

# The vacuum UV photoabsorption spectrum of methyl bromide (CH<sub>3</sub>Br) and its perdeuterated isotopomer CD<sub>3</sub>Br: a vibrational analysis

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## Abstract

The fine structure of the vacuum UV photoabsorption spectrum of CH<sub>3</sub>Br and CD<sub>3</sub>Br has been analyzed in the 6.9-10.2 eV photon energy range. A large number of lines have been observed, classified and assigned to the vibrational excitation accompanying a series of Rydberg transitions. The effects of the Jahn-Teller distortion and of the spin-orbit splitting of the ground electronic state of the ion have been considered. The former effect has been evaluated by ab initio calculations, showing that the <sup>2</sup>E state (in the C<sub>3v</sub> symmetry group) splits into <sup>2</sup>A' and <sup>2</sup>A'' states in the C<sub>s</sub> symmetry group. Even though the energy difference of about 1 meV is extremely small, the <sup>2</sup>A' state is energetically the lowest component whereas the <sup>2</sup>A'' is found to be a transition state. The Jahn-Teller stabilization energy and the wavenumbers associated with all vibrational modes have been calculated. Experimentally, the entire fine structure could be described in terms of three vibrational modes, i.e.,  $hc\omega_4 = 146 \pm 6$  meV ( $1178 \pm 48$  cm<sup>-1</sup>),  $hc\omega_5 = 107 \pm 6$  meV ( $863 \pm 48$  cm<sup>-1</sup>) and  $hc\omega_6 = 71 \pm 4$  meV ( $572 \pm 32$  cm<sup>-1</sup>), respectively, as resulting from an average over all analyzed Rydberg states. In CD<sub>3</sub>Br the corresponding energies are  $hc\omega_4 = 104 \pm 3$  meV ( $839 \pm 24$  cm<sup>-1</sup>),  $hc\omega_5 = 82 \pm 4$  meV ( $661 \pm 32$  cm<sup>-1</sup>) and  $hc\omega_6 = 62 \pm 4$  meV ( $500 \pm 32$  cm<sup>-1</sup>). These values are in fairly good agreement with those predicted by the present ab initio calculations for the ionic ground state. The experimental isotopic ratio  $\rho_i = [\omega/\omega_{\text{isot}}]_i$  is  $1.15 \pm 0.14$ ,  $1.31 \pm 0.14$  and  $1.39 \pm 1.0$  and is predicted to be 1.04, 1.34 and 1.36, respectively, for  $\omega_6$ ,  $\omega_5$  and  $\omega_4$ . On the basis of the present study an alternative assignment of the CH<sub>3</sub>Br<sup>+</sup>( $\tilde{X}^2E$ ) photoelectron band structure is proposed.

**Keywords:** Photoabsorption; Vacuum UV; Rydberg series; CH<sub>3</sub>Br; Jahn-Teller effect; CD<sub>3</sub>Br; Vibrational analysis; Ab initio calculations; Photo-electron spectrum

## 1. INTRODUCTION

In previous papers, we investigated in detail the photoabsorption and photoionization dynamics of fluoro and chloromethanes [1-3]. Their vacuum UV photo-absorption spectrum proved to be an essential piece of information for the puzzling interpretation of the threshold photoelectron spectrum (TPES), constant ion state spectra (CIS) and the fragment ion yields in photoionization mass spectrometry.

The previous paper is devoted to a detailed analysis of the pure electronic Rydberg excitations in CH<sub>3</sub>Br and CD<sub>3</sub>Br [4] between 6 and 12 eV photon energy. In these spectra, numerous weaker and generally broader features are identified. Previous studies of these structures are very scarce in the literature and are limited to a narrow low photon energy range.

Essentially, two papers contributed to the analysis of the vibrational fine structure of the Rydberg series in CH<sub>3</sub>Br. First, Causley and Russell [5] examined the photoabsorption spectrum of CH<sub>3</sub>Br and other bromomethanes in the 6-10 eV photon energy range. These authors proposed a vibrational analysis of the first *ns*- and *np*-type Rydberg states converging to both spin-orbit ionization limits  $\tilde{X}^2E_{3/2}$ - $\tilde{X}^2E_{1/2}$ . The spectrum of CD<sub>3</sub>Br was not included in this work.

Felps et al. [6] restricted their investigation to the study of the vacuum UV photoabsorption spectrum of CH<sub>3</sub>Br in the 54,000-64,000 cm<sup>-1</sup> (6.69-7.93 eV) spectral region which corresponds to the 2e → 5s Rydberg transition. An extensive vibrational analysis is presented. This study was extended to CD<sub>3</sub>Br. The pressure dependence of the absorption spectrum has also been examined.

The aim of the present work is to identify and classify most of the weak features present in the vacuum

UV absorption spectrum of both CH<sub>3</sub>Br and CD<sub>3</sub>Br over the 6.9-10.2 eV spectral region. Our assignments are supported by ab initio quantum mechanical calculation of the wavenumbers associated with the vibrational normal modes of CH<sub>3</sub>Br<sup>+</sup> and CD<sub>3</sub>Br<sup>+</sup>. This will allow us to make a comparison between the experimental and predicted isotope effect on the vibrational wavenumbers.

## 2. EXPERIMENTAL

### 2.1. Experimental set-up

The experimental set-up used in this work has already been described in detail elsewhere [7]. Only the most salient features will be reported here.

Synchrotron radiation available from the BESSY I facility (Berlin, Germany) is dispersed with a modified vacuum UV normal incidence 225 McPherson mono-chromator with a focal length of 1.5 m, instead of 1 m in the commercial version (Im-NIM-2 beamline). A laminar Zeiss grating is used for the efficient reduction of the second spectral order. It is gold coated with 1200 l/mm and its transmission vanishes above 26 eV (210,000 cm<sup>-1</sup> or 47 nm). The width of the entrance and exit slits of 100 μm provides a 0.1 nm resolution. The light passes through a 1 mm thick stainless steel microchannel plate necessary to maintain a differential pressure of 1:1000 before entering a 30 cm long stainless steel absorption cell. The vapor pressure in the cell is measured by a Balzers capacitor manometer. CH<sub>3</sub>Br and CD<sub>3</sub>Br vapors are introduced at a pressure of 20 μbar. The light is detected by a sodium salicylate sensitized photomultiplier located at the end of the absorption cell and in front of the monochromator exit slit. The recording of an absorption spectrum requires one scan with gas in the absorption cell and one with the empty cell. The stability of the synchrotron radiation and of the pressure in the cell ensures reliable absorption data. If required, the spectra presented in the following sections are corrected for any pressure drift. The commercially available CH<sub>3</sub>Br, purchased from Praxair and of 99.5% purity, was used without further purification. The CD<sub>3</sub>Br, purchased from Merck, Sharp and Dohme, is certified at 99 at.% purity. No noticeable impurity was observed by mass spectrometry at 21.2 eV photon energy. Therefore, the sample was used without further purification.

### 2.2. Data handling and error estimation

The wavelength calibration of the monochromator has been performed by using the Ar<sup>+</sup> absorption spectrum between the <sup>2</sup>P<sub>3/2</sub> and <sup>2</sup>P<sub>1/2</sub> ionic states. The accuracy of this calibration was estimated to be 2 meV. In the photoabsorption spectra extending between 6 and 12 eV photon energy, an energy increment of 1.5 meV has been adopted. The precision on the energy position of a feature is estimated to be of the order of 2 meV. Therefore, in these cases the assigned total error would be 4 meV. This evaluation is confirmed by the reproducibility of energy positions measured in four different spectra recorded over a two year interval.

## 3. EXPERIMENTAL RESULTS

### 3.1. The CH<sub>3</sub>Br photoabsorption spectrum

Fig. 1(a)-(c) reproduces the photoabsorption spectrum of CH<sub>3</sub>Br on an expanded photon energy scale. The assignments of the observed fine structure to various vibrational progressions have been inserted in this figure as far as not overcrowded.

They will be discussed in Section 5.

