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The Formation of Electronically Excited Fragments by the Electron Impact of Furan and Related Five-membered Heterocycles

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In the wavelength region of 200—600 nm, photoemissions from electronically excited H, CH, C_2, and CS (only from thiophene and tetrahydrothiophene) were observed when furan, tetrahydrofuran, thiophene, and tetrahydrothiophene were excited by electron impact (0—70 eV). Hydrogen atoms (n=4) and CH($A^2\Delta$) radicals were produced from these five-membered heterocycles *via* single collision excitations, while CS($A^1\Pi$) radicals from thiophene and tetrahydrothiophene were partly formed in secondary processes. The appearance potentials for the hydrogen Balmer β and the CH($A^2\Delta$-$X^2\Pi$) bands from these five-membered heterocycles are determined, and the dissociation processes forming H(n=4) and CH(A) are discussed.

The excited electronic states of furan, tetrahydrofuran, thiophene, and tetrahydrothiophene have been investigated by means of their ultraviolet absorption spectra for more than sixty years. Recently, the excited electronic states of these heterocycles have also been studied by means of ultraviolet photoelectron spectroscopy.[1,2] Several decay processes from the electronically excited states of these five-membered heterocycles have been investigated by means of photolysis,[3] flash photolysis,[4] and electron-impact mass spectroscopy.[5—7] However, we have only a little information about electronically excited fragments from five-membered heterocycles and their fragmentation mechanisms. There seem to be only a few papers[8,9] on this subject.

In a previous paper, we have reported on the emission spectra of the fragment species from pyrrole and pyrrolidine.[10] The appearance potentials for the hydrogen Balmer β (H_β), CH($A^2\Delta$-$X^2\Pi$), and NH($A^3\Pi$-$X^3\Sigma$) bands from pyrrole and pyrrolidine are 18—23 eV about twice as large as the first ionization potentials of the parent heterocycles. In these cases, it appears that an ionic fragment is a by-product of the formation of neutral fragments.[10]

This paper will present the emission spectra of the fragments produced by the electron-impact dissociation of furan, tetrahydrofuran, thiophene, and tetrahydrothiophene. Further, the appearance potentials for the H_β and CH(A-X) emissions from these heterocycles are determined and possible dissociation processes forming H(n=4) and CH(A) are discussed.

Experimental

The apparatus consists of a collision chamber, a photon-detection system, and a control system. The collision chamber and the photon-detection system have been described in detail previously.[9] The sample pressures in the collision chamber during the emission measurements, as measured by means of an ionization gauge, were 5—40 mPa. An HTV R585 photomultiplier and an HTV C1230 photon-counter were used with the spectral resolution of 0.6 nm (FWHM). Electron-beam currents of 10 μA near the threshold and 40—50 μA at higher energies were used for the measurement of the excitation function.

A schematic electronic block diagram of the automatic control system used for the measurement of the excitation function is shown in Fig. 1. An AD converter (ICL 7109) is interfaced to a microcomputer (MZ-80K). After a preset counting time, the current electron-accelerating potential, the electron-beam current, and the photo-electron current are measured. These measurements are repeated several times at the same electron-accelerating potential. At the end of a counting cycle, the microcomputer sends a signal to a motor to advance the voltage regulator to the next voltage, thus setting a new counting cycle. After the experiment, the three values are recorded with a cassette tape recorder. These data, as well as the calculated excitation function, can be printed with a dot printer, while this excitation function can be plotted with as MIPLOT WX4671.

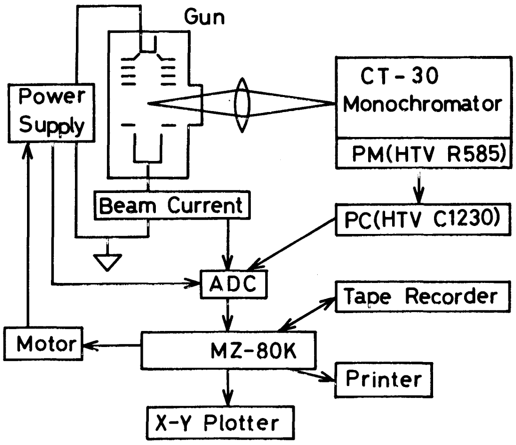

Fig. 1. The schematic electronic block diagram for the automatic control system.

