

# Vacuum Ultraviolet Spectra of Bromoethylene and Dibromoethylenes

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**Abstract:** The vacuum ultraviolet spectra of bromoethylene, 1,1-dibromoethylene, and *cis*- and *trans*-1,2-dibromoethylene are reported. The  $V \leftarrow N(\pi^* \leftarrow \pi)$  transition energies ( $52\,200$ – $46\,500\text{ cm}^{-1}$ ) are lower than those reported for the corresponding chloroethylenes and decrease upon additional bromine substitution. Other assignments made are *ns*, *np*, and *nd* Rydberg series converging on the  $\pi$  and nonbonding ionization potentials and associated vibrational components. As determined by this means, the  $\pi$  ionization potentials are: bromoethylene,  $9.90 \pm 0.01\text{ eV}$ ; 1,1-dibromoethylene,  $9.78 \pm 0.01\text{ eV}$ ; *cis*-1,2-dibromoethylene,  $9.63 \pm 0.01\text{ eV}$ ; and *trans*-1,2-dibromoethylene,  $9.55 \pm 0.01\text{ eV}$ . From the spectral data observed, a comparison is made of the relative stabilities of the nonbonding molecular orbitals, and evidence is presented indicating a high degree of interaction between the bromine substituents and the rest of the molecule.

General interest in molecular excited states is primarily based on the fact that many chemical reactions occur via excited states. Studies of such states are, therefore, of broad potential use in areas concerned with reaction mechanisms, especially those photochemically induced. There have been numerous studies of the spectral properties of the halogenated ethylenes, but the vacuum ultraviolet spectra of the bromoethylenes have not yet been reported. This study is concerned with this series of compounds and their absorption spectra in the region  $40\,000$ – $90\,000\text{ cm}^{-1}$  ( $250$ – $110\text{ nm}$ ). The principal features of these spectra are molecular Rydberg transitions and intravalent transitions associated with the  $\pi$  electrons and the bromine nonbonding p electrons. The absorptions attributed to Rydberg transitions were assigned using the Rydberg series expression:<sup>1</sup>

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

where  $\bar{\nu}_n$  is the observed transition energy, IP is the ionization potential, and  $R$  is the Rydberg constant.  $\delta$  is the quantum defect, and  $n - \delta$  is therefore an effective quantum number.  $R/(n - \delta)^2$ , the term value of the transition, is equal to the difference between the IP of the ground state and the observed energy of the Rydberg transition and can therefore be thought of as the ionization potential of the specific Rydberg state. For each of the compounds in this study, it was observed that the term values of the Rydberg levels were relatively constant, regardless of the originating molecular orbital. The regularity of these energies was of predictive value in making Rydberg assignments.

Rydberg orbitals are characterized by having a greater principal quantum number,  $n$ , than the highest filled valence shell orbital, and this quantum number is then modified by a value of  $\delta$  which reflects the extent of orbital penetration into the molecular core. Therefore, the first Rydberg transition from a C=C bonding orbital is considered to terminate at an  $n = 3$  level, with  $\delta$  values in the range of  $0.1$ – $1.0$ , while the corresponding transition from a nonbonding orbital on bromine is to an  $n = 5$  Rydberg orbital with  $\delta$  values between  $2.0$  and  $3.0$ .<sup>2</sup> In the bromoethylenes, absorptions associated with both types of transitions are observed, and the choice is whether to number the first Rydberg levels differently depending on the originating molecular orbital or to number consistently beginning with either  $n = 3$  or  $5$  regardless of assignment. Because of reasons to be presented later concerning the high degree of interaction between the bromine substituents and the rest of the molecule, it was decided to begin all Rydberg series with the  $n = 5$  member. In any case, the distinction is more

philosophical than practical, since the resulting  $n - \delta$  term is numerically identical for the two choices.

In order to determine the term values of the absorptions, the ionization potentials of the compounds are required. The available photoelectron ionization potential values are listed in Table I, together with the assignments given in the two previous studies.<sup>3,4</sup> There is some disagreement, both in numerical values and in assignments, between these two studies, and it is hoped that this investigation will clear up the ambiguities. In determining the symmetry labels for the orbitals, the highest-fold rotation axis is the  $z$  axis, and the  $x$  and  $y$  axes are then assigned according to the right-hand rule. Some previous studies are cited where the axes were labeled differently. In such cases, the symmetry labels will be translated into those consistent with the above described method to facilitate comparison.