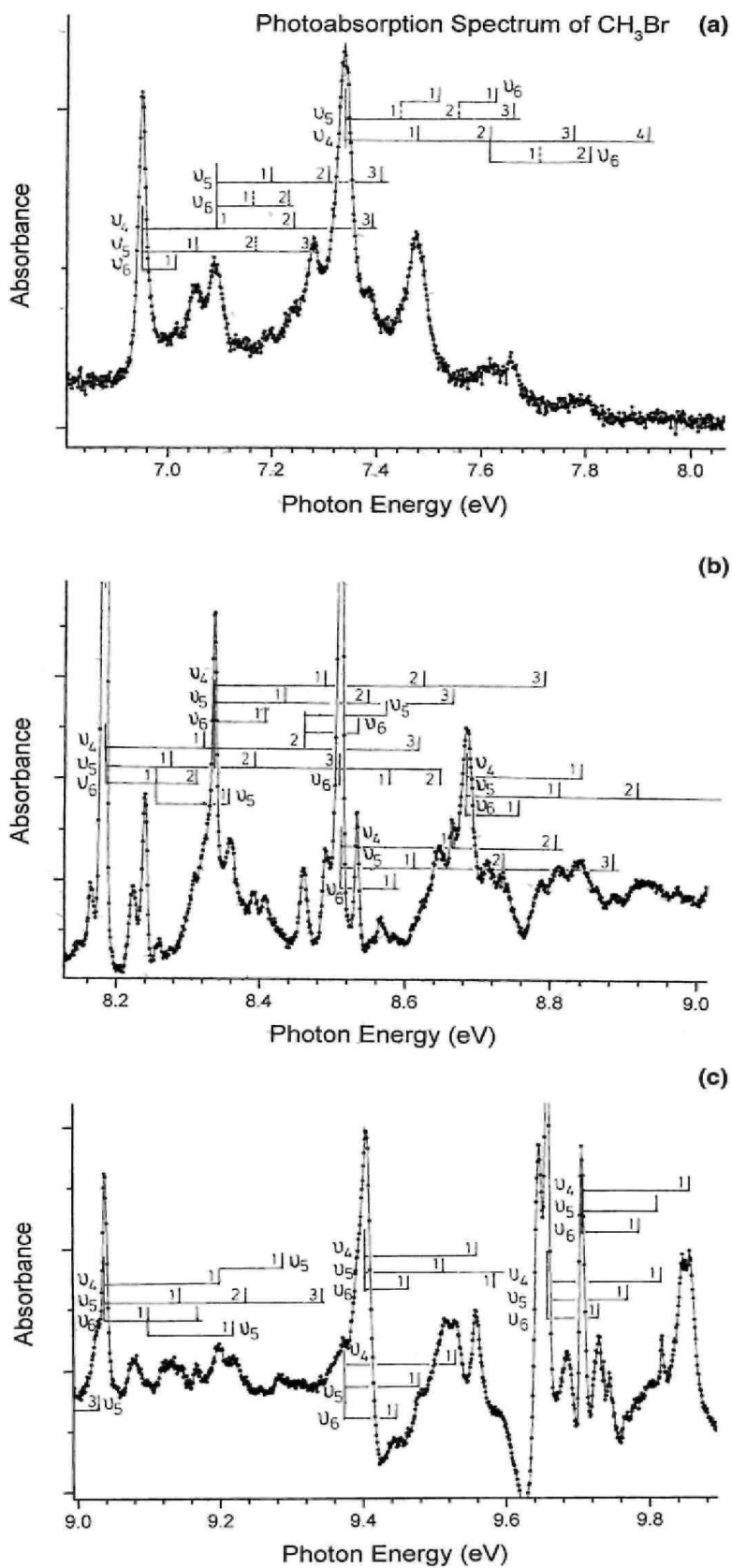
### 3.2. The CD<sub>3</sub>Br photoabsorption spectrum

The photoabsorption spectrum of CD<sub>3</sub>Br has been recorded between 6 and 12 eV photon energy. The fine structures, assigned to excitation of vibrational progressions in the successive Rydberg states, are clearly identified in an expanded photon energy scale, as shown in Fig. 2(a)-(c).

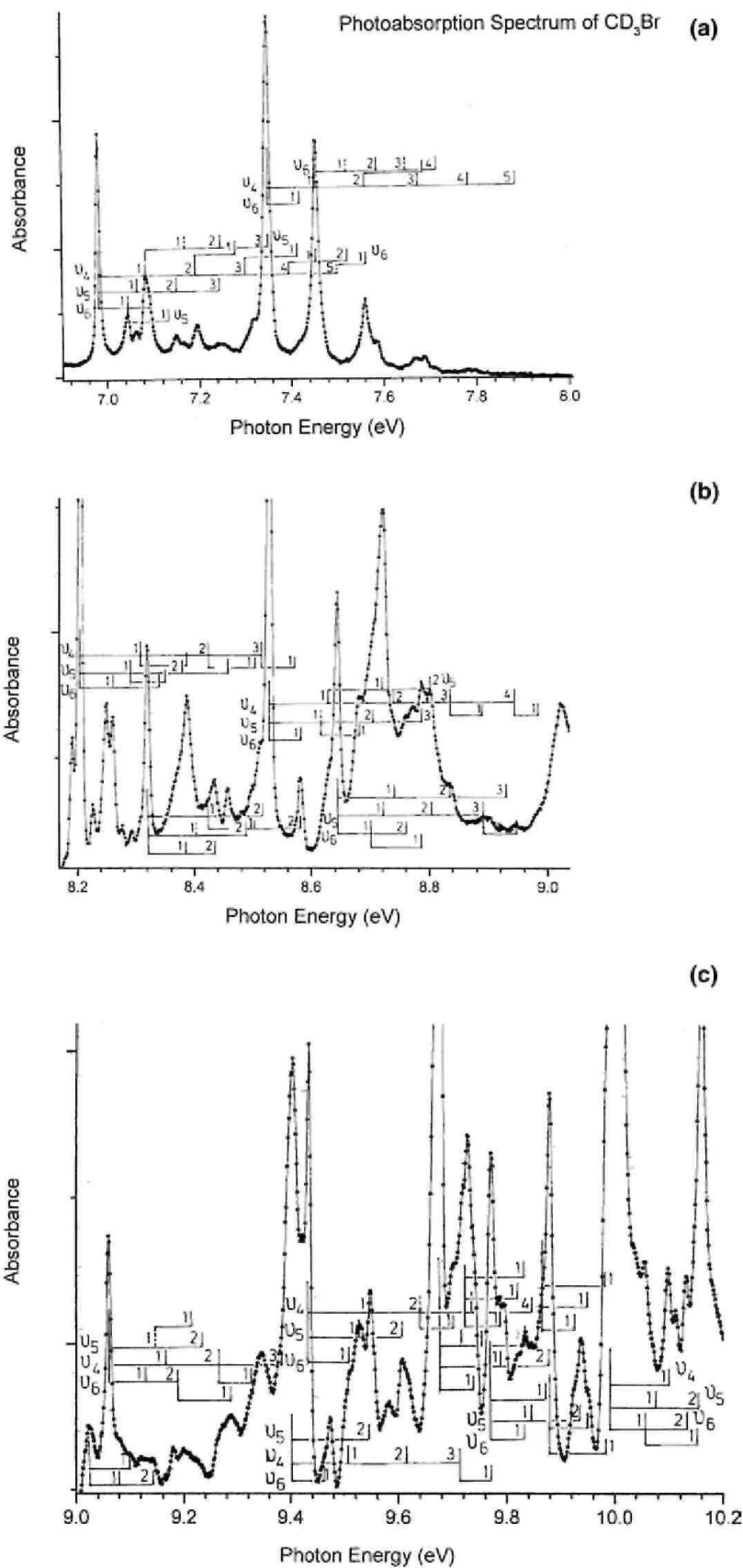
## 4. AB INITIO CALCULATIONS: METHODS AND RESULTS

Ab initio quantum mechanical calculation of the geometry and the vibrational wavenumbers of the cation proved to be very helpful for the interpretation of the vacuum UV spectroscopy of CH<sub>3</sub>Cl and CD<sub>3</sub>Cl [3]. A similar extensive ab initio calculation on the ground state of CH<sub>3</sub>Br and CD<sub>3</sub>Br and their cations has been performed.

**Fig. 1.** The vacuum UV photoabsorption spectrum of  $\text{CH}_3\text{Br}$  on an expanded photon energy scale between 6.9 and 10.0 eV (a)-(c). The assignments are inserted by vertical bars.



**Fig. 2.** The vacuum UV photoabsorption spectrum of  $CD_3Br$  on an expanded photon energy scale between 6.9 and 10.0 eV (a)-(c). The assignments are inserted by vertical bars.



The latest high level ab initio quantum mechanical calculations on  $\text{CH}_3\text{Br}^+$  and  $\text{CD}_3\text{Br}^+$  were reported by Lugez et al. [8]. They investigated the infrared spectrum of the methyl halides cations, i.e., the  $\text{CH}_3\text{Br}^+$  and  $\text{CD}_3\text{Br}^+$  cations trapped in a frozen neon matrix. The discussion of their experimental results was based upon ab initio calculations at MP2 and QCISD levels with different basis sets (in the frozen core approximation, 6-311+G\*\* for C and H and HW 2111+G\*\* for Br). The  $\text{CH}_3\text{Br}^+$  and its isomeric ylidion  $\text{H}_2\text{CBrH}^+$  were investigated. Contrarily to the results on  $\text{CH}_3\text{F}$ , the latter isomer is less stable than the former one. With respect to the neutral molecule, the C-Br bond length increases slightly upon ionization whereas a shortening was calculated in  $\text{CH}_3\text{F}^+$  and  $\text{CH}_3\text{Cl}^+$ . These results were corroborated by the experimental data.

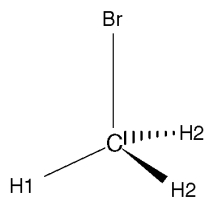
Furthermore, these authors [8] calculated the vibrational wavenumbers in  $\text{CH}_3\text{Br}^+$  and compared the theoretical results with their infrared data and with the values obtained for the cation by photoelectron spectroscopy [9]. However, this work was restricted to the lowest energy component  $^2\text{A}'$  of the Jahn-Teller split  $^2\text{E}$  ground state of the  $\text{CH}_3\text{Br}^+$  cation. No information is provided about the second component  $^2\text{A}''$ .

