra. Later, the absorption spectrum of thiirane had been assigned to three Rydberg series converging to the first ionization potential (IP).² Unfortunately, this result is inconsistent with the assignments of the *4s* and *4p* Rydberg members based on the electric dichroism spectrum.⁴ As for thietane, an excellent investigation has been conducted on Rydberg transitions: i.e., Whiteside and Warsop³ have assigned two Rydberg transitions converging to the first IP and concluded that the ground state of thietane ion is nonplanar on the basis of the vibrational analysis of Rydberg transitions. Nevertheless, from the analysis of divalent sulfides such as CH₃SH⁵ and (CH₃)₂S,⁶ we expect that additional Rydberg series are identified in the VUV spectra of thiirane and thietane. In this context, a reinvestigation of the absorption spectrum of thiirane and thietane is needed for an understanding of the Rydberg transition of molecules containing a second-row atom.

The present study is concerned with the assignment of absorption bands in the VUV region to the Rydberg transitions. Many Rydberg transitions of thiirane and thietane have been observed to possess vibronic structures. From the analysis of these vibrational progressions and molecular orbital considerations, the molecular geometries and force fields of the Rydberg state are discussed.

II. EXPERIMENTAL

The experimental setup has been described in a previous paper.⁵ In brief, synchrotron radiation provided by the electron storage ring (UVSOR) at Okazaki was dispersed by a 1 m Seya–Namioka monochromator before entering the gas cell. The transmitted VUV light was converted into UV light by a sodium salicylate-coated LiF window. The intensity of transmitted light and emission are monitored by each Ha-

mamatsu R585 photomultiplier. The photoabsorption cross section was derived from the attenuation of incident light by sample vapor. They fail to give any emission in the 180–650 nm region at the sensitivities available to us.

The thiirane was purchased from Aldrich with a stated purity of better than 99% and thietane was purchased from Tokyo Kasei with a stated purity of better than 98%. No further purification was made except several freeze–pump–thaw degassing. Fresh sample vapor was constantly introduced into the gas cell and slowly pumped with a rotary pump. The vapor pressure was monitored by an MKS Baratron. All data were measured at vapor pressures lower than 2.8 Pa.

III. RESULTS

The VUV absorption cross sections of thiirane and thietane are shown in Figs. 1 and 2 with the Rydberg progressions identified. There are a number of sharp peaks in the absorption spectra of thiirane and thietane. Many of lower Rydberg transitions are observed to be accompanied by vibrational structures. These progressions have been analyzed in terms of the totally symmetric vibration on the basis of the analogy between the vibrational frequencies for the Rydberg states and those for the ground state of thiirane⁷ and thietane.⁸ The experimental uncertainty in the absorption cross section was estimated to be within $\pm 15\%$ of the given value.

Tentative identifications of the Rydberg transitions were made by calculating the effective quantum number by use of the published values of IP.^{9–11} These observed transitions were grouped and then within each series the value of IP and the quantum defect (δ) were refined by a least-square method. In each case, a number of absorptions were found to fit the Rydberg progressions of the form

$$\bar{\nu}_n = \text{IP} - R/(n - \delta)^2, \quad (1)$$

where *R* is the Rydberg constant. The central sulfur atom of these molecules is a second-row atom possessing low-lying empty 3*d* orbitals. Thus, in all spectra, the initial member of

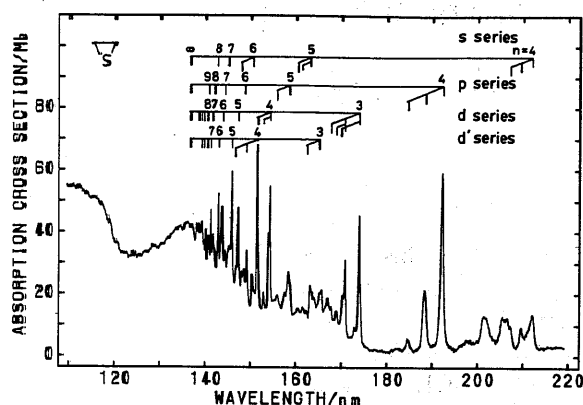


FIG. 1. The absorption cross sections of thiirane in the 110–220 nm region measured at a spectral resolution of 0.2 nm ($1 \text{ Mb} = 10^{-22} \text{ m}^2$). The four Rydberg series converging to the first IP are displayed.

s- or *p*-type Rydberg series is assigned an n of 4, which restricts δ to values between one and two, whereas the initial member of *d*-type series is assigned an n of 3, which restricts δ to zero and one.