## Experimental Section

The instrumentation used to obtain the spectra has been described in detail elsewhere.<sup>5</sup> The compounds were obtained from Columbia Organic Chemicals. These were of the highest purity available and were further purified by low-temperature vacuum distillation. In obtaining the spectra of *cis*- and *trans*-1,2-dibromoethylene, it was found necessary to introduce a fresh sample after scanning across the  $\pi^* \leftarrow \pi$  absorption. 1,2-Dichloroethylene has been shown<sup>6</sup> to undergo *cis*-*trans* isomerization upon excitation of the  $\pi^* \leftarrow \pi$  transition, and as expected the analogous bromo compounds behave similarly.

## Spectral Assignments

**Bromoethylene.** The vacuum ultraviolet spectrum of bromoethylene is given in Figure 1, with the assigned Rydberg absorptions indicated. The A band is broad and fairly intense ( $\epsilon = 7780\text{ l.}/(\text{mol cm})$ ), with its maximum at about  $52\,200\text{ cm}^{-1}$ . It is assigned to the  $V \leftarrow N(\pi^* \leftarrow \pi)$  transition, in comparison with data from chloroethylene,<sup>7</sup> which has the intensity maximum of its  $\pi^* \leftarrow \pi$  band at  $54\,000\text{ cm}^{-1}$  and  $\epsilon = 8000\text{ l.}/(\text{mol cm})$ . Superimposed on the higher energy side are three weak absorptions separated by  $1344\text{ cm}^{-1}$ , the C=C symmetric stretch, decreased from its value of  $1605\text{ cm}^{-1}$  in the ground state.<sup>8</sup> These absorptions are assigned to the first member of an *ns*  $\leftarrow \pi$  Rydberg series ( $\delta\,2.97$ ,  $n = 5$ – $9$ ) converging to a limit of  $9.90\text{ eV}$ .

In the  $59\,000$ – $64\,000\text{ cm}^{-1}$  region of the spectrum, a number of sharp peaks are present and assigned to Rydberg transitions. The strong peak at  $62\,759\text{ cm}^{-1}$  is the first member of an *ns* Rydberg series ( $\delta\,2.96$ ,  $n = 5$ – $10$ ) converging to the ionization potential attributed to the in-plane nonbonding electrons. The band system beginning at  $61\,862\text{ cm}^{-1}$  is assigned to the first member of an *np*  $\leftarrow \pi$  Rydberg series ( $\delta\,2.57$ ,  $n = 5$ – $10$ ). It has three members of the in-plane C–C–Br

**Table I.** Photoelectron Ionization Potentials of Bromoethylene and Dibromoethylenes<sup>a</sup>

Compd	IP <sup>b</sup>	IP <sup>c</sup>
CH <sub>2</sub> =CHBr	9.87 (a'')	9.80 (a'')
	10.87 (a')	10.90 (a')
<i>trans</i> -CHBr=CHBr	12.30 (a'')	12.28 (a'')
	9.55 (a <sub>u</sub> )	9.44 (a <sub>u</sub> )
	11.04 (a <sub>g</sub> )	11.05 (a <sub>g</sub> )
	11.04 (b <sub>u</sub> )	11.05 (b <sub>g</sub> )
	11.57 (b <sub>g</sub> )	11.60 (b <sub>u</sub> )
<i>cis</i> -CHBr=CHBr	12.90 (a <sub>u</sub> )	13.00 (a <sub>u</sub> )
	9.63 (b <sub>2</sub> )	9.44 (b <sub>2</sub> )
	10.74 (b <sub>1</sub> )	10.74 (b <sub>1</sub> )
	11.23 (a <sub>1</sub> )	11.24 (a <sub>2</sub> )
	11.53 (a <sub>2</sub> )	11.56 (a <sub>1</sub> )
CH <sub>2</sub> =CBr <sub>2</sub>	12.86 (b <sub>2</sub> )	12.85 (b <sub>2</sub> )
	9.78 (b <sub>2</sub> )	
	10.73 (b <sub>1</sub> )	
	11.23 (a <sub>1</sub> )	
	11.60 (a <sub>2</sub> )	
	13 (b <sub>2</sub> )	

<sup>a</sup> Values in electron volts and assignments in parentheses. <sup>b</sup> Reference 3. <sup>c</sup> Reference 4.