In order to obtain a more complete picture, we performed ab initio calculations on  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Br}^+$  using the Gaussian-03 program [10]. The geometries of the neutral ground state and the cations are fully optimized at several levels including electronic correlation, using either a perturbational method (MP2 [11]), variational-related methods (QCISD [12], CCSD [13]) or working within the density functional theory (DFT [14]) framework with the B3LYP hybrid functionals [15]. The geometries are optimized in the  $\text{C}_{3v}$  and the  $\text{C}_s$  symmetry point groups for  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Br}^+$ , respectively. The effect of isotopic substitution has been evaluated by performing the same calculations on  $\text{CD}_3\text{Br}$  and  $\text{CD}_3\text{Br}^+$ . The vibrational wavenumbers of the neutral and ionic species were calculated at the MP2 and the B3LYP levels. Two basis sets were used, i.e., the 6-311++G\*\* [16] and cc-pVTZ [17], respectively. The results related to the geometry of the neutral and ionized species are shown in Table 1 for  $\text{CH}_3\text{Br}(\tilde{\chi}^1\text{A}_1)$  and  $\text{CH}_3\text{Br}^+(^2\text{A}' \text{ and } ^2\text{A}'')$  together with the results provided by the calculations reported by Lugez et al. [8]. The  $^2\text{A}''$  component is a transition state (TS) connecting two minima corresponding to the lowest Jahn-Teller distorted potential energy surface.

**Table 1-** Optimized geometries of  $\text{CH}_3\text{Br}(\tilde{\chi}^1\text{A}_1)$  in the  $\text{C}_{3v}$  symmetry group and  $\text{CH}_3\text{Br}^+(^2\text{A}' \text{ and } ^2\text{A}'')$  in the  $\text{C}_s$  symmetry group calculated at the MP2/6-311G\*\*, QCISD/6-311++G\*\* and CCSD/cc-pVTZ levels

| Level   | C-Br   | C-H1   | C-H2   | H1-C-Br | H2-C-Br | H2-C-Br-H1 |
|---|--------|--------|--------|---------|---------|------------|
| $\text{CH}_3\text{Br}(\tilde{\chi}^1\text{A}_1)$ $\text{C}_{3v}$ symmetry |        |        |        |         |         |            |
| MP2   | 1.9343 | 1.0876 | 1.0876 | 108.40  | 108.40  | 120.0      |
| QCISD   | 1.9452 | 1.0894 | 1.0894 | 108.26  | 108.26  | 120.0      |
| CCSD  | 1.9342 | 1.0835 | 1.0835 | 108.16  | 108.16  | 120.0      |
| Ref. [8]  | 1.955  | -      | -      | -       | -       | 120.0      |
| Experimental [19]   | 1.939  | 1.113  | 1.113  | -       | -       |            |
| $\text{CH}_3\text{Br}^+(^2\text{A}')$ in $\text{C}_s$ symmetry            |        |        |        |         |         |            |
| MP2   | 1.9374 | 1.0974 | 1.0882 | 103.13  | 107.31  | 117.80     |
| QCISD   | 1.9606 | 1.0983 | 1.0896 | 103.06  | 106.76  | 117.95     |
| CCSD  | 1.9406 | 1.0947 | 1.0844 | 102.50  | 106.86  | 117.65     |
| Ref. [8]  | 1.971  | -      | -      | -       | -       | -          |
| $\text{CH}_3\text{Br}^+(^2\text{A}'')$ in $\text{C}_s$ symmetry           |        |        |        |         |         |            |
| MP2   | 1.9377 | 1.0860 | 1.0939 | 108.09  | 104.90  | 122.04     |
| QCISD   | 1.9616 | 1.0875 | 1.0949 | 107.46  | 104.54  | 121.90     |
| CCSD  | 1.9415 | 1.0819 | 1.0906 | 107.63  | 104.29  | 122.15     |

Distances in Å and angles in °. Comparison is made with previous calculations at their highest level [8] and experimental results [19].



In agreement with these authors [8], a slight lengthening of the C-Br bond is obtained upon ionization in either the  $^2\text{A}'$  or the  $^2\text{A}''$  component of the Jahn-Teller splitting. For both the  $^2\text{A}'$  and the  $^2\text{A}''$  states, the largest C-H bond change involves the lengthening of either the C-H1 ( $^2\text{A}'$ ) or the C-H2 ( $^2\text{A}''$ ) (about 0.01 Å) whereas the other C-H remains almost unchanged (for the H atoms numbering, see figure in Table 1). The most important change of valence angle is the decrease of H1-C-Br ( $^2\text{A}'$ ) or H2-C-Br ( $^2\text{A}''$ ) by about 5° whereas the other H-C-

Br angle changes only slightly. The dihedral angle is decreased by about 2° in the  ${}^2A'$  state and increased by the same amount in the  ${}^2A''$  state.

**Table 2**-Vibrational normal modes and their corresponding wavenumbers ( $\text{cm}^{-1}$ ) resulting from *ab initio* calculations at the MP2/6-311G\*\* and B3LYP/6-311++G\*\* levels, for  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}(\tilde{X}^1A_1)$  and  $\text{CH}_3\text{Br}^+$  and  $\text{CD}_3\text{Br}^+$  ( ${}^2A'$  and  ${}^2A''$ ), respectively, in the  $C_{3v}$  and  $C_s$  symmetry group

| Designation   | Description in Fig. 3 | Experiment [19,20]        |                    | Calculated wavenumbers (this work) |                    |                    |                    |
|---|-----------------------|---------------------------|--------------------|------------------------------------|--------------------|--------------------|--------------------|
|   |                       |                           |                    | MP2                                |                    | B3LYP              |                    |
|   |                       | CH <sub>3</sub> Br        | CD <sub>3</sub> Br | CH <sub>3</sub> Br                 | CD <sub>3</sub> Br | CH <sub>3</sub> Br | CD <sub>3</sub> Br |
| CH <sub>3</sub> Br and CD <sub>3</sub> Br $X^1A_1$ in the $C_{3v}$ symmetry                             |                       |                           |                    |                                    |                    |                    |                    |
| $a_1$ symmetry  |                       |                           |                    |                                    |                    |                    |                    |
| V1  | $m_7$                 | 2972                      | 2151               | 3122                               | 2233               | 3081               | 2201               |
| v <sub>2</sub>  | $m_3$                 | 1305.1                    | 987                | 1381                               | 1049               | 1335               | 1006               |
| v <sub>3</sub>  | $m_{11}$              | 611                       | 577                | 649                                | 607                | 587                | 554                |
| $e$ symmetry  |                       |                           |                    |                                    |                    |                    |                    |
| v <sub>4</sub>  | $m_9 + m_{10}$        | 3056.3                    | 2293               | 3237                               | 2404               | 3188               | 2368               |
| v <sub>5</sub>  | $m_2 + m_6$           | 1443.1                    | 1053               | 1496                               | 1084               | 1475               | 1070               |
| v <sub>6</sub>  | $m_1 + m_2$           | 953.8                     | 717                | 990                                | 738                | 964                | 716                |
| CH <sub>3</sub> Br <sup>+</sup> and CD <sub>3</sub> Br <sup>+</sup> ${}^2A'$ in the $C_s$ symmetry      |                       |                           |                    |                                    |                    |                    |                    |
|   |                       | Calculated wavenumber [8] |                    | Calculated wavenumbers (this work) |                    |                    |                    |
|   |                       | CH <sub>3</sub> Br        | CD <sub>3</sub> Br | MP2                                |                    | B3LYP              |                    |
|   |                       |                           |                    | CH <sub>3</sub> Br                 | CD <sub>3</sub> Br | CH <sub>3</sub> Br | CD <sub>3</sub> Br |
| $a'$ symmetry   |                       |                           |                    |                                    |                    |                    |                    |
| V1  | $m_9$                 | 3180                      | 2356               | 3197                               | 2363               | 3107               | 2282               |
| v <sub>2</sub>  | $m_7$                 | 3056                      | 2183               | 3064                               | 2191               | 2953               | 2120               |
| v <sub>3</sub>  | $m_6$                 | 1448                      | 1059               | 1455                               | 1065               | 1406               | 1033               |
| v <sub>4</sub>  | $m_3$                 | 1341                      | 997                | 1350                               | 1002               | 1276               | 939                |
| v <sub>5</sub>  | $m_1$                 | 888                       | 660                | 891                                | 667                | 836                | 624                |
| V <sub>6</sub>  | $m_{11}$              | 506                       | 423                | 542                                | 513                | 488                | 467                |
| $a''$ symmetry  |                       |                           |                    |                                    |                    |                    |                    |
| V7  | $m_{10}$              | 3175                      | 2343               | 3195                               | 2358               | 3095               | 2279               |
| V <sub>8</sub>  | $m_2$                 | 1313                      | 933                | 1312                               | 931                | 1181               | 837                |
| V <sub>9</sub>  | $m_2$                 | 558                       | 481                | 585                                | 447                | 417                | 320                |
| CH <sub>3</sub> Br <sup>+</sup> and CD <sub>3</sub> Br <sup>+</sup> ${}^2A''$ -TS in the $C_s$ symmetry |                       |                           |                    |                                    |                    |                    |                    |
| $a'$ symmetry   |                       |                           |                    |                                    |                    |                    |                    |
| v' <sub>1</sub>   | $m_9$                 | -                         | -                  | 3268                               | 2430               | 3211               | 2386               |
| v' <sub>2</sub>   | $m_7$                 | -                         | -                  | 3075                               | 2195               | 2983               | 2130               |
| v' <sub>3</sub>   | $m_6$                 | -                         | -                  | 1441                               | 1054               | 1400               | 1025               |
| V' <sub>4</sub>   | $m_3$                 | -                         | -                  | 1348                               | 996                | 1271               | 930                |
| v' <sub>5</sub>   | $m_1$                 | -                         | -                  | 1007                               | 751                | 973                | 726                |
| V' <sub>6</sub>   | $m_{11}$              | -                         | -                  | 545                                | 518                | 489                | 469                |
| $a''$ symmetry  |                       |                           |                    |                                    |                    |                    |                    |
| v' <sub>7</sub>   | $m_{10}$              | -                         | -                  | 3069                               | 2244               | 2927               | 2135               |
| v' <sub>8</sub>   | $m_2$                 | -                         | -                  | 1346                               | 959                | 1195               | 849                |
| v' <sub>9</sub>   | $m_2$                 | -                         | -                  | <b>i561</b>                        | <b>i431</b>        | <b>i371</b>        | <b>i286</b>        |

The  ${}^2A''$  state corresponds to a transition state (TS).