A. Thiirane: $(\text{CH}_2)_2\text{S}$

Four Rydberg series of thiirane thus constructed are

s series: $\bar{\nu}_n = 73\,076 - R/(n - 1.907)^2$, $n = 4-8$,

p series: $\bar{\nu}_n = 73\,144 - R/(n - 1.663)^2$, $n = 4-9$,

d series: $\bar{\nu}_n = 73\,048 - R/(n - 0.351)^2$, $n = 3-10$,

d' series: $\bar{\nu}_n = 73\,117 - R/(n - 0.072)^2$, $n = 3-11$.

These Rydberg series converging to the first IP are designated to the *s*, *p*, *d*, *d'* series for brevity. The goodness of the fit of these series is displayed in Table I. The weighted average of the series limits for the four Rydberg transitions is $73\,090 \pm 60 \text{ cm}^{-1}$ ($9.072 \pm 0.008 \text{ eV}$), which is in good agreement with the published values of 9.05 and 9.03 eV obtained by photoelectron spectrum.^{9,11}

Many of lower members of the four Rydberg series possess vibrational progressions. The vibronic frequency intervals and their assignments obtained are listed in Table II.

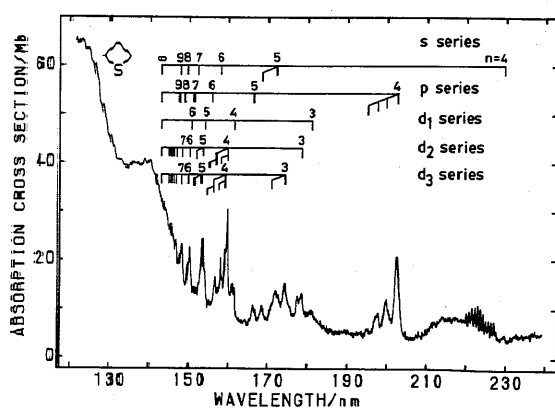


FIG. 2. The absorption cross sections of thietane in the 120–240 nm region measured at a spectral resolution of 0.2 nm. The five Rydberg series converging to the first IP are displayed.

TABLE I. Rydberg progressions of thiirane (in cm^{-1}).

n	$\bar{\nu}_{\text{obs}}$	$\bar{\nu}_{\text{calc}}$	$\Delta\nu$	n	$\bar{\nu}_{\text{obs}}$	$\bar{\nu}_{\text{calc}}$	$\Delta\nu$
<i>s</i> series				<i>d</i> series			
4	47 137	48 017	-880	3	57 508	57 407	101
5	61 286	61 602	-316	4	64 821	64 805	16
6	66 520	66 524	-4	5	67 939	67 970	-31
7	68 856	68 844	12	6	69 604	69 609	-5
8	70 112	70 119	-7	7	70 567	70 566	1
				8	71 159	71 172	-13
				9	71 597	71 581	16
				10	71 886	71 869	17
<i>p</i> series				<i>d'</i> series			
4	52 029	53 048	-1019	3	60 507	60 317	190
5	63 119	63 288	-169	4	66 011	66 005	6
6	67 308	67 309	-1	5	68 592	68 598	-6
7	69 286	69 291	-5	6	69 984	69 994	-10
8	70 428	70 411	17	7	70 812	70 831	-19
9	71 095	71 105	-10	8	71 383	71 371	12
				9	71 762	71 740	22
				10	71 999	72 004	-5
				11	72 197	72 198	-1