**Table II.** Rydberg Assignments for Bromoethylene

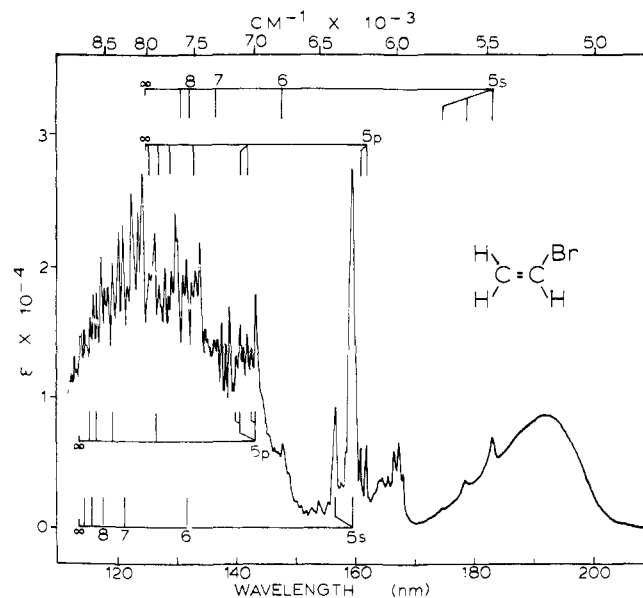
First IP, 79 860 cm <sup>-1</sup>					
<i>ns</i> ← π, δ 2.97		<i>np</i> ← π, δ 2.57			
<i>n</i>	$\bar{\nu}_{\text{obsd}}$	<i>n</i>	$\bar{\nu}_{\text{obsd}}$		
5	54 735	5	61 862		
6	67 801	6	70 577		
7	73 137	7	74 278		
8	75 560	8	76 086		
9	76 865	9	77 202		
		10	77 899		

Second IP, 87 880 cm <sup>-1</sup>					
<i>ns</i> ← n, δ 2.96		<i>np</i> ← n, δ 2.55		<i>nd</i> ← n, δ 2.11	
<i>n</i>	$\bar{\nu}_{\text{obsd}}$	<i>n</i>	$\bar{\nu}_{\text{obsd}}$	<i>n</i>	$\bar{\nu}_{\text{obsd}}$
5	62 759	5	69 881	5	74 722
6	75 959	6	78 765	6	80 678
7	81 162	7	82 332	7	83 285
8	83 493	8	84 189	8	84 717
9	84 875	9	85 244	9	85 521
10	85 668				

bending frequency associated with it, unchanged from its ground state value<sup>8</sup> for 345 cm<sup>-1</sup>. There is a system of peaks beginning at 59 584 cm<sup>-1</sup> which are assigned to a second 5p ← π Rydberg transition (δ 2.67). The corresponding 6p ← π absorption appears as a shoulder on the 69 881 cm<sup>-1</sup> peak to be discussed below, but higher members of the series could not be assigned because of the rapid decrease in peak intensities. Underlying the 59 584 cm<sup>-1</sup> band system is a broad absorption attributed to the π\* ← n transition, as consideration of the relative energies of the states would place this transition in this region.

The higher energy region of the spectrum beginning with the sharp band at 69 881 cm<sup>-1</sup> consists mainly of molecular Rydberg absorptions, including the higher members of the second ionization potential (*np*, δ 2.55, *n* = 5–9; *nd*, δ 2.11, *n* = 5–9). These energies are listed in Table II. There is, in addition, a very strong, sharp absorption at 80 431 cm<sup>-1</sup> which could not be fit to any of the above mentioned series, but has the proper term value for a 5p Rydberg absorption associated with the third ionization potential. Unfortunately, other

**Figure 1.** Absorption spectrum of bromoethylene. The assigned *ns* and *np* Rydberg series are shown.

members of this series are beyond the accessible region, thus this assignment must remain tentative at this time.

The absorptions in this spectrum offer insight into the nature of the excited states of bromoethylene. According to group theory, transitions to all three possible p Rydberg states are allowed for each of the molecular energy levels. However, it was not possible to assign three p Rydberg series for any of the ion states, which suggests that the p Rydberg electron is experiencing a higher degree of symmetry from the core than expected in the C<sub>s</sub> point group. Because of the significance of unresolved splittings in the absorption spectrum, attention will be focussed on the p Rydberg states associated with the first ionization potential, since the first members of these series occur in a relatively uncrowded region of the spectrum (59 000–64 000 cm<sup>-1</sup>).