The energy scale for the impinging electron was calibrated on the basis of both the peak of the excitation function for the (0, 0) band of the N_2($C^3\Pi$-$B^3\Pi$) emission reported by Finn *et al.*[11] and the appearance potential for the (0,0) band of the N_2^+($B^2\Sigma$-$X^2\Sigma$) emission reported by Borst and Zipf.[12] Nitrogen was mixed with the sample vapor, and their excitation functions were measured alternately.

The furan, thiophene, and tetrahydrothiophene (Nakarai guaranteed grade), and tetrahydrofuran (Wako guaranteed grade) were dried over sodium for several days. All the samples were subjected to several freeze-pump-thaw cycles just before use.

Results

Emission Spectra and Emission Intensities of Excited Fragment. Figure 2 shows the emission spectra produced by the electron impact of furan and tetrahydrofuran at an electron energy of 70 eV. Many

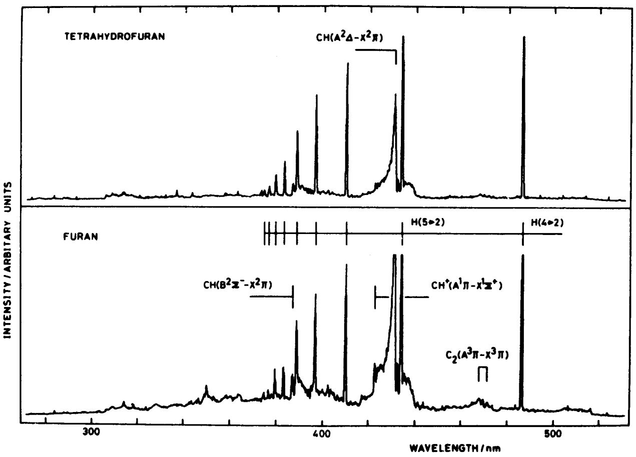

Fig. 2. Emission spectra by electron impact (70 eV, 0.5 mA) of tetrahydrofuran at 26 mPa and furan at 27 mPa.

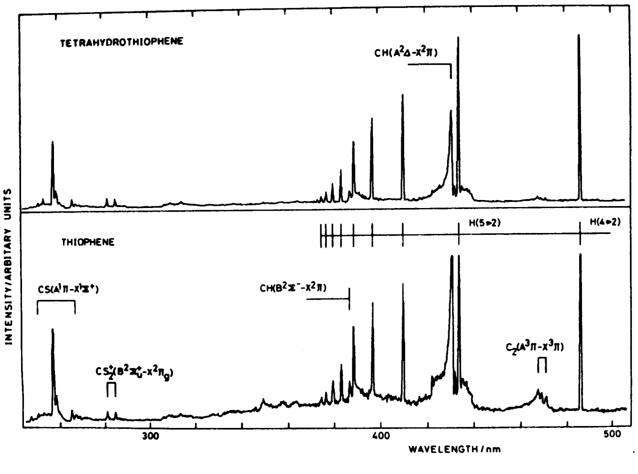

Fig. 3. Emission spectra by electron impact (70 eV, 0.5 mA) of tetrahydrothiophene at 27 mPa and thiophene at 27 mPa.

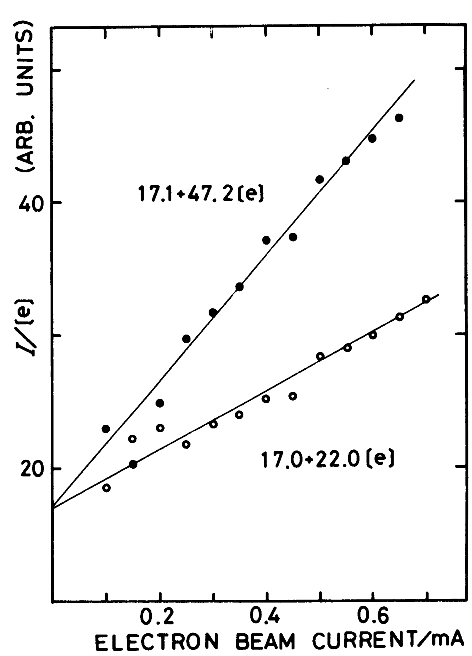

Fig. 4. Dependence of the photoemission intensity divided by the electron-beam current, $[I]/[e]$, on the electronbeam current. CS(A-X) emissionf rom thiophene (○), and from tetrahydrothiophene (●).