B. Thietane: $(\text{CH}_2)_3\text{S}$

A great number of transitions of thietane are classified into the following Rydberg series:

s series: $\bar{\nu}_n = 69\,817 - R/(n - 1.911)^2$, $n = 4-9$,

p series: $\bar{\nu}_n = 69\,786 - R/(n - 1.586)^2$, $n = 4-9$,

*d*₁ series: $\bar{\nu}_n = 69\,852 - R/(n - 0.286)^2$, $n = 3-6$,

*d*₂ series: $\bar{\nu}_n = 69\,821 - R/(n - 0.162)^2$, $n = 3-11$,

*d*₃ series: $\bar{\nu}_n = 69\,844 - R/(n - 0.057)^2$, $n = 3-11$.

These transitions are abbreviated to the *s*, *p*, *d*₁, *d*₂, and *d*₃ series, respectively. The observed and calculated wave

TABLE II. Observed vibronic frequency intervals in the Rydberg states of thiirane and thietane (in cm^{-1}).

Thiirane state	ν_4	ν_5	Thietane state	ν_5	ν_7
\bar{X}^1A_1		626 ^a	\bar{X}^1A_1	1226 ^c	698 ^c
		1048 ^b		1268 ^b	787 ^b
4 <i>s</i>	1081	562	4 <i>p</i>		630
4 <i>p</i>	1060		3 <i>d</i> ₃	1148	
3 <i>d</i>	1060	620	5 <i>s</i>	1192	
3 <i>d'</i>	1081		5 <i>p</i>		717
5 <i>s</i>	1047	614	4 <i>d</i> ₂	1192	680
5 <i>p</i>	1037		4 <i>d</i> ₃	1167	688
4 <i>d</i>		586	6 <i>s</i>		704
4 <i>d'</i>	1054		5 <i>d</i> ₂	1202	704
6 <i>s</i>	1057		5 <i>d</i> ₃	1202	708
5 <i>d</i>	1041		6 <i>d</i> ₂		672
\bar{X}^2B_1	1088 ^b	526 ^b	\bar{X}^2B_1	1268 ^b	738 ^b

^a Observed value reported in Ref. 7.

^b Calculated value in the present study. See Tables V and VII for the descriptions.

^c Observed value reported in Ref. 8.

numbers for these Rydberg series are listed in Table III. The weighted average of the series limit for the five Rydberg transitions converging to the first IP is $69\,830 \pm 50 \text{ cm}^{-1}$ ($8.668 \pm 0.006 \text{ eV}$), which is in good agreement with the published values of 8.65 eV obtained by photoelectron spectrum¹⁰ and with the series limit obtained from two Rydberg series.³

Many of lower members of the four Rydberg series except the weak d_1 series are vibrationally structured. The vibrational frequency intervals together with their assignments are listed in Table II.

IV. MOLECULAR ORBITAL CALCULATIONS

There has been very limited information about the molecular geometries for the excited states of parent molecules.³ In order to estimate the change in the molecular structure on the excitation to the Rydberg states, *ab initio* calculations based on the GAUSSIAN 82 system¹² were carried out about the ground state of parents and their ions.¹³ Moreover, consistent sets of vibrational frequencies for the ground state of parents and their ions were calculated for the purpose of the assignment of vibrational progressions.

The basis set used is 4-31G*, which includes *d*-type polarization functions on carbon and sulfur atoms. All SCF calculations were carried out within the restricted Hartree-Fock (HF) formalism for the ground state of parents and within the unrestricted HF formalism for the ground state of parent ions. Geometries were optimized using an analytic energy gradient method and vibrational frequencies were computed analytically. It is well known that the vibrational frequencies calculated at the HF level are usually larger than the observed values. Thus, we find a scale factor in the case of the ground state of parent in bringing the HF/4-31G* harmonic frequencies into agreement with the observed values.^{7,8}

TABLE III. Rydberg progressions of thietane (in cm^{-1}).