Of the three allowed (π<sub>1</sub>, 5p) transitions (A' ← A' and 2(A'' ← A')) only two could be assigned, which suggests that two of the three p Rydberg states are accidentally degenerate. Since formal degeneracy is the result of symmetry, it is of interest to consider the possible excited-state symmetries that could lead to such a degeneracy in the p Rydberg states. If the core exerts a planar symmetric field on the Rydberg electron, only one transition is allowed. If, however, the predominant effect is one of linear symmetry, two transitions are expected, corresponding to excitations in which the transition moment is oriented parallel and perpendicular to the internuclear axis, respectively.

For a molecule which is linear in its ground state, the situation where the angular momentum of the excited electron is not coupled to the internuclear axis is referred to as Hund's coupling case d. Such a coupling scheme is most readily achieved in Rydberg states, where the Rydberg electron occupies an orbital that is larger and more diffuse than valence shell orbitals.<sup>9</sup> Since the results for bromoethylene indicate linear core symmetry in its p Rydberg states, it may be thought of as approaching case d coupling in these states. The effect, however, is less pronounced than in a molecule that is linear in both ground and excited states.

**1,1-Dibromoethylene.** The spectrum of 1,1-dibromoethylene and the assigned Rydberg series are given in Figure 2. Again, the A band region is broad and fairly intense; however, it is more highly structured than in bromoethylene. The first absorption has its maximum at 47 820 cm<sup>-1</sup> and is followed by another at 49 020 cm<sup>-1</sup>. These are assigned to the π\* ← π

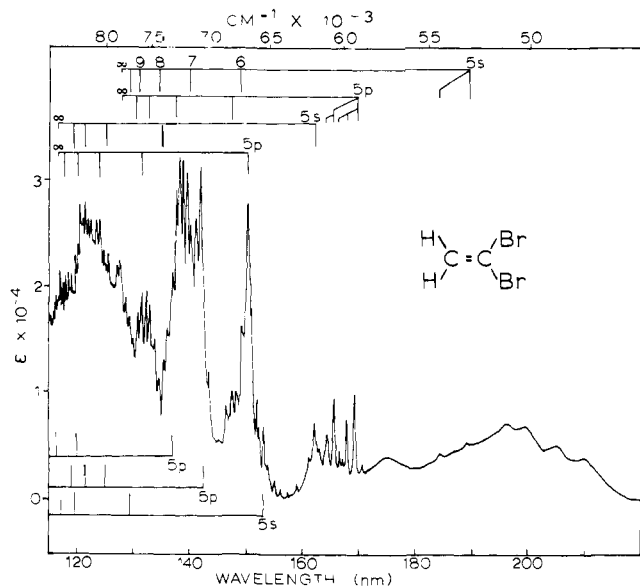


Figure 2. Absorption spectrum of 1,1-dibromoethylene, with assigned  $ns$  and  $np$  Rydberg series indicated.

transition and a single vibrational component of the symmetric C=C stretch<sup>8</sup> decreased to  $1150\text{ cm}^{-1}$  from the ground state value of  $1593\text{ cm}^{-1}$ . Following these is a more intense pair of bands at  $50\,350$  and  $51\,230\text{ cm}^{-1}$ , which is believed to be the result of torsional motion. The molecule possesses a low-lying  $\sigma^*$  orbital of  $b_1$  symmetry. A transition to this  $\sigma^*$  orbital from the  $b_2\pi$  orbital is forbidden for the planar molecule; however, upon twisting the transition becomes allowed. The torsional mode responsible for the nonplanarity was noted in the electronic spectra of ethylene and deuterated ethylene.<sup>10</sup>

Superimposed on the high energy side of these bands is the first member of an  $ns \leftarrow \pi$  Rydberg series ( $\delta\,2.95$ ,  $n = 5-9$ ) converging to a limit which correlates well with the reported PE value. Following this Rydberg peak is a very broad, structureless absorption which is assigned to a  $\pi^* \leftarrow n$  transition. The spectral position of this band is where the transition to the  $\pi^*$  level from the  $a_1$  nonbonding level would be expected.