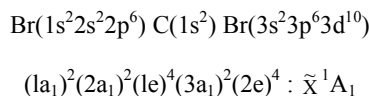
The vibrational wavenumbers of the neutral molecule ground state and of the  ${}^2A'$  and the  ${}^2A''$  states of the cation have been calculated. As we have worked with different basis sets, the correction factor recommended by Scott and Radom [18] has not been applied. The results are displayed in Table 2 for  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Br}^+$  ( ${}^2A'$  and  ${}^2A''$ ) and for  $\text{CD}_3\text{Br}$  and  $\text{CD}_3\text{Br}^+$  in the corresponding electronic states. The nuclear motions associated with the nine normal modes are described with reference to symmetry coordinates ( $m_1$  to  $m_{11}$ ) represented in Fig. 3.

For both neutral species  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$  in the  $\tilde{X}^1A_1$  state, the present calculated and the experimental wavenumbers [19,20] are in fairly good agreement. Concerning the  ${}^2A'$  state of the normal  $\text{CH}_3\text{Br}^+$  and perdeuterated  $\text{CD}_3\text{Br}^+$  cations, the results provided by the present calculations satisfactorily agree with those reported by Lugez et al. [8] working at the QCISD level. For the  ${}^2A''$  TS the wavenumbers obtained in this work are listed in Table 2.

The stabilization brought about by the Jahn-Teller distortion is 36 meV, i.e., slightly lower than that calculated in the case of  $\text{CH}_3\text{Cl}^+$  (40 meV) [3] and is negligible compared with the spin-orbit splitting (319 meV [9]). The energy difference between the minima and the TS is vanishing (1 meV).

## 5. DISCUSSION OF THE EXPERIMENTAL DATA

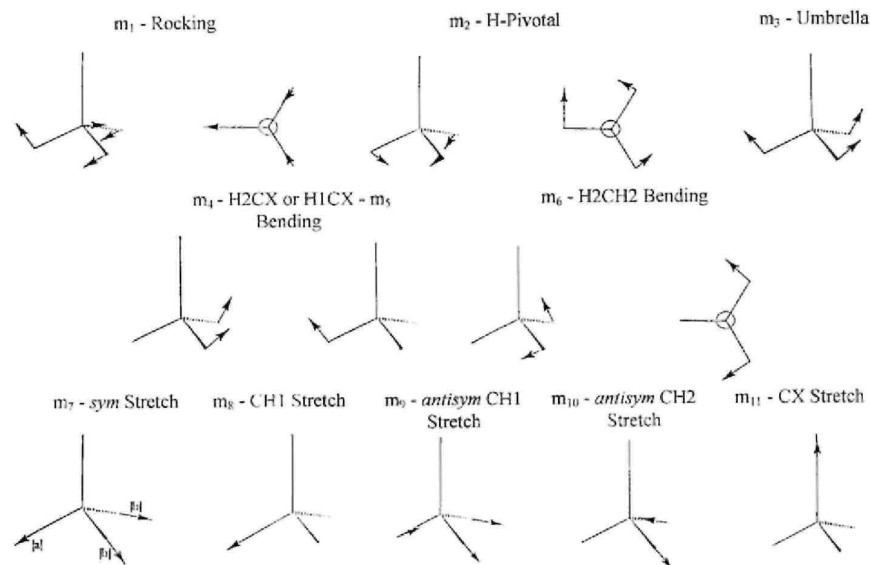
For clarity in the following discussion of the experimental results, the molecular orbital configuration of  $\text{CH}_3\text{Br}$  in the  $C_{3v}$  point group is



where the  $1e$ ,  $3a_1$  and  $2e$  molecular orbitals have outer-valence character. The most accurate and vibrationally well-resolved He(I) photoelectron spectrum reported by Karlsson et al. [9] provide the adiabatic ionization energy of the ground ionic state. This state shows a large spin-orbit splitting of  $319 \pm 6$  meV ( $2573 \pm 50$   $\text{cm}^{-1}$ ), i.e., ionization energies measured at  $10.543 \pm 0.003$  and  $10.862 \pm 0.003$  eV [9]. These quantities were used to calculate the effective quantum numbers  $n^*$  associated with each Rydberg state as described earlier [4]. It has also been considered that their values are independent of the vibrational energy. Therefore, it is considered to be constant for each electronic Rydberg state, within experimental accuracy.

The He(I) photoelectron spectra of  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$  have been measured in our laboratory [21] to (i) determine accurately the ionization energies of  $\text{CD}_3\text{Br}$  and (ii) allow us to reexamine the vibrational fine structure of the lowest ionic states of  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$ . The ionization energies corresponding to the spin-orbit split ground state  $\tilde{X}$  ( ${}^2E_{3/2}$ - ${}^2E_{1/2}$ ) of  $\text{CD}_3\text{Br}$  are  $10.565 \pm 0.004$  and  $10.902 \pm 0.004$  eV [21].

**Fig. 3.** Schematic representation and description of nuclear symmetry coordinates  $m$ , of  $\text{CH}_3\text{X}^+$  in the  $C_3$  point group.



For convenience we denote the Rydberg series by the ionic core and the successive molecular ( $n1a_1/e$ ) Rydberg orbitals. In the absence of generally accepted rules, the starting values of the principal quantum number were chosen to be as in the correlated Kr atom [4], i.e.,  $n = 5$  for s- and p-type orbitals and  $n = 4$  for d- and f-type orbitals.

### 5.1. The ( ${}^2E_{3/2}$ - ${}^2E_{1/2}$ ) $5s a_1$ series

Owing to the absence of overlap, the lowest Rydberg transition will be discussed separately for both  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$ . The energy positions and associated effective principal quantum numbers are listed in Tables 3 and 4. Another reason for a separated discussion is that the two previous reports [5,6] are essentially limited to the vibrational analysis of these transitions only.

As a general remark it has to be pointed out that the  $5s_{a_1}$  Rydberg states in both molecules show very different vibrational intensity patterns. This is not completely surprising because, as we showed in a previous paper [4], the first member of this Rydberg series is the only state that corresponds to a coupling case intermediate between Hund's cases (a) and (c). The two optically active states deriving from the  $(2e)^3(5s_{a_1})^1$  configuration have therefore different potential energy surfaces.

From the data obtained in the present work for  $\text{CH}_3\text{Br}$ , and the ionization limits measured by high resolution He(I) photoelectron spectroscopy [9], we are able to propose a reasonable vibrational assignment for the fine structure observed in both  $5s_{a_1}$  Rydberg states. However, several convergence limits (listed in braces in Table 3), e.g., at 10.611, 11.005 and 11.026 eV, are frequently measured. These have probably not been observed in the photoelectron spectrum [9] owing to lack of resolution and/or sensitivity. Otherwise, all observed transitions correspond to a fairly constant effective principal quantum number whose average value and standard deviation are  $n^*_{3/2} = 1.944 \pm 0.002$  and  $n^*_{1/2} = 1.963 \pm 0.006$  (see Table 3). As already mentioned, the progressions converging to  ${}^2E_{3/2}$  and  ${}^2E_{1/2}$  are different not only with respect to the vibrational intensity distribution but also regarding the nature of the vibrational modes excited in each state. In the  $({}^2E_{3/2})5s_{a_1}$  state three vibrational normal modes (and their overtones and/or combinations) appear to be active upon excitation. By contrast, in the  $({}^2E_{1/2})5s_{a_1}$  state the vibrational structure is clearly dominated by only one normal mode.

According to our calculations, the vibrational motions are identified as being the  $\nu_6$ ,  $\nu_5$  and  $\nu_4$  modes. Averaging over the energy intervals available for the  $({}^2E_{3/2})5s_{a_1}$  component (see Table 4)  $hc\omega_6 \approx 71$  meV (573  $\text{cm}^{-1}$ ),  $hc\omega_5 \approx 108$  meV (871  $\text{cm}^{-1}$ ) and  $hc\omega_4 \approx 147$  meV (1185  $\text{cm}^{-1}$ ) are obtained. From the analysis of the  $({}^2E_{1/2})5s_{a_1}$  component a value of about  $hc\omega_4 \approx 145$  meV (1170  $\text{cm}^{-1}$ ) is deduced from the observation of  $\nu_4$  ( $\nu = 1-3$ ). These first estimations have to be compared with the predicted wavenumbers (see Table 2) of  $\omega_6 = 488$   $\text{cm}^{-1}$  for the C-Br stretching vibration,  $\omega_5 = 836$   $\text{cm}^{-1}$  for the  $\text{CH}_3$ -rocking mode and  $\omega_4 = 1276$   $\text{cm}^{-1}$  for the  $\text{CH}_3$ -umbrella mode. Only the  $\nu_5$  mode is Jahn-Teller active.