<i>n</i>	$\bar{\nu}_{\text{obs}}$	$\bar{\nu}_{\text{calc}}$	$\Delta\nu$	<i>n</i>	$\bar{\nu}_{\text{obs}}$	$\bar{\nu}_{\text{calc}}$	$\Delta\nu$
<i>s</i> series				<i>d</i> ₂ series			
4	43 552	44 669	- 1117	3	55 982	56 195	- 213
5	58 102	58 316	- 214	4	62 567	62 370	197
6	63 247	63 253	- 6	5	65 142	65 132	10
7	65 595	65 579	16	6	66 596	66 601	- 5
8	66 854	66 857	- 3	7	67 458	67 474	- 16
9	67 627	67 633	- 6	8	68 013	68 034	- 21
<i>p</i> series				9	68 404	68 416	- 12
4	49 371	50 955	- 1584	10	68 714	68 687	27
5	60 107	60 371	- 264	11	68 903	68 886	17
6	64 152	64 154	- 2	<i>d</i> ₃ series			
7	66 055	66 042	13	3	57 349	57 171	178
8	67 100	67 119	- 19	4	62 784	62 784	0
9	67 797	67 790	7	5	65 347	65 352	- 5
<i>d</i> ₁ series				6	66 725	66 737	- 12
3	55 203	54 958	245	7	67 600	67 567	33
4	61 893	61 898	- 5	8	68 106	68 104	2
5	64 931	64 914	17	9	68 498	68 472	26
6	66 480	66 491	- 11	10	68 714	68 734	- 20
				11	68 903	68 927	- 24

TABLE IV. Equilibrium geometries for the \tilde{X}^1A_1 and $(3b_1)^{-1}\tilde{X}^2B_1$ ion states of thiirane (in Angstrom and degree).

Parameter	\tilde{X}^1A_1 4-31G*	Obs. ^a	$(3b_1)^{-1}\tilde{X}^2B_1$ 4-31G*
$r(\text{C-S})$	1.800	1.815	1.847
$r(\text{C-C})$	1.474	1.484	1.452
$r(\text{C-H})$	1.075	1.083	1.076
$\angle(\text{C-S-C})$	48.3	48.3	46.3
ϕ^b	150.8	151.8	159.4
$\angle(\text{H-C-H})$	114.5	115.8	116.0

^a r_s structure. Reference 15.

^b Angle between HCH bisector and C-C bond.

The thiirane molecule has a C_{2v} symmetry^{14,15}; here we use the geometry that the *z* axis is the C_2 symmetry axis and the plane of the molecule is in the *yz* plane. The electronic configuration of the occupied valence shell in the ground state is

$$(2b_1)^2(7a_1)^2(1a_2)^2(8a_1)^2(4b_2)^2(3b_1)^2.$$

The outermost $3b_1$ orbital is almost nonbonding and its main component is $3p_x$ orbital (n_s) of sulfur atom (93%) which is perpendicular to the plane of the ring. The ground state of thiirane ion corresponds to the removal of a $3b_1$ (n_s) electron. The resulting equilibrium geometries for the ground and $(3b_1)^{-1}$ ion states are summarized in Table IV. The calculated values of the totally symmetric vibrational frequencies are summarized in Table V together with the experimental values.⁷

The ring-puckering motion of thietane has been studied by Harris *et al.*¹⁶ and the potential function is found to have a double minimum with a barrier of 274 cm^{-1} at the planar configuration. Thus, the thietane molecule has a C_s symmetry.¹⁷ On the other hand, the vibrational assignment has been discussed in terms of a planar-ring structure (C_{2v} symmetry).⁸ The averaged conformation of the ring is probably approximated to be planar since the barrier height is comparable with the thermal energy. In this context, geometrical parameters and vibrational frequencies have been mainly analyzed under the constraint of C_{2v} symmetry.

TABLE V. Predicted totally symmetric vibrational frequencies for the \tilde{X}^1A_1 and $(3b_1)^{-1}\tilde{X}^2B_1$ ion states of thiirane (in cm^{-1}).