Beginning at  $59\,411\text{ cm}^{-1}$ , there is an extensive vibrational envelope with three quanta of symmetric C=C stretch decreased to  $1280\text{ cm}^{-1}$ . In addition, each has associated with it at least one  $490\text{ cm}^{-1}$  interval, which is the symmetric CBr<sub>2</sub> vibration (ground state  $467\text{ cm}^{-1}$ ).<sup>8</sup> These vibrational energy changes are consistent with the assignment of the  $59\,411\text{ cm}^{-1}$  peak to an  $np$  Rydberg series ( $\delta\,2.64$ ,  $n = 5-10$ ) converging to the  $\pi$  ionization potential. Since this  $\pi$  orbital has both C-C bonding and C-Br antibonding character, removal of an electron would be expected to have the observed vibrational effect.

The remaining sharp absorptions in the spectrum are assigned to Rydberg transitions. These energies are listed in Table III. A significant feature of interest is not the Rydberg series that are assigned but one that is absent. As indicated in Table III, both  $ns$  and  $np$  Rydberg series have been found converging to each of the first three ionization potentials, but for the fourth, only a three-member ( $\delta\,2.64$ ,  $n = 5-7$ ) series beginning at  $74\,047\text{ cm}^{-1}$  was assigned. Using the average term value of  $25\,500\text{ cm}^{-1}$  found for the other series for the first  $s$  Rydberg member, the first peak in an  $ns$  series leading to the fourth ionization potential would be expected at about  $68\,000\text{ cm}^{-1}$ , a region in which there are no absorptions. Of the molecular orbitals derived from the nonbonding and  $\pi$  electrons, only the  $A_2 \leftarrow A_1$  ( $ns \leftarrow a_2$ ) Rydberg transition is symmetry forbidden. Accordingly, the fourth ionization po-

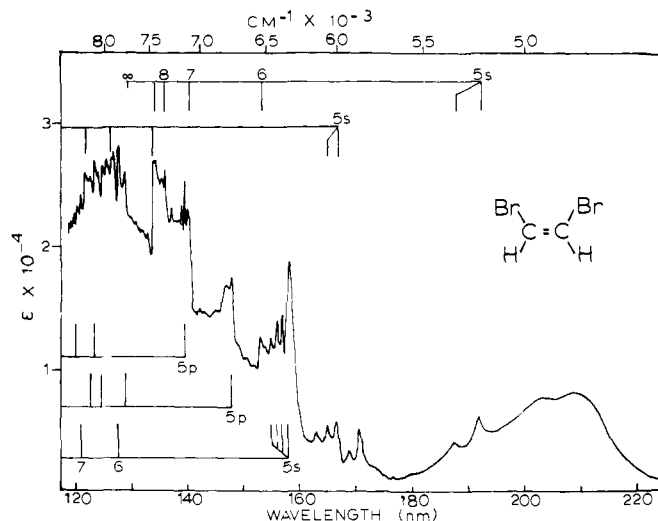


Figure 3. Absorption spectrum of *cis*-1,2-dibromoethylene, including  $ns$  and  $np$  Rydberg series.

Table III. Rydberg Assignments for 1,1-Dibromoethylene

First IP, $78\,910\text{ cm}^{-1}$			
$ns \leftarrow \pi$ ( $b_2$ ), $\delta\,2.95$		$np \leftarrow \pi$ ( $b_2$ ), $\delta\,2.64$	
$n$	$\bar{\nu}_{\text{obsd}}$	$n$	$\bar{\nu}_{\text{obsd}}$
5	53 129	5	59 411
6	67 114	6	69 190
7	72 213	7	73 137
8	74 599	8	75 180
9	75 930	9	76 200

Second IP, $86\,560\text{ cm}^{-1}$			
$ns \leftarrow n$ ( $b_1$ ), $\delta\,2.99$		$np \leftarrow n$ ( $b_1$ ), $\delta\,2.66$	
$n$	$\bar{\nu}_{\text{obsd}}$	$n$	$\bar{\nu}_{\text{obsd}}$
5	60 790	5	66 948
6	74 360	6	76 589
7	79 669	7	80 749
8	82 196	8	82 699
9	83 500	9	83 808

Third IP, $90\,690\text{ cm}^{-1}$			
$ns \leftarrow n$ ( $a_1$ ), $\delta\,2.94$		$np \leftarrow n$ ( $a_1$ ), $\delta\,2.64$	
$n$	$\bar{\nu}_{\text{obsd}}$	$n$	$\bar{\nu}_{\text{obsd}}$
5	65 673	5	70 927
6	78 989	6	81 018
7	84 062	7	84 930
8	86 410	8	86 861

tential is assigned to the  $a_2$  orbital. This point will be dealt with further in the Discussion section (see below).