To improve these assignments, the same analysis has been applied to the same transitions observed in  $\text{CD}_3\text{Br}$  (see Fig. 2 and Table 4). In this molecule the vibrational energies are  $hc\omega_6 \approx 64$  meV (516  $\text{cm}^{-1}$ ),  $hc\omega_5 \approx 84$  meV (677  $\text{cm}^{-1}$ ) and  $hc\omega_4 \approx 103$  meV (831  $\text{cm}^{-1}$ ). These values can be compared to those predicted by our calculations, i.e.,  $hc\omega_6 = 467$   $\text{cm}^{-1}$ ,  $hc\omega_5 = 624$   $\text{cm}^{-1}$  and  $hc\omega_4 = 939$   $\text{cm}^{-1}$ .

An argument supporting the present assignments is the calculated ratio  $\rho_i = [\omega/\omega_{\text{isot}}]_i$ , i.e.,  $\rho_6 = 1.04$ ,  $\rho_5 = 1.34$  and  $\rho_4 = 1.36$  and its comparison with the corresponding provisional experimental values 1.11, 1.29 and 1.41. However, the confidence of these numbers could be improved by the analysis of the vibrational structure observed at higher energies.

The present results on  $\text{CH}_3\text{Br}$  can directly be compared with the data reported by Causley and Russell [5] and Felps et al. [6]. As shown in Table 3 there is a general agreement between the three photoabsorption spectra, within about 100  $\text{cm}^{-1}$ . Though present in the spectra reproduced in Figs. 4 and 5 in their paper, Causley and Russell do not mention several structures in their Table V [5]. For  $\text{CD}_3\text{Br}$  a comparison could only be made with the work of Felps et al. [6]. It has to be noted that in the latter work the photoabsorption spectra of  $\text{CH}_3\text{Br}$  were recorded in a pressure range of 120-6000  $\mu\text{bar}$  and for  $\text{CD}_3\text{Br}$  the pressure ranged from 30 to 18,600  $\mu\text{bar}$ . Therefore, several features tabulated in [6] are only detected under high pressure conditions.

In both papers, the authors discussed the assignments in the frame of the  $C_{3v}$  symmetry of the neutral ground state of the molecule. Causley and Russell [5] measured four energy intervals of about (i) 2673  $\text{cm}^{-1}$ , (ii) 1173  $\text{cm}^{-1}$ , (iii) 861  $\text{cm}^{-1}$ , and (iv) 533  $\text{cm}^{-1}$  and assigned them to the C-H symmetric stretching,  $\text{CH}_3$  umbrella,  $\text{CH}_3$ -rocking and C-Br stretching modes, respectively. The last three values are in good agreement with the values determined in this work. The energy interval of 2673  $\text{cm}^{-1}$  will be assigned differently, as will be discussed below.

Felps et al. [6] investigated the two  $2e \rightarrow 5s_{a_1}$  Ryd-berg transitions in  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{Br}$ . In the former molecule they measured energy differences of (i) 2647  $\text{cm}^{-1}$ , (ii) 1310  $\text{cm}^{-1}$ , (iii) 1127  $\text{cm}^{-1}$ , (iv) 840  $\text{cm}^{-1}$ , and (v) 560  $\text{cm}^{-1}$ . In  $\text{CD}_3\text{Br}$  the corresponding differences are (i) 2010  $\text{cm}^{-1}$ , (ii) 950  $\text{cm}^{-1}$  (iii) 845  $\text{cm}^{-1}$  (iv) 685  $\text{cm}^{-1}$ , and (v) 527  $\text{cm}^{-1}$ . The last figures have to be compared with those determined in this work, i.e., 831, 677 and 516  $\text{cm}^{-1}$ , respectively. As for  $\text{CH}_3\text{Br}$ , the wavenumber at 2647  $\text{cm}^{-1}$  (2010  $\text{cm}^{-1}$ ) has to be discussed at a later stage. The wavenumber of 1310  $\text{cm}^{-1}$  (950  $\text{cm}^{-1}$ ) is not detected in our spectra and its observation is likely only possible at high pressures.

**Table 3-** Energies (eV), wavenumbers ( $\text{cm}^{-1}$ ), effective principal quantum numbers ( $n^*$ ), convergence limits (eV) and assignments (0-0 meaning vibrationless transition) of vibrational progressions of ( ${}^2E_{3/2}$  or  ${}^2E_{1/2}$ )[ $nl(a_1$  or  $e)$ ]



Rydberg series in  $CH_3Br$  converging to the  $\tilde{X}^1E_{3/2}$  and  $\tilde{X}^2E_{1/2}$  states of  $CH_3Br^+$  (1 eV = 8065.545  $cm^{-1}$  [22])

| Rydberg              | eV                   | This work            |                      |                       |                       | Assignment        | Ref. [5] | Ref. [6] |
|----------------------|----------------------|----------------------|----------------------|-----------------------|-----------------------|-------------------|----------|----------|
|                      |                      | $cm^{-1}$            | $n^*$                | Limit                 |                       |                   |          |          |
| $(^2E_{3/2}) 5sa_1$  | 6.944                | 56,010               | 1.944                | 10.543                | 0-0                   | 56,030            | 56,023   |          |
|                      | 7.015                | 56,580               | 1.945                | {10.611} <sup>c</sup> | $v_6$                 | 56,590            | 56,556   |          |
|                      | 7.052                | 56,878               | 1.945                | 10.648                | $v_5$                 | 56,870            | 56,884   |          |
|                      | 7.089                | 57,177               | 1.940                | 10.703                | $v_4$                 | 57,170            | 57,160   |          |
|                      | 7.151                | 57,677               | 1.943                | 10.750                | $2v_5$                | 57,670            | 57,655   |          |
|                      |                      |                      |                      |                       | $v_4 + v_6$           |                   |          |          |
|                      | 7.188                | 57,975               | 1.943                | {10.798} <sup>c</sup> | $v_4 + v_5$           | 58,005            | 57,975   |          |
|                      | 7.225                | 58,273               | 1.944                | {10.815} <sup>c</sup> | $2v_4$                | 58,305            | 58,371   |          |
|                      |                      |                      |                      |                       | $v_4 + 2v_6$          |                   |          |          |
|                      | 7.262                | 58,573               | 1.944                | 10.862                | $3v_5$                | 58,345            |          |          |
|                      | 7.275                | 58,677               | (1.944) <sup>b</sup> | (10.875) <sup>b</sup> |                       | 58,715            | 58,693   |          |
|                      | 7.290                | 58,798               | (1.944) <sup>b</sup> | (10.890) <sup>b</sup> | $v_4 + 2v_5$          |                   |          |          |
|                      |                      |                      |                      |                       | $2v_4 + v_6$          |                   |          |          |
|                      | [7.332] <sup>a</sup> | 59,136               | 1.944                | 10.930                | $2v_4 + v_5$          | 59,165            | 59,175   |          |
|                      | 7.380                | 59,524               | 1.946                | {10.972} <sup>c</sup> | $3v_4$                | 59,560            | 59,564   |          |
|                      | 7.393                | 59,629               | 1.941                | {11.005} <sup>c</sup> | $3v_5 + 2v_6$         | -                 | -        |          |
|                      | 7.419                | 59,838               | 1.942                | {11.026} <sup>c</sup> | $v_4 + 3v_5$          | -                 | -        |          |
|                      | $(^2E_{1/2}) 5sa_1$  | [7.332] <sup>a</sup> | 59,136               | 1.963                 | 10.862                | 0-0               | 59,165   | 59,175   |
|                      |                      | 7.474                | 60,282               | 1.963                 | {11.005} <sup>c</sup> | $v_4$             | 60,280   | 60,275   |
| 7.510                |                      | 60,572               | 1.968                | {11.026} <sup>c</sup> | $v_5 + v_6$           | 60,670            | -        |          |
| 7.605                |                      | 61,338               | 1.976                | 11.090                | $2v_5$                | 61,210            | -        |          |
| 7.626                |                      | 61,509               | 1.957                | 11.179                | $2v_4$                | 61,450            | 61,430   |          |
| 7.657                |                      | 61,758               | 1.954                | 11.220                | $3v_5$                | 61,775            | 61,810   |          |
|                      |                      |                      |                      |                       |                       |                   |          |          |
| 7.785                |                      | 62,790               | 1.963                | 11.290                | $3v_4$                | 62,685            | -        |          |
| 7.823                |                      | 63,097               | 1.963                | 11.354                | $2v_4 + 2v_5$         | 62,845            | -        |          |
| 7.920                |                      | 63,879               | 1.963                | 11.451                | $4v_4$                | 63,875            | -        |          |
|                      |                      |                      |                      |                       |                       |                   |          |          |
|                      |                      |                      |                      |                       |                       |                   | Ref. [5] |          |
| This work            |                      |                      |                      |                       |                       |                   |          |          |
| Rydberg              | eV                   | $cm^{-1}$            | $n^*$                | Limit                 | Assignment            |                   |          |          |
| $(^2E_{3/2}) 5pa_1$  | 8.179                | 65,968               |                      | 2.399                 | 10.543                | 0-0               | 66,004   |          |
|                      | 8.223                | 66,323               |                      |                       |                       | n.a. <sup>d</sup> | 66,341   |          |
|                      | 8.239                | 66,452               |                      |                       |                       | n.a. <sup>d</sup> | 66,482   |          |
|                      | 8.254                | 66,573               |                      | 2.402                 | {10.611} <sup>c</sup> | $v_6$             | -        |          |
|                      | 8.260                | 66,621               |                      |                       |                       | n.a. <sup>d</sup> | 66,650   |          |
|                      | 8.275                | 66,742               |                      | 2.394                 | 10.648                | $v_5$             | -        |          |
|                      | 8.309                | 67,017               |                      | 2.407                 | {10.657} <sup>c</sup> | $2v_6$            | 66,990   |          |
|                      | 8.321                | 67,113               |                      | 2.397                 | 10.703                | $v_4$             | 67,093   |          |
|                      | 8.359                | 67,420               |                      | 2.401                 | {10.720} <sup>c</sup> | $v_5 + v_6$       | 67,437   |          |
|                      | 8.364                | 67,460               |                      |                       |                       |                   |          |          |
|                      | 8.390                | 67,670               |                      | 2.400                 | 10.752                | $2v_5$            | -        |          |
|                      | 8.394                | 67,702               |                      |                       |                       |                   | 67,720   |          |
|                      | 8.460                | 68,234               |                      | 2.404                 | {10.815} <sup>c</sup> | $2v_4$            | 68,256   |          |
|                      |                      |                      |                      |                       |                       | $2v_5 + v_6$      |          |          |
|                      | [8.508] <sup>a</sup> | 68,621               |                      | 2.404                 | 10.862                | $3v_5$            | 68,659   |          |
|                      | [8.533] <sup>a</sup> | 68,823               |                      | (2.400) <sup>b</sup>  | (10.895) <sup>b</sup> | $v_4 + 2v_5$      | 68,848   |          |
|                      |                      |                      |                      |                       |                       | $2v_4 + v_6$      |          |          |
|                      | [8.564] <sup>a</sup> | 69,073               |                      | 2.400                 | 10.931                | $2v_4 + v_5$      | 69,105   |          |
|                      | [8.623] <sup>a</sup> | 69,549               |                      | 2.407                 | {10.972} <sup>c</sup> | $3v_4$            | 69,581   |          |
| 8.646                | 69,735               |                      | 2.401                | {11.005} <sup>c</sup> | $3v_5 + 2v_6$         | -                 |          |          |
| [8.663] <sup>a</sup> | 69,872               |                      | 2.399                | {11.026} <sup>c</sup> | $v_4 + 3v_5$          | -                 |          |          |
| $(^2E_{3/2}) 5pe$    | 8.335                | 67,226               |                      | 2.482                 | 10.543                | 0-0               | 67,246   |          |
|                      | 8.408                | 67,815               |                      | 2.485                 | {10.611} <sup>c</sup> | $v_6$             | -        |          |
|                      | [8.460] <sup>a</sup> | 68,234               |                      | 2.493                 | 10.648                | $v_5$             | 68,256   |          |
|                      | 8.490                | 68,476               |                      | 2.479                 | 10.703                | $v_4$             | 68,504   |          |
|                      | [8.533] <sup>a</sup> | 68,823               |                      | 2.494                 | {10.720} <sup>c</sup> | $v_5 + v_6$       | 68,848   |          |
|                      | [8.564] <sup>a</sup> | 69,073               |                      | 2.495                 | 10.758                | $3v_6/2v_5$       | 69,105   |          |
|                      | [8.584] <sup>a</sup> | 69,235               |                      | 2.490                 | {10.779} <sup>c</sup> | $v_4 + v_5$       | -        |          |
|                      | [8.623] <sup>a</sup> | 69,549               |                      | 2.491                 | {10.815} <sup>c</sup> | $2v_4$            | 69,581   |          |
|                      |                      |                      |                      |                       |                       | $v_4 + 2v_6$      |          |          |
|                      |                      |                      |                      |                       |                       |                   |          |          |