Assignment	Approximate description	\tilde{X}^1A_1 4-31G**a	Obs. ^b	$(3b_1)^{-1}\tilde{X}^2B_1$ 4-31G**a
ν_1	CH ₂ str.	3003	3017	3012
ν_2	CH ₂ scis.	1497	1471	1477
ν_3	CH ₂ wagg. + CC str.	1125	1107	1157
ν_4	CH ₂ wagg. + ring breath.	1048		1088
ν_5	CS sym. str.	634	626	526

^a The scaled frequencies have been reduced by 9.5%.

^b Reference 7.

TABLE VI. Equilibrium geometries of the \tilde{X}^1A_1 and $(4b_1)^{-1}\tilde{X}^2B_1$ ion states of thietane under the constraint of C_s or C_{2v} symmetry (in Angstrom and degree).

Parameter	\tilde{X}^1A_1	C_s Obs. ^a	C_{2v} 4-31G*	$(4b_1)^{-1}\tilde{X}^2B_1$	
	C_s 4-31G*			C_s 4-31G*	C_{2v} 4-31G*
$r(\text{C-S})$	1.832	1.847(2)	1.843	1.832	1.839
$r(\text{C-C})$	1.540	1.549(3)	1.541	1.544	1.542
$r(\text{C}_\alpha\text{-H})$	1.088		1.081	1.082	1.079
$r(\text{C}_\beta\text{-H})$	1.087	1.100(6)	1.079	1.082	1.081
$\angle(\text{C-S-C})$	77.5	76.8(0.3)	77.0	78.4	77.7
δ^b	19.6	26(2)	0 (fix)	17.0	0 (fix)
$\angle(\text{H-C}_\alpha\text{-H})$	109.1	112(4)	109.9	109.0	108.7
$\angle(\text{H-C}_\beta\text{-H})$	108.4	114(5)	108.9	108.9	109.6
$\angle(\text{C-C-S})$	91.4	90.6(0.3)	92.1	92.2	92.7
$\angle(\text{C-C-C})$	96.2	95.6(0.4)	96.2	97.2	96.9

^a Reference 17.^b Dihedral angle of the ring.

The electronic configuration of the occupied valence shell in the ground state under the C_{2v} geometry is

$$(8a_1)^2(2b_1)^2(9a_1)^2(1a_2)^2(4b_2)^2 \\ \times (3b_1)^2(5b_2)^2(10a_1)^2(4b_1)^2.$$

The outermost $4b_1$ orbital is almost nonbonding and is mainly composed of $3p_x$ orbital (n_s) of sulfur atom (86%). The ground state of thietane ion corresponds to the removal of a $4b_1(n_s)$ electron. The resulting equilibrium geometries for the ground and $(4b_1)^{-1}$ ion states are summarized in Table VI. The calculated values of the totally symmetric vibrational frequencies under C_{2v} geometry are summarized in Table VII together with the experimental values.⁸

V. DISCUSSION

A. Assignments of Rydberg transitions

For thiirane, a number of peaks are assigned to the four Rydberg series in the present study (see Table I). This assignment, however, differs from the assignment of Basco and Morse²: i.e., the p and d series in the present study correspond to the ns and np series, respectively, in their assignments. We believe that the assignment and conclusion of Basco and Morse² must be revised for the following reasons:

First, the δ values for the ns and np Rydberg series of sulfur-containing molecules are evaluated to be 1.90–2.00 and 1.55–1.60, respectively^{5,6,18–21}; second, the np Rydberg series with $\delta \approx 1.3$ is not identified except for H_2S^{21} ; third, the assignment of the $4p$ and $4d$ Rydberg members based on electric dichroism spectra⁴ agrees with the present result. Hence, the δ value of 1.72 for the ns series in their assignments is considerably smaller than those of other sulfides. Accordingly, the ns , np , and nd Rydberg series² must be assigned to the np , nd , and ns series, respectively.