***cis*-1,2-Dibromoethylene.** The spectrum of this compound is given in Figure 3, together with the assigned Rydberg series. The  $\pi^* \leftarrow \pi$  band has its maximum at  $48\,200\text{ cm}^{-1}$ , followed by a second band at an interval of  $1191\text{ cm}^{-1}$ .<sup>8</sup> On the shoulder of this absorption appears the first member of an  $ns \leftarrow \pi$  Rydberg series ( $\delta\,2.90$ ,  $n = 5-9$ ). Associated with this peak are two vibrational components of  $1284\text{ cm}^{-1}$ , again the symmetric C=C stretch, but reduced from its ground state frequency to a lesser extent.

The remainder of the spectrum contains the higher members of the  $ns \leftarrow \pi$  Rydberg series and the peaks assigned to four additional series. Band positions for the Rydberg assignments

**Table IV.** Rydberg Assignments for *cis*-1,2-Dibromoethylene

First IP, 77 710 cm <sup>-1</sup> <i>ns</i> ← $\pi$ ( <i>b</i> <sub>2</sub> ), $\delta$ 2.90			
<i>n</i>	$\bar{\nu}_{\text{obsd}}$		
5	52 042		
6	66 432		
7	71 220		
8	73 486		
9	74 778		
Second IP, 86 640 cm <sup>-1</sup>			
<i>ns</i> ← <i>n</i> ( <i>b</i> <sub>1</sub> ), $\delta$ 2.96		<i>np</i> ← <i>n</i> ( <i>b</i> <sub>1</sub> ), $\delta$ 2.61	
<i>n</i>	$\bar{\nu}_{\text{obsd}}$	<i>n</i>	$\bar{\nu}_{\text{obsd}}$
5	60 346	5	68 199
6	74 778	6	77 095
7	79 917	7	80 945
8	82 320	8	82 843
Third IP, 90 590 cm <sup>-1</sup>			
<i>ns</i> ← <i>n</i> ( <i>a</i> <sub>1</sub> ), $\delta$ 2.95		<i>np</i> ← <i>n</i> ( <i>a</i> <sub>1</sub> ), $\delta$ 2.61	
<i>n</i>	$\bar{\nu}_{\text{obsd}}$	<i>n</i>	$\bar{\nu}_{\text{obsd}}$
5	64 387	5	71 906
6	78 821	6	81 215
7	83 900	7	84 981

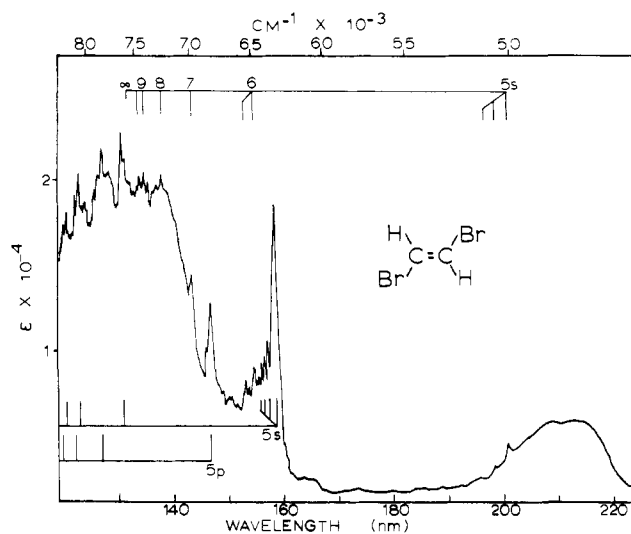
are listed in Table IV. There is a peak at 59 260 cm<sup>-1</sup> with the proper term value for a 5*p* ←  $\pi$  Rydberg transition (18 450 cm<sup>-1</sup>). The corresponding *n* = 6 member appears as a shoulder on the 68 199 cm<sup>-1</sup> band. The band at 60 346 cm<sup>-1</sup> which begins a *ns* ← *n* (*b*<sub>1</sub>) Rydberg series ( $\delta$  2.96, *n* = 5–8) has two members of C–Br stretching frequency associated with it, unchanged from its ground state value<sup>8</sup> of 573 cm<sup>-1</sup>. Another *s* Rydberg series begins with the very strong peak at 64 387 cm<sup>-1</sup> followed by three quanta of a 372 cm<sup>-1</sup> vibrational interval (C–C–Br bend).<sup>8</sup>