(continued on next page)

Table 3 (continued)

| Rydberg  | This work            |                  |            |                       |                                   | Ref. [5] |
|--|----------------------|------------------|------------|-----------------------|-----------------------------------|----------|
|  | eV                   | cm <sup>-1</sup> | <i>n</i> * | Limit                 | Assignment                        |          |
|  | [8.663] <sup>a</sup> | 69,872           | 2.487      | 10.862                | 3v <sub>5</sub>                   | 69,932   |
|  | 8.736                | 70,460           | 2.490      | 10.931                | 2v <sub>4</sub> + v <sub>5</sub>  | -        |
|  | 8.789                | 70,888           | 2.495      | {10.972} <sup>c</sup> | 3v <sub>4</sub>                   | -        |
|  | 8.811                | 71,065           | 2.490      | {11.005} <sup>c</sup> | 3v <sub>5</sub> + 2v <sub>6</sub> | -        |
| ( <sup>2</sup> E <sub>1/2</sub> ) 5pa <sub>1</sub> | [8.508] <sup>a</sup> | 68,621           | 2.404      | 10.862                | 0-0                               | 68,659   |
|  | [8.584] <sup>a</sup> | 69,235           | 2.407      | 10.931                | v <sub>6</sub>                    |          |
|  | 8.609                | 69,436           | 2.399      | {10.972} <sup>c</sup> | v <sub>5</sub>                    | 69,581   |
|  | 8.663                | 69,872           | 2.410      | {11.005} <sup>c</sup> | v <sub>4</sub>                    |          |
|  | 8.736                | 70,460           | 2.404      | 11.090                | 2v <sub>5</sub>                   |          |
|  | 8.811                | 71,065           | 2.397      | 11.179                | 2v <sub>4</sub>                   |          |
|  | 8.864                | 71,493           | 2.403      | 11.220                | 3v <sub>5</sub>                   |          |
| ( <sup>2</sup> E <sub>1/2</sub> ) 5pe              | 8.684                | 70,041           | 2.499      | 10.862                | 0-0                               | 70,083   |
|  | 8.752                | 70,590           | 2.499      | 10.931                | v <sub>6</sub>                    |          |
|  | 8.811                | 71,065           | 2.498      | {10.991} <sup>c</sup> | v <sub>5</sub>                    |          |
|  | 8.839                | 71,291           | 2.506      | {11.005} <sup>c</sup> | v <sub>4</sub>                    |          |
|  | 8.924                | 71,977           | 2.506      | 11.090                | 2v <sub>5</sub>                   |          |
|  | 9.025                | 72,791           | 2.490      | 11.220                | 3v <sub>5</sub>                   |          |
| ( <sup>2</sup> E <sub>3/2</sub> ) 4f               | 9.038                | 72,896           | 3.006      | 10.543                | 0-0                               |          |
|  | 9.112                | 73,493           | 3.013      | {10.611} <sup>c</sup> | v <sub>6</sub>                    |          |
|  | 9.146                | 73,767           | 3.010      | 10.648                | v <sub>5</sub>                    |          |
|  | 9.167                | 73,937           | 3.018      | {10.660} <sup>c</sup> | 2v <sub>6</sub>                   |          |
|  | 9.199                | 74,195           | 3.008      | 10.703                | v <sub>4</sub>                    |          |
|  | 9.219                | 74,356           | 3.011      | {10.720} <sup>c</sup> | v <sub>5</sub> + v <sub>6</sub>   |          |
|  | 9.237                | 74,501           | 2.999      | 10.750                | 2v <sub>5</sub>                   |          |
|  | 9.282                | 74,864           | 3.015      | {10.779} <sup>c</sup> | v <sub>4</sub> + v <sub>5</sub>   |          |
|  | [9.372] <sup>a</sup> | 75,590           | 3.022      | 10.862                | 3v <sub>5</sub>                   |          |
| ( <sup>2</sup> E <sub>3/2</sub> ) 6pa <sub>1</sub> | [9.372] <sup>a</sup> | 75,590           | 3.409      | 10.543                | 0-0                               |          |
|  | 9.443                | 76,163           | 3.428      | {10.611} <sup>c</sup> | v <sub>6</sub>                    |          |
|  | 9.480                | 76,461           | 3.413      | 10.648                | v <sub>5</sub>                    |          |
|  | [9.530] <sup>a</sup> | 76,865           | 3.408      | 10.701                | v <sub>4</sub>                    |          |
| ( <sup>2</sup> E <sub>3/2</sub> ) 6pe              | 9.405                | 75,856           | 3.458      | 10.543                | 0-0                               |          |
|  | 9.463                | 76,324           | 3.443      | {10.611} <sup>c</sup> | v <sub>6</sub>                    |          |
|  | 9.515                | 76,744           | 3.465      | 10.648                | v <sub>5</sub>                    |          |
|  | [9.530] <sup>a</sup> | 76,865           | 3.470      | {10.660} <sup>c</sup> | 2v <sub>6</sub>                   |          |
|  | 9.557                | 77,082           | 3.449      | 10.701                | v <sub>4</sub>                    |          |
|  | 9.590                | 77,349           | 3.470      | {10.720} <sup>c</sup> | v <sub>5</sub> + v <sub>6</sub>   |          |
| ( <sup>2</sup> E <sub>3/2</sub> ) 5d               | 9.659                | 77,905           | 3.923      | 10.543                | 0-0                               |          |
|  | 9.729                | 78,470           | 3.927      | {10.611} <sup>c</sup> | v <sub>6</sub>                    |          |
|  | 9.765                | 78,760           | 3.925      | 10.648                | v <sub>5</sub>                    |          |
|  | 9.818                | 79,188           | 3.921      | 10.703                | v <sub>4</sub>                    |          |
| ( <sup>2</sup> E <sub>3/2</sub> ) 5f               | 9.706                | 78,195           | 4.022      | 10.543                | 0-0                               |          |
|  | 9.784                | 78,913           | 4.056      | {10.611} <sup>c</sup> | v <sub>6</sub>                    |          |
|  | 9.800                | 79,042           | 4.005      | 10.648                | v <sub>5</sub>                    |          |
|  | [9.857] <sup>a</sup> | 79,502           | 4.010      | 10.703                | v <sub>4</sub>                    |          |

<sup>a</sup> Data in brackets have different possible assignments or their intensity has different contributions.