There are a few bands below 180 nm which cannot be assigned to the Rydberg transition originating from a $3b_1$ electron of thiirane. Nevertheless, these bands are successfully assigned to the lower Rydberg transitions correlating with the second or the third IP as shown in Table VIII. In the assignment, we used the polished values of IP.^{9,11}

In addition to the unambiguous Rydberg transitions thus assigned, several peaks have been observed above 180 nm. Two of these transitions possessing vibrational progressions are tentatively assigned to the $4s$ and $4p$ Rydberg members (see Fig. 1 and Table I). However, they do not fit their Rydberg equations very well and are severely perturbed: The putative $4s$ and $4p$ Rydberg members lie to the red of predicted position. Thus, the $4s$ and $4p$ Rydberg states must possess mixed Rydberg-valence characters. The $4s$

TABLE VII. Predicted totally symmetric vibrational frequencies for the \tilde{X}^1A_1 and $(4b_1)^{-1}\tilde{X}^2B_1$ ion states of thietane under C_{2v} geometry (in cm^{-1}).

Assignment	Approximate description	\tilde{X}^1A_1	Obs. ^b	$(4b_1)^{-1}\tilde{X}^2B_1$
		4-31G**		4-31G**
ν_1	CH_2 str.	2943	2950	2967
ν_2	CH_2 str.	2923	2950	2952
ν_3	CH_2 bend.	1507	1460	1490
ν_4	CH_2 bend.	1470	1460	1429
ν_5	CH_2 wagg.	1268	1226	1268
ν_6	C-C str.	911	932	911
ν_7	C-S str.	787	698	738
ν_8	ring def.	551	528	508

^a The scaled frequencies have been reduced by 9.7%.^b Reference 8.TABLE VIII. Lower Rydberg transitions of thiirane originating from the $4b_2$ and $8a_1$ orbitals.

$\bar{\nu}_{\text{obs}}$ (cm^{-1})	Assignment ^a	δ
64 982	$4b_2 \rightarrow 4s$	2.02–2.04
74 507	$4b_2 \rightarrow 4p$	1.52–1.55
77 622	$4b_2 \rightarrow 3d$	0.25–0.29
77 966	$8a_1 \rightarrow 4p$	1.50–1.62
80 238	$4b_2 \rightarrow 5s$	1.94–2.00
80 691	$8a_1 \rightarrow 3d$	0.26–0.42

^a The assignments by using the published values of IP for the $4b_2(\sigma_{\text{SC}}, \sigma_{\text{CC}}^*)$ and $8a_1(\sigma_{\text{SC}}, \sigma_{\text{CC}})$ electrons, which are 11.32–11.37 and 11.72–11.93 eV, respectively (Refs. 9 and 11).

Rydberg member is overlapped with the 195–212 nm band, which has been assigned to the $b_2 \rightarrow b_2^*$ transition¹ or the $a_1 \rightarrow b_2^*(\sigma \rightarrow \sigma^*)$ transition.²² The present study offers no information for either assignment other than the result that the 204–212 nm band has the 4s Rydberg character.

For thietane, the five Rydberg series have been assigned. Among these series the d_2 series is the most prominent. The d_2 and d_3 series correspond to Series I and II, respectively, assigned by Whiteside and Warsop.³ Although they have assigned Series I to the s type, the δ value of 2.14 is slightly larger than other sulfides.^{5,6,8–21} Therefore, we believe that Series I must be assigned to the d type since the other series with $\delta = 1.91$ has been constructed for the s type in the present study (see Table II).

All of the observed peaks below 180 nm have been unambiguously assigned to the five Rydberg series. The broad 181 nm band has been tentatively assigned to the $4d_1$ Rydberg member. On the other hand, Whiteside and Warsop³ have attributed this band to the intravalence transition (the $10a_1 \rightarrow 11a_1$ or the $4b_1 \rightarrow 6b_2$ transition). The intense 203 nm band assigned to the $4p$ Rydberg transition^{1,23,24} is considerably shifted to the blue of the predicted position. The $4p$ Rydberg state has been shown to be nonplanar for the ring.³ The putative 4s Rydberg transition lies to the red of the predicted position and is overlapped with the 208–235 nm band, which is a transition with extensive vibrational structure.³ This structure has been interpreted as an excitation to a planar state.