***trans*-1,2-Dibromoethylene.** The spectrum of the *trans*-dibromo isomer (Figure 4) is given with the members of the assigned Rydberg series (Table V). The band assigned to the *V* ← *N*( $\pi^*$  ←  $\pi$ ) transition has a maximum at 46 000 cm<sup>-1</sup>, followed by a second band at an interval of 1210 cm<sup>-1</sup> which is the symmetric C=C stretch (ground state value 1578 cm<sup>-1</sup>).<sup>8</sup> On the higher energy side of this band is the *n* = 5 member of an *ns* ←  $\pi$  Rydberg series ( $\delta$  2.94, *n* = 5–10). As predicted by the parity selection rule, no *np* ←  $\pi$  series was observed. The absence of this series was also reported for the centrosymmetric chloroethylenes.<sup>11</sup>

Following these absorptions, there is a relatively flat region terminated at about 63 500 cm<sup>-1</sup> by the presence of a sharp band assigned to an *s* Rydberg series converging to a limit slightly higher than the PE value of the second ionization po-

**Table V.** Rydberg Assignments for *trans*-1,2-Dibromoethylene

First IP, 77 040 cm <sup>-1</sup> <i>ns</i> ← $\pi$ , $\delta$ 2.94		Second IP, 89 135 cm <sup>-1</sup> <i>np</i> ← <i>n</i> ( <i>a</i> <sub>g</sub> ), $\delta$ 2.62		Third IP, 89 490 cm <sup>-1</sup> <i>ns</i> ← <i>n</i> ( <i>b</i> <sub>u</sub> ), $\delta$ 2.94	
<i>n</i>	$\bar{\nu}_{\text{obsd}}$	<i>n</i>	$\bar{\nu}_{\text{obsd}}$	<i>n</i>	$\bar{\nu}_{\text{obsd}}$
5	51 140	5	69 725	5	63 529
6	65 368	6	79 605	6	77 748
7	70 363	7	83 431	7	82 843
8	72 754	8	85 350	8	85 192
9	74 069				
10	74 839				

**Figure 4.** Absorption spectrum of *trans*-1,2-dibromoethylene, with *ns* and *np* Rydberg series shown.

tential (89 490 cm<sup>-1</sup> vs. 89 135 cm<sup>-1</sup>). Associated with this band are four quanta of a 225 cm<sup>-1</sup> vibrational interval, which is the in-plane C–C–Br bend,<sup>8</sup> relatively unchanged from its ground state value of 218 cm<sup>-1</sup>. Beginning at 69 725 cm<sup>-1</sup> is a *p* Rydberg series which converges to the value of the second photoelectron ionization potential, and also has the 218 cm<sup>-1</sup> vibration associated with it. This ionization potential has been assigned<sup>3,4</sup> to degenerate in-plane 4*b*<sub>u</sub> and 5*a*<sub>g</sub> orbitals. Since this is a centrosymmetric molecule, the presence of both *s* and *p* Rydberg series converging to approximately the same limit supports the near coincidence of these levels.

## Discussion

In the bromoethylenes, each bromine atom is considered to have two nonbonding *p* orbitals, one in the molecular plane and one perpendicular to it, the third *p* orbital being mainly involved in the C–Br  $\sigma$  bond. The out-of-plane *p* orbital is capable of conjugation with the  $\pi$  bond to form two split  $\pi$  levels. This splitting is larger in the bromoethylenes than in the chloro compounds.<sup>12</sup> This  $\pi$  level splitting is attributed to the resonance effect, which is dependent on the ability of the halogen to conjugate with the  $\pi$  orbital and is largely a function of the similarity in energy of the conjugating levels. On comparing the ethylene  $\pi$  IP (10.51 eV)<sup>13</sup> with the *p* orbital IP's of bromine and chlorine (12.18 and 13.37 eV, respectively),<sup>14</sup> it is expected that bromine would exert a greater resonance effect, as is observed.