sharp bands were assigned to the hydrogen Balmer series ($n=4-10\rightarrow 2$), the CH($A^2\Delta$-$X^2\Pi$) band around 431 nm, the CH($B^2\Sigma$-$X^2\Pi$) band around 388 nm, the CH^+($A^1\Pi$-$X^1\Sigma$) band around 423 nm, and the C_2($A^3\Pi$-$X^3\Pi$) band around 470 nm. Further, weak emissions from CO and CO^+ were observed in the region of 240—470 nm. Figure 3 shows the emission spectra obtained from thiophene and tetrahydrothiophene. Besides the emission spectra for the hydrogen Balmer series and the CH(A-X) and CH(B-X) bands, the CS($A^1\Pi$-$X^1\Sigma$) band around 258 nm and the CS_2^+($B^2\Sigma$-$X^2\Pi$) band around 282 nm were observed.

The photoemission intensities of the H_β and CH(A-X) bands from furan, tetrahydrofuran, thiophene, and tetrahydrothiophene were proportional to the electron-beam current up to 0.5 mA and to the sample pressure up to 35 mPa in the collision chamber.

The emissions of the CS(A-X) band from thiophene and tetrahydrothiophene were weak. The intensities of the CS(A-X) band measured at a sample pressure of 30 mPa were found to deviate significantly from the proportional increase with the electron-beam current. If we assume that the emission intensity of the CS(A-X) band, $[I]$, includes the quadratic term on the electron-beam current, $[e]$, the emission intensity divided by the electron-beam current, $[I]/[e]$, can be represented by the following formula,[13] where A and B are adjustable constants:

$$[I]/[e] = A + B[e]. \tag{1}$$

Figure 4 shows the plot of $[I]/[e]$ as a function of $[e]$ for the CS(A-X) bands from thiophene and tetrahydro-

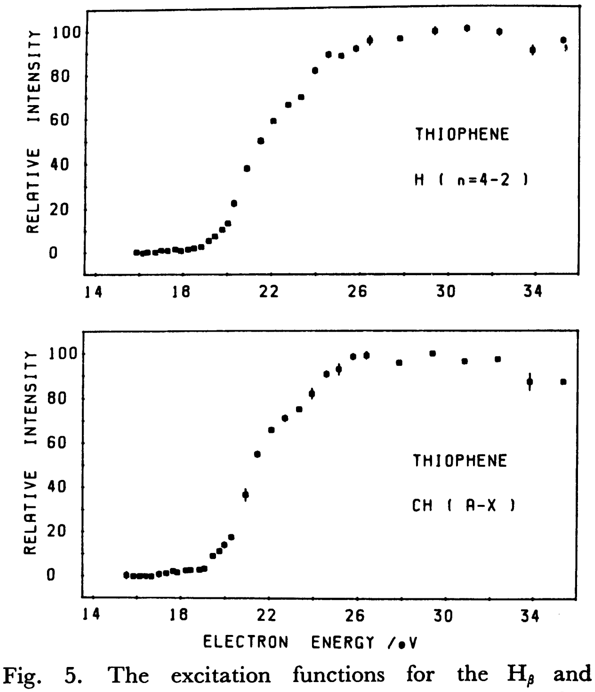

Fig. 5. The excitation functions for the H_β and CH(A-X) bands from thiophene. The error bar represents ± one standard deviation.

Table 1. Dissociation processes for the formation of H(n=4)

Dissociation process	Threshold/eV	
	Estd	Obsd
$(CH)_4O \longrightarrow C_4H_3O\cdot + H(n=4)$	17.6[a]	20.5±0.8
$(CH_2)_4O \longrightarrow C_4H_7O\cdot + H(n=4)$	17.1[b]	18.7±0.8
$(CH)_4S \longrightarrow C_4H_3S\cdot + H(n=4)$	17.6[a]	18.9±0.8
$(CH_2)_4S \longrightarrow C_4H_7S\cdot + H(n=4)$	17.1[b]	19.7±0.8

a) Estimated from the bond-dissociation energy of the C–H bond for benzene.[14] b) Estimated from the bond-dissociation energy of C–H for saturated hydrocarbon.[15]

thiophene. The reasonable fit to a straight line in each plot indicates that the emission intensities of the CS(A-X) band fairly well include the quadratic term on the electron-beam current. On the other hand, the emission intensities of the CS(A-X) band from thiophene and tetrahydrothiophene were found to be proportional to the sample pressure up to 35 mPa. This is probably because the number density of target molecules in the column of the electron beam is about two orders of magnitude lower than the electron density.