Following the notation of Wang *et al.*,²⁵ the Rydberg orbitals under C_{2v} symmetry where the z axis is the C_2 symmetry axis are

$$ns: a_1(\sigma_g) \quad \text{for } n \geq 4,$$

$$np: b_2(\sigma_u), a_1(\pi_u), b_1(\pi_u) \quad \text{for } n \geq 4,$$

$$nd: a_1(\sigma_g), a_2(\pi_g), b_2(\pi_g),$$

$$a'_1(\delta_g), b_1(\delta_g) \quad \text{for } n \geq 3,$$

where the notations in parentheses correspond to $D_{\infty h}$; the y axis is the C_∞ symmetry axis. Among the transitions from the b_1 orbital in the ground state to the Rydberg orbitals, all transitions $(b_1)^{-1}n b_2^1 A_2 \leftarrow \tilde{X}^1 A_1$ are forbidden in the electric-dipole approximation. Thus, one s series, two p series, four d series (i.e., a total of seven series) should be observed. Among four d series, two series are identified from thiirane and three series from thietane.

It is well known that for diatomic molecules built up from atoms from the first period the quantum defect of a Rydberg series depends mainly on the Rydberg orbital and is approximately independent of the nature of the molecule and of the initial orbit of the electron.²⁶ This is also confirmed in small molecules containing a central atom from the second period.²³ In the present study, the assignment of the Rydberg series is based on the analogy between the quantum defects of thiirane or thietane and those of H_2S^{21} and $(CH_3)_2S^6$ which have the same C_{2v} geometry. Although, thietane belongs to the C_s symmetry, it is assumed that the local symmetry of C_{2v} can be applied to the C–S–C skeleton in order to compare with thiirane.²⁴ Consequently, the members of the s and p Rydberg series of thiirane or thietane

have been easily assigned to the $n_s(b_1) \rightarrow n s a_1$ and $n_s(b_1) \rightarrow n p b_1$ transitions, respectively. This is consistent with the assignments of 4s and 4p Rydberg members of thiirane and of 4p Rydberg member of thietane obtained by electric dichroism spectra.^{4,24}

The d Rydberg series with $\delta = 0.35$ of thiirane and the d_1 series with $\delta = 0.29$ of thietane undoubtedly correspond to the $2b_1 \rightarrow n d a_1(\sigma_g)$ Rydberg series with $\delta = 0.34$ of H_2S^{21} on the basis of the analogy among the quantum defects. Next, the quantum defects of 0.072 for the d' series of thiirane and that of 0.057 for the d_3 series of thietane reasonably agree with that ($\delta = 0.037$) of the $2b_1 \rightarrow n d a'_1(\delta_g)$ Rydberg series of H_2S .²¹ On the other hand, the d_2 series of thietane cannot be attributed to either the $n d a_2$ or the $n d b_1$ Rydberg transition.

B. Vibrational analysis

Many of the Rydberg members are observed to possess vibronic structure except the weak d_1 series of thietane. Vibrational analyses were performed on the lower Rydberg members from thiirane and thietane (see Table II). The predicted vibrational frequencies for the $\tilde{X}^2 B_1$ ion state are in approximate agreement with the observed and predicted values for the ground state of parents (see Tables V and VII). This agreement can be applied to the vibrational frequencies for the Rydberg states and the molecular geometries seem to be nearly unchanged upon excitation to the Rydberg states (see Tables IV and VI). Therefore, the most intense peak in each transition is assigned to the 0–0 band. The vibrational spacing were analyzed in terms of the ν_4 and ν_5 modes of the excited states for thiirane and the ν_5 and ν_7 modes for thietane.