In the dibromoethylenes, the four nonbonding orbitals combine to form four linear combinations. In *C*<sub>2v</sub> symmetry these are: *a*<sub>1</sub> and *b*<sub>1</sub>, in-plane combinations; and *a*<sub>2</sub> and *b*<sub>2</sub>, out-of-plane combinations. In *C*<sub>2h</sub> point group, the corresponding orbitals are labeled *a*<sub>g</sub> and *b*<sub>u</sub>, in-plane, and *a*<sub>u</sub> and *b*<sub>g</sub>, out-of-plane (see Figure 5).

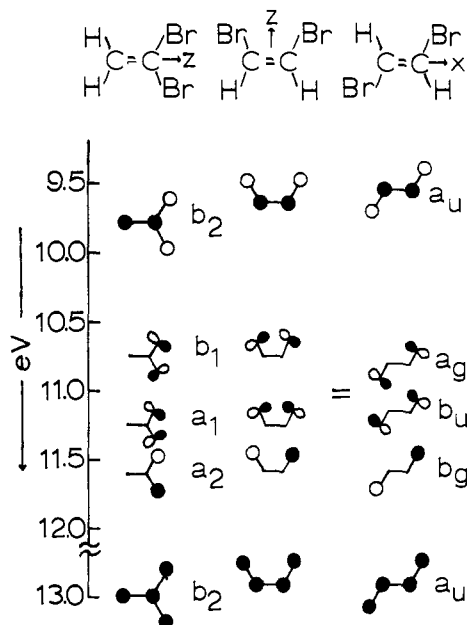


Figure 5. Molecular orbital correlation diagram for the dibromoethylenes.

The two published reports<sup>3,4</sup> of the PE spectra of these compounds disagree with respect to the relative stability of the nonbonding levels. In *cis*-1,2-dibromoethylene, Wittel and Bock<sup>3</sup> assign the energy levels in order of increasing ionization potential as  $2b_2$ ,  $4b_1$ ,  $5a_1$ ,  $1a_2$ , and  $1b_2$ , and in the 1,1-dibromo compound, the same ordering is given. However, in the study of Chadwick et al.,<sup>4</sup> the order of the  $5a_1$  and  $1a_2$  levels is reversed in *cis*-1,2-dibromoethylene. They do not report the spectrum of the 1,1-dibromo compound.

Considering these assignments, there is some basis for doubt concerning the relative energies of the  $5a_1$  and  $1a_2$  levels. As pictured in Figure 5, the  $5a_1$  orbital is in the molecular plane and capable of bonding overlap between the two bromine substituents, whereas the out-of-plane  $1a_2$  orbital is Br-Br antibonding. However, in this study, as discussed earlier, the presence of both *s* and *p* Rydberg series leading to the third ionization potential, and the absence of an *s* series leading to the fourth, indicates that the  $1a_2$  level is more stable than the  $5a_1$ . In support of this assignment, it may also be noted that both the in-plane  $5a_1$  and  $4b_1$  levels are of the proper symmetry to interact with molecular orbitals of the ethylene  $\sigma$  framework, specifically the  $1b_{3g}$  and  $3a_g$  orbitals. Since the IP's of the bromine levels are lower<sup>13</sup> than those of the corresponding ethylene orbitals (12.38 and 14.47 eV respectively),<sup>13</sup> they will

be further destabilized by the interaction. Therefore, the result is not that the out-of-plane  $1a_2$  orbital is more stable than would be expected but that both in-plane orbitals are less stable.

An additional interesting observation in these two molecules is the degeneracy of the ionization potentials assigned to the in-plane nonbonding molecular orbitals. This indicates that any through-space interaction of these orbitals is effectively overridden by the through-bond conjugation with the ethylene framework, since the spatial distributions in these molecules should not be the same. Again, conjugative interaction involving the entire molecule predominates over the localized Br-Br interaction. The other degeneracy of energy levels noted is that of the out-of-plane orbitals ( $a_2$  and  $b_g$ ) in all three of the dibromo compounds. The symmetries of these levels restricts interaction with the rest of the molecule.

The haloethylenes have previously been treated as  $\pi$  systems perturbed by the halogens, and the validity of this approach with other halogen substituents has been amply demonstrated.<sup>2,16</sup> However, the results present here indicate that bromine is capable of interacting with the ethylene framework to such an extent that the effect is too large to be considered a perturbation. An adequate explanation of the results required taking into account all orbitals capable of interaction. Instead of considering an isolated set of halogen orbitals, it is necessary to consider the molecule in its entirety.

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