<sup>b</sup> Data in parentheses have the proposed assignment by using the mentioned *n*\* value.

<sup>c</sup> Data in braces are ionization limits observed by PES [21]. For explanation see text.

<sup>d</sup> n.a. = not assigned: see text.

## 5.2. The (<sup>2</sup>E<sub>3/2</sub>-<sup>2</sup>E<sub>1/2</sub>)nsa<sub>1</sub>, npa<sub>1</sub>, npe, nd(a<sub>1</sub>) and nf(nde) series (n > 5)

Table 3 shows a tentative classification and assignments of the fine structure above 8 eV photon energy. Only the lower energy part of these results can be compared with the work reported by Causley and Russell [5]. To the best of our knowledge, no other analysis has been reported in the literature. As can be seen from Table 3, comparing columns 3 and 7, a good agreement is found between both experimental results.

**Table 4** - Energies (eV), wavenumbers (cm<sup>-1</sup>) and assignments (0-0 meaning vibrationless transition) of vibrational progressions of (<sup>2</sup>E<sub>3/2</sub> or <sup>2</sup>E<sub>1/2</sub>)[nl(a<sub>1</sub> or e)] Rydberg series in CD<sub>3</sub>Br converging to the  $\tilde{X}^2E_{3/2}$  and  $\tilde{X}^2E_{1/2}$  states of CD<sub>3</sub>Br<sup>+</sup> (1 eV = 8065.545 cm<sup>-1</sup> [22])

| Rydberg  | This work            |                  |   | Assignment                        | Felps et al. [6] |
|--|----------------------|------------------|---|-----------------------------------|------------------|
|  | eV                   | cm <sup>-1</sup> |   |                                   |                  |
| <sup>(2</sup> E <sub>3/2</sub> )5sa <sub>1</sub> | 6.981                | 56,306           |   | 0-0                               | 56,285           |
|  | -                    | -                |   | -                                 | 56,435           |
|  | -                    | -                |   | -                                 | 56,720           |
|  | 7.045                | 56,822           |   | v <sub>6</sub>                    | 56,795           |
|  | 7.062                | 56,959           |   | v <sub>5</sub>                    | 56,945           |
|  | 7.084                | 57,136           |   | v <sub>4</sub>                    | 57,125           |
|  | 7.092                | 57,201           |   | (2v <sub>6</sub> )                | 57,190           |
|  | 7.128                | 57,491           |   | v <sub>5</sub> + v <sub>6</sub>   | -                |
|  | 7.150                | 57,669           |   | 2v <sub>5</sub>                   | 57,650           |
|  | -                    | -                |   | -                                 | 57,780           |
|  | 7.194                | 58,031           | } | 2v <sub>4</sub>                   | 58,010           |
|  | -                    | -                |   | v <sub>5</sub> + 2v <sub>6</sub>  | -                |
|  | 7.240                | 58,394           |   | 3v <sub>5</sub>                   | 58,370           |
|  | 7.261                | 58,564           |   | v <sub>4</sub> + 2v <sub>5</sub>  | 58,460           |
|  | 7.279                | 58,709           |   | 2v <sub>4</sub> + v <sub>5</sub>  | 58,650           |
|  | -                    | -                |   | -                                 | 58,860           |
|  | 7.308                | 58,943           | } | 3v <sub>4</sub>                   | 58,995           |
|  | -                    | -                |   | 3v <sub>5</sub> + v <sub>6</sub>  | -                |
|  | [7.350] <sup>a</sup> | 59,282           |   | 3v <sub>5</sub> + v <sub>4</sub>  | 59,255           |
|  | [7.394] <sup>a</sup> | 59,637           |   | 4v <sub>4</sub>                   | -                |
|  | [7.411] <sup>a</sup> | 59,774           |   | 3v <sub>4</sub> + 2v <sub>6</sub> | 59,810           |
|  | -                    | -                |   | -                                 | 59,965           |
|  | [7.453] <sup>a</sup> | 60,113           |   | 4v <sub>4</sub> + v <sub>6</sub>  | 60,105           |
|  | -                    | -                |   | -                                 | 60,225           |
|  | [7.520] <sup>a</sup> | 60,653           |   | 4v <sub>4</sub> + 2v <sub>6</sub> | 60,625           |
|  | -                    | -                |   | -                                 | 60,810           |
|  | [7.560] <sup>a</sup> | 60,975           |   | 5v <sub>4</sub> + v <sub>6</sub>  | 60,960           |
| <sup>(2</sup> E <sub>1/2</sub> )5sa <sub>1</sub> | [7.350] <sup>a</sup> | 59,282           |   | 0-0                               | 59,255           |
|  | [7.411] <sup>a</sup> | 59,774           |   | v <sub>6</sub>                    | 59,810           |
|  | [7.453] <sup>a</sup> | 60,113           |   | v <sub>4</sub>                    | 60,105           |
|  | -                    | -                |   | -                                 | 60,225           |
|  | [7.520] <sup>a</sup> | 60,653           |   | v <sub>4</sub> + v <sub>6</sub>   | 60,625           |
|  | -                    | -                |   | -                                 | 60,810           |
|  | [7.560] <sup>a</sup> | 60,975           |   | 2v <sub>4</sub>                   | 60,960           |
|  | -                    | -                |   | -                                 | 61,035           |
|  | 7.584                | 61,169           |   | v <sub>4</sub> + 2v <sub>6</sub>  | 61,175           |
|  | -                    | -                |   | -                                 | 61,390           |
|  | -                    | -                |   | -                                 | 61,685           |
|  | 7.668                | 61,847           |   | 3v <sub>4</sub>                   | 61,815           |
|  | 7.686                | 61,992           |   | 2v <sub>4</sub> + 2v <sub>6</sub> | 61,995           |
|  | 7.709                | 62,177           |   | v <sub>4</sub> + 4v <sub>6</sub>  | 62,180           |
|  | -                    | -                |   | -                                 | 62,560           |
|  | 7.771                | 62,677           |   | 4v <sub>4</sub>                   | 62,735           |
|  | -                    | -                |   | -                                 | 62,825           |
|  | 7.835                | 63,193           |   | 4v <sub>4</sub> + v <sub>6</sub>  | 63,030           |
|  | -                    | -                |   | -                                 | 63,390           |
|  | 7.884                | 63,589           |   | 5v <sub>4</sub>                   | 63,660           |
| -  | -                    |                  | - | 63,820                            |                  |
| -  | -                    |                  | - | 64,610                            |                  |
| <sup>(2</sup> E <sub>3/2</sub> )5pa <sub>1</sub> | 8.201                | 66,145           |   | 0-0                               |                  |
|  | 8.225                | 66,339           |   | na <sup>b</sup>                   |                  |
|  | 8.247                | 66,517           |   | na <sup>b</sup>                   |                  |
|  | 8.259                | 66,613           |   | v <sub>6</sub>                    |                  |
|  | 8.273                | 66,726           |   | na <sup>b</sup>                   |                  |
|  | 8.289                | 66,855           |   | v <sub>5</sub>                    |                  |
|  | 8.304                | 66,975           |   | v <sub>4</sub>                    |                  |
|  | 8.336                | 67,234           |   | 2v <sub>6</sub>                   |                  |
|  | 8.355                | 67,388           |   | v <sub>5</sub> + v <sub>6</sub>   |                  |
|  | 8.377                | 67,565           |   | 2v <sub>5</sub>                   |                  |

(continued on next page)