Appearance Potentials for the H_β and CH(A-X) Bands. Figure 5 shows the excitation functions for the H_β and CH(A-X) emissions from thiophene from their thresholds to 35 eV. The appearance potentials thus obtained for H(n=4) are listed in the third column of Table 1, while those for CH(A) are listed in the third column of Table 2.

Discussion

Photoemissions from Electronically Excited Fragments. The intensities of the hydrogen Balmer line and the CH(A-X) band from furan, tetrahydrofuran, thiophene, and tetrahydrothiophene were proportional to the electron-beam current and the sample pressure in the collision chamber. The excitation functions for the H_β and CH(A-X) band from these heterocycles were measured at sample pressures of 5—11 mPa; the appearance potentials were found to be independent of the sample pressure. Therefore, the H atoms and CH radicals from these heterocycles seem to be formed by fragmentation *via* a single-collision excitation. The two-step collision with another electron seems to be negligible.

On the other hand, the photoemission intensities of the CS(A-X) band from thiophene and tetrahydrothiophene fairly well include the quadratic term on the electron-beam current. Unknown secondary processes seem to participate in the formation of CS(A) to an appreciable extent; that is, the formation of CS(A) by way of a two-step excitation *via* an unidentified intermediate species is comparable to that by single-collision excitation at a beam current of more than 0.2 mA. The formation rates of CS(A) *via* single-collision excitations from thiophene and tetrahydrothiophene are of the same order of magnitude, for the A values for thiophene and tetrahydrothiophene, which were measured under similar experimental conditions, are nearly equal (see Fig. 4). The relative contributions of the two-electron excitation process to the single-electron excitation process, B/A, for thiophene and tetrahydrothiophene are estimated to be 1.3 and 2.8 respectively from the slope of $[I]/[e]$ and its extrapolation with beam-current to zero. That is, secondary processes in the formation of CS(A) from tetrahydrothiophene are twice

Table 2. Dissociation processes for the formation of CH($A^2\Delta$) and heat of formation for radicals and ions

Dissociation process		Threshold/eV	
		Estd	Obsd
$(CH)_4O$	$\longrightarrow C_2H_2(X) + CHO(X) + CH(A)$	11.4[a]	19.6±0.8
	$\longrightarrow C_3H_3^+(X) + O + CH(A)$	16.3—25.1[b]	
	$\longrightarrow C_3H_2^+(X) + OH(X) + CH(A)$	17.7—25.4[b]	
$(CH_2)_4O$	$\longrightarrow CH_3OH(X) + C_2H_3(X) + CH(A)$	10.3[a]	18.8±1.0
	$\longrightarrow C_2H_3^+(X) + CH_3OH(X) + CH(A)$	20.4[a]	
	$\longrightarrow C_3H_6^+(X) + OH(X) + CH(A)$	21.2[a]	
$(CH)_4S$	$\longrightarrow C_2H_2S^+(X) + CH(X) + CH(A)$	15.5—25.4[b]	18.7±1.0
	$\longrightarrow CHS^+(X) + C_2H_2(X) + CH(A)$	>17.0[b]	
$(CH_2)_4S$	$\longrightarrow C_2H_4S^+(X) + CH_3(X) + CH(A)$	19.8[a]	20.1±1.1
	$\longrightarrow C_2H_3S^+(X) + CH_4(X) + CH(A)$	19.4[a]	

Species	ΔH_f^0/kJ mol^{-1}	Ref.
CH	500.78 ± 0.4	16
OH	38.9 ± 1.2	16
CH_3	149.03 ± 0.84	16
C_2H_3	274—282	Estimated
CHO	−19.6	17
$C_2H_3^+$	1125	18
$C_3H_6^+$	960	18
$C_2H_4S^+$	866	6
$C_2H_3S^+$	1037.6	6

a) Estimated from the heat of formation. b) Estimated from the appearance potential of the by-product ion.[5]

as abundant as those from thiophene.