For thiirane the two vibrational spacings of 560–620 and 1040–1080 cm^{-1} have been observed. The only prominent vibrational spacing reported for thiirane is 1050 cm^{-1} in the analysis of the Rydberg transitions of thiirane.² In the photoelectron spectrum of thiirane, Frost *et al.*⁹ have also reported the vibrational spacing of 1090 cm^{-1} , which is assigned to the ν_3 modes on comparing with the observed vibrational frequencies for the ground state of thiirane.⁷ Unfortunately, Thompson and Cave⁷ did not mention the frequency of the ν_4 mode in the vibrational analysis. In the present study, the ν_3 and ν_4 modes for the ground and $(3b_1)^{-1}$ ion states are assigned to the CH_2 wagging + CC stretching and CH_2 wagging (+ ring breathing) vibrations, respectively. We prefer the ν_4 mode for the observed spacing of 1040–1080 cm^{-1} . For thietane, the two vibrational spacings of 630–720 and 1150–1200 cm^{-1} have been observed. The former corresponds the ν_5 (CS stretching) mode and the later ν_7 (CH_2 wagging) mode in the excited states. This assignment is the same as the result obtained by the VUV absorption spectrum³ and the photoelectron spectrum.¹⁰

All of the Rydberg transitions converging to the first IP involve the promotion of a nonbonding electron into diffuse atomic orbitals. This suggests that neither the force field nor the molecular geometry is changed upon ionization. The observed vibrational frequencies of the Rydberg transitions from thiirane and thietane are in approximate agreement with the values for the ground state. Therefore, the force

field for the excited states is estimated to be almost unchanged from that for the ground state. On the other hand, the observation of the vibrational progressions is interpreted as molecular geometries for the excited states are partly changed from that for the ground state on the assumption of the Franck-Condon principle.

For thiirane, two of the five a_1 vibrational modes are seen to be active in the Rydberg transition. Molecular geometries of the $(3b_1)^{-1}$ ion state evaluated by MO calculations are partly changed from those of the ground state: $r(\text{C-S})$ is lengthened about 0.05 Å and ϕ enlarges about 10°. This change in geometry is caused by the change in the character of the $4b_2$ orbital upon ionization. The $4b_2$ orbital in the ground state is composed of the $3p_y$ orbital of sulfur (52%) and the $2p_z$ orbital of two carbon atoms ($2 \times 24\%$) and then its character is $\sigma_{\text{CS}} + \sigma_{\text{CC}}^*$. When the $3b_1$ electron ionizes, the C-S bond weakens and the C-C bond strengthens since the $3p_y$ component increases about 10% and the $2p_z$ component decreases.

For thietane, the ν_5 and ν_7 modes of the excited states are active among the eight a_1 vibrational modes. Unfortunately, molecular geometries for the $(4b_1)^{-1}$ ion state are almost equal to those for the ground state from MO calculations. The character of the $4b_1$ orbital in the ground state is n_{S} (86%) and π_{CH_2} of α methylene groups ($2 \times 7\%$), while the character in the $(4b_1)^{-1}$ ion state is n_{S} (55%) and π_{CH_2} of three methylene groups ($3 \times 15\%$). On the other hand, the component of the $5b_2$ orbital is mainly σ_{CS} in the ground state, while π_{CC}^* character increases upon ionization. When the $4b_1$ electron ionizes, molecular geometries of thietane are almost unchanged since the effects by the $4b_1$ and $5b_2$ orbitals compensate each other.

VI. SUMMARY

This analysis of the VUV absorption spectra of thiirane and thietane applying the C_{2v} point group shows that a number of peaks are assigned to the Rydberg series converging to the first IP. Lower members of these Rydberg transitions manifest vibronic structures. Two vibrational spacing observed from both molecules are essentially unchanged from their ground state on comparing with the observed and calculated vibrational frequencies. The vibrational analysis together with the calculated molecular geometries for thiirane gives rise to partly changed structure of the excited states with respect to the ground state; that is the lengthened C-S bond and enlarged angle between HCH bisector and C-C bond.

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