Ogawa *et al.*[13,19] have reported several similar results and have classified the excited species the emission intensities of which show non-linear relationships with the electron-beam current into the following two groups: (a) Fragments which have at least two heavy atoms and which are produced through the scission of two skeletal bonds, and (b) fragments with a new chemical bond. The CS(A) from thiophene and tetrahydrothiophene can be classified in Group (a). This result is consistent with the fact that the CS_2^+(B-X) band from thiophene and tetrahydrothiophene appears upon electron impact. The formation of the CS_2^+ ion can be classified in Group (b).

*Formation of H(*n*=4).* The onsets for the H_β emissions from furan, tetrahydrofuran, thiophene, and tetrahydrothiophene are found at 20.5 ± 0.8, 18.7 ± 0.8, 18.9 ± 0.8, and 19.7 ± 0.8 eV respectively. The dissociation processes which are expected to play an important role in the formation of H(n=4) and CH(A) near their thresholds are shown in the first column of Tables 1 and 2. The threshold energies of the dissociation processes listed in the second column of Table 1 are calculated by using the excitation energy of H(n=4), 12.75 eV,[20] and the bond dissociation energy of the C–H bond, 4.86 eV from benzene[14] or 4.31 eV from saturated hydrocarbons.[15] The excess energy of 1.3—2.9 eV for the difference between the observed and estimated thresholds in these processes is probably dissipated as the kinetic energy of the leaving hydrogen atom. These dissociation processes for the formation of excited H atoms following neither the cleavage of skeletal bonds nor new bond formation are similar to those with benzene,[9,21] pyridine and pyrazine[69] and pyrrolidine.[10]

Derrick *et al.*[22,23] have reported the structure of the Rydberg series in the photoelectron spectra of furan and thiophene and the associated ionization potentials. They have assigned the vertical ionization potentials of 17.5, 19.0, and 19.5 eV in furan to the $7a_1$, $6a_1$, and $4b_2$ orbitals respectively. This energy region is close to the onset of H(n=4). The approximate descriptions of the bonding orbitals have shown[22] that the r-type orbital, $7a_1$, is C–H bonding; the s-type orbital, $6a_1$, is C–C bonding, and the s-type orbital, $4b_2$, is strongly C–H bonding. On the basis of the character of the molecular orbitals and the comparison between the onset of H(n=4) and the ionization potentials, H(n=4) from furan seems to be produced *via* the Rydberg state, converging to the $4b_2$ ionization potential. The vertical ionization potentials of 16.16, 17.6, and 18.3 eV in thiophene have been assigned to the $7a_1$, $4b_2$ and $6a_1$ orbitals respectively by Derrick *et al.*[23] According to the approximate descriptions of the bonding orbitals,[23] the r-type orbital, $7a_1$, is characterized as C–H bonding, and the s-type orbitals, $4b_2$ and $6a_1$, as strongly C–H bonding. In similar considerations of the characters of the molecular orbitals and the ionization potentials, it is concluded that H(n=4) from thiophene is produced *via* the Rydberg state, converging to the $4b_2$ or the $6a_1$ ionization potential.

Formation of CH(A). The onsets for the CH(A-X) band from furan, tetrahydrofuran, thiophene, and tetrahydrothiophene are found at 19.6 ± 0.8, 18.8 ± 1.0, 18.7 ± 1.0, and 20.1 ± 1.1 eV respectively. The dissociation processes leading to the formation of CH(A) from these heterocycles are still uncertain because the available data of the heat of formation of ionic products are insufficient. Nevertheless, if one assumes that the threshold energy consists of the electron-excitation energy of CH(A) and the heat of formation, the main dissociation processes leading to the formation of CH(A) seem to include an ionic by-product. The appearance potentials observed for CH(A) are much higher than the first ionization potentials for furan, 9.06 eV;[24] for tetrahydrofuran, 9.57 eV;[25] for thiophene, 8.87 eV,[26] and for tetrahydrothiophene, 8.57 eV.[6] Accordingly, it is possible that an ionic fragment is a by-product in the formation of CH(A). The threshold energies of the dissociation processes leading to the formation of CH(A) from tetrahydrofuran and tetrahydrothiophene, listed in the second column of Table 2, are calculated from the excitation energy of CH(A) and the heat of formation. The threshold energies for these processes from furan and thiophene are calculated from the excitation energy of CH(A) and the appearance potential for a by-product ion reported by Hissel.[5] The heat of formation and the appearance potentials used for the calculation of the thresholds are summarized in Table 2. The by-product ions in the dissociation processes forming CH(A) (see Table 2) are abundant in mass-spectroscopy measurements.[5,6]

Another possibility for the formation of CH(A) is that by-products are formed in their electronically excited states. It is not possible to derive the processes which may be involved, because the relevant dissociation energies and the electronic energies are not known.

The onsets for the CH(A-X) band resulting from the formation of only neutral fragments are estimated to be 10—16 eV.[9,20] On the basis of the electron-impact energy-loss spectra of furan and thiophene[27] and the photoelectron spectra of furan[22] and thiophene,[23] we may expect the excitation cross-sections for the collision of electrons with furan and thiophene in these energy regions to be relatively large; these excitations seem to be spin-forbidden transitions, mainly in the 11—13 eV region. However, no onset for the CH(A-X) band from any five-membered heterocycles were observed in the 10—16 eV region; competing processes, such as ionization or radiationless decay, may be abundant.

References

1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," John Wiley & Sons, London (1970).

2) K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules," Japan Sci. Soc. Press, Tokyo (1981).

3) B. C. Roquitte, *J. Am. Chem. Soc.*, **91**, 7664 (1969).

4) S. L. N. G. Krishnamachari and T. V. Venkitachalam, *Chem. Phys. Lett.*, **55**, 116 (1978).

5) J. Hissel, *Bull. Soc. Roy. Sci. Liege*, **21**, 457 (1952).

6) E. J. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **66**, 136

(1962).

7) A. S. Siegel, *Tetrahedron Lett.*, **1970**, 4113.

8) T. Ogawa, M. Toyoda, and N. Ishibashi, *Eng. Sci. Repts. Kyushu Univ.*, **2**, 17 (1980).

9) I. Tokue and M. Ikarashi, *Bull. Chem. Soc. Jpn.*, **54**, 2565 (1981).

10) I. Tokue, M. Ikarashi, and Y. Ito, *Bull. Chem. Soc. Jpn.*, **55**, 1250 (1982).

11) T. G. Finn, J. F. M. Aarts, and J. P. Doering, *J. Chem. Phys.*, **56**, 5632 (1972).

12) W. L. Borst and E. C. Zipf, *Phys. Rev. A*, **1**, 834 (1970).

13) M. Tsuji, T. Ogawa, Y. Nishimura, and N. Ishibashi, *Bull. Chem. Soc. Jpn.*, **50**, 2432 (1977).

14) A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **89**, 4578 (1967).

15) J. D. Coxon and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York (1970).

16) D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd ed, Nt. Stand. Ref. Data Ser., Nat. Bur. Stand., **37**, 1141 (1971).

17) R. I. Reed and J. C. D. Brand, *Trans. Faraday Soc.*, **54**, 478 (1958).

18) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6**, Suppl. No. 1 (1977).

19) T. Ogawa, T. Iwasaka, M. Toyoda, M. Tsuji, and N. Ishibashi, *Bull. Chem. Soc. Jpn.*, **48**, 645 (1975).

20) S. Bashkin and J. O. Stoner, Jr., "Atomic Energy Levels and Grotrian Diagrams," North-Holland, Amsterdam (1975), Vol. 1.

21) C. I. M. Beenakker and F. J. de Heer, *Chem. Phys. Lett.*, **29**, 89 (1974).

22) P. J. Derrick, L. Asbrink, O. Edqvist, B.-O. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 161 (1971).

23) P. J. Derrick, L. Asbrink, O. Edqvist, B.-O. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 177 (1971).

24) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

25) A. D. Bain, J. C. Bunzli, D. C. Frost, and L. Weiler, *J. Am. Chem. Soc.*, **95**, 291 (1973).

26) R. A. W. Johnstone and F. A. Mellon, *J. Chem. Soc., Faraday Trans. 2*, **69**, 1155 (1973).

27) W. M. Flicker, O. A. Mosher, and A. Kuppermann, *J. Chem. Phys.*, **64**, 1315 (1976).