**Table 4** (continued)

| Rydberg  | This work            |                                   | Assignment                         |
|--|----------------------|-----------------------------------|------------------------------------|
|  | eV                   | cm <sup>-1</sup>                  |                                    |
| <sup>(2)E<sub>3/2</sub></sup> 5pe              | 8.383                | 67,613                            | } v <sub>4</sub> + v <sub>5</sub>  |
|  | 8.385                | 67,630                            |                                    |
|  | 8.415                | 67,871                            | 2v <sub>4</sub>                    |
|  | 8.426                | 67,960                            | v <sub>5</sub> + 2v <sub>6</sub>   |
|  | 8.434                | 68,025                            | v <sub>4</sub> + 2v <sub>6</sub>   |
|  | 8.439                | 68,065                            |                                    |
|  | 8.455                | 68,194                            | 3v <sub>5</sub>                    |
|  | 8.466                | 68,283                            | } 2v <sub>4</sub> + v <sub>6</sub> |
|  | 8.473                | 68,339                            |                                    |
|  | 8.493                | 68,501                            | 2v <sub>4</sub> + v <sub>5</sub>   |
|  | 8.510                | 68,638                            | 3v <sub>4</sub>                    |
|  | 8.526                | 68,767                            | 2v <sub>4</sub> + 2v <sub>6</sub>  |
|  | 8.563                | 69,065                            | 3v <sub>4</sub> + v <sub>6</sub>   |
|  | 8.318                | 67,089                            | 0-0                                |
|  | [8.377] <sup>a</sup> | 67,565                            | } v <sub>6</sub>                   |
| [8.383] <sup>a</sup>                           | 67,613               |                                   |                                    |
| [8.385] <sup>a</sup>                           | 67,630               | } v <sub>4</sub>                  |                                    |
| [8.426] <sup>a</sup>                           | 67,960               |                                   |                                    |
| [8.434] <sup>a</sup>                           | 68,025               | } 2v <sub>6</sub>                 |                                    |
| [8.439] <sup>a</sup>                           | 68,065               |                                   |                                    |
| [8.466] <sup>a</sup>                           | 68,283               | } v <sub>5</sub> + v <sub>6</sub> |                                    |
| [8.473] <sup>a</sup>                           | 68,339               |                                   |                                    |
| [8.493] <sup>a</sup>                           | 68,501               | 2v <sub>5</sub>                   |                                    |
| [8.510] <sup>a</sup>                           | 68,638               | v <sub>4</sub> + v <sub>5</sub>   |                                    |
| [8.526] <sup>a</sup>                           | 68,767               | 2v <sub>4</sub>                   |                                    |
| [8.563] <sup>a</sup>                           | 69,065               | v <sub>4</sub> + 2v <sub>6</sub>  |                                    |
| 8.583  | 69,089               | v <sub>4</sub> + 2v <sub>5</sub>  |                                    |
| <sup>(2)E<sub>1/2</sub></sup> 5pa <sub>1</sub> | [8.526] <sup>a</sup> | 68,767                            | 0-0                                |
|  | [8.583] <sup>a</sup> | 69,227                            | v <sub>6</sub>                     |
|  | 8.630                | 69,606                            | v <sub>4</sub>                     |
|  | 8.681                | 70,017                            | v <sub>5</sub> + v <sub>6</sub>    |
|  | 8.702                | 70,186                            | 2v <sub>5</sub>                    |
|  | 8.721                | 70,340                            | v <sub>4</sub> + v <sub>5</sub>    |
|  | 8.737                | 70,469                            | 2v <sub>4</sub>                    |
|  | 8.760                | 70,654                            | } 2v <sub>5</sub> + v <sub>6</sub> |
|  |                      |                                   |                                    |
|  | 8.773                | 70,759                            | 3v <sub>5</sub>                    |
|  | 8.788                | 70,880                            | 2v <sub>4</sub> + v <sub>6</sub>   |
|  | 8.802                | 70,993                            | v <sub>4</sub> + 2v <sub>5</sub>   |
|  | 8.812                | 71,073                            | 2v <sub>4</sub> + v <sub>5</sub>   |
|  | 8.831                | 71,227                            | 3v <sub>4</sub>                    |
|  | 8.888                | 71,686                            | 3v <sub>4</sub> + v <sub>6</sub>   |
| 8.942  | 72,122               | 4v <sub>4</sub>                   |                                    |
| 8.986  | 72,477               | 4v <sub>4</sub> + v <sub>6</sub>  |                                    |
| <sup>(2)E<sub>1/2</sub></sup> 5pe              | [8.643] <sup>a</sup> | 69,710                            | 0-0                                |
|  | [8.702] <sup>a</sup> | 70,186                            | v <sub>6</sub>                     |
|  | [8.721] <sup>a</sup> | 70,340                            | v <sub>5</sub>                     |
|  | [8.737] <sup>a</sup> | 70,469                            | v <sub>4</sub>                     |
|  | [8.760] <sup>a</sup> | 70,654                            | 2v <sub>6</sub>                    |
|  | [8.788] <sup>a</sup> | 70,880                            | } v <sub>5</sub> + v <sub>6</sub>  |
|  | [8.802] <sup>a</sup> | 70,993                            |                                    |
|  | [8.812] <sup>a</sup> | 71,073                            | } 2v <sub>5</sub>                  |
|  | [8.831] <sup>a</sup> | 71,227                            |                                    |
|  | [8.888] <sup>a</sup> | 71,686                            | 2v <sub>4</sub>                    |
|  | [8.924] <sup>a</sup> | 71,976                            | 3v <sub>5</sub>                    |
|  | [8.942] <sup>a</sup> | 72,122                            | 3v <sub>4</sub>                    |
| <sup>(2)E<sub>3/2</sub></sup> 6sa <sub>1</sub> | 9.019                | 72,743                            | 3v <sub>5</sub> + v <sub>6</sub>   |
|  | 9.075                | 73,195                            | 0-0                                |
|  | 9.094                | 73,348                            | v <sub>6</sub>                     |
|  | 9.141                | 73,727                            | v <sub>5</sub>                     |
|  |                      |                                   | 2v <sub>6</sub>                    |

(continued on next page)

**Table 4** (continued)

| Rydberg  | This work                                      |                      | Assignment                        |                |
|--|--|----------------------|-----------------------------------|----------------|
|  | eV   | cm <sup>-1</sup>     |                                   |                |
| <sup>(2)E<sub>3/2</sub></sup> 4f               | 9.058  | 73,057               | 0-0                               |                |
|  | 9.133  | 73,663               | v <sub>5</sub>                    |                |
|  | 9.160  | 73,880               | v <sub>4</sub>                    |                |
|  | 9.179  | 74,034               | 2v <sub>6</sub>                   |                |
|  | 9.192  | 74,138               | v <sub>5</sub> + v <sub>6</sub>   |                |
|  | 9.223  | 74,388               | 2v <sub>5</sub>                   |                |
|  | 9.264  | 74,719               | 2v <sub>4</sub>                   |                |
|  | 9.280  | 74,848               | v <sub>4</sub> + 2v <sub>6</sub>  |                |
|  | 9.321  | 75,179               | 2v <sub>4</sub> + v <sub>6</sub>  |                |
|  | 9.343  | 75,356               | 2v <sub>4</sub> + v <sub>5</sub>  |                |
|  | 9.370  | 75,574               | 3v <sub>4</sub>                   |                |
|  | 9.420  | 75,977               | 3v <sub>4</sub> + v <sub>6</sub>  |                |
|  | 9.450  | 76,219               | 3v <sub>4</sub> + v <sub>5</sub>  |                |
|  | <sup>(2)E<sub>1/2</sub></sup> 6sa <sub>1</sub> | [9.343] <sup>a</sup> | 75,356                            | 0-0            |
| [9.401] <sup>a</sup>                           |  | 75,824               | v <sub>6</sub>                    |                |
| [9.420] <sup>a</sup>                           |  | 75,977               | v <sub>5</sub>                    |                |
| [9.450] <sup>a</sup>                           |  | 76,219               | v <sub>4</sub>                    |                |
| [9.466] <sup>a</sup>                           |  | 76,348               | 2v <sub>6</sub>                   |                |
| <sup>(2)E<sub>3/2</sub></sup> 6pa <sub>1</sub> | 9.401  | 75,824               | 0-0                               |                |
|  | 9.466  | 76,348               | v <sub>6</sub>                    |                |
|  | 9.504  | 76,655               | v <sub>4</sub>                    |                |
|  | 9.519  | 76,776               | na                                |                |
|  | 9.540  | 76,945               | v <sub>5</sub> + v <sub>6</sub>   |                |
|  | 9.547  | 77,002               | 2v <sub>5</sub>                   |                |
|  | 9.583  | 77,292               | v <sub>4</sub> + v <sub>5</sub>   |                |
|  | 9.606  | 77,478               | 2v <sub>4</sub>                   |                |
|  | 9.716  | 78,365               | 3v <sub>4</sub>                   |                |
|  | 9.726  | 78,445               | 2v <sub>4</sub> + 2v <sub>6</sub> |                |
|  | 9.770  | 78,800               | 3v <sub>4</sub> + v <sub>6</sub>  |                |
|  | <sup>(2)E<sub>3/2</sub></sup> 6pe              | 9.431                | 76,066                            | 0-0            |
|  |  | [9.504] <sup>a</sup> | 76,655                            | v <sub>6</sub> |
| [9.519] <sup>a</sup>                           |  | 76,776               | v <sub>5</sub>                    |                |
| [9.540] <sup>a</sup>                           |  | 76,945               | v <sub>4</sub>                    |                |
| [9.583] <sup>a</sup>                           |  | 77,292               | v <sub>5</sub> + v <sub>6</sub>   |                |
| 9.600  |  | 77,429               | 2v <sub>5</sub>                   |                |
| [9.606] <sup>a</sup>                           |  | 77,478               | v <sub>4</sub> + v <sub>6</sub>   |                |
| [9.699] <sup>a</sup>                           |  | 78,228               | 2v <sub>4</sub> + v <sub>6</sub>  |                |
| [9.716] <sup>a</sup>                           |  | 78,365               | v <sub>4</sub> + v <sub>5</sub>   |                |
| 9.737  |  | 78,534               | 3v <sub>4</sub>                   |                |
| [9.770] <sup>a</sup>                           |  | 78,800               | 2v <sub>4</sub> + 2v <sub>6</sub> |                |
| 9.796  |  | 79,010               | 3v <sub>4</sub> + v <sub>6</sub>  |                |
| [9.812] <sup>a</sup>                           |  | 79,139               | 3v <sub>4</sub> + v <sub>5</sub>  |                |
| [9.845] <sup>a</sup>                           |  | 79,405               | 4v <sub>4</sub>                   |                |
| <sup>(2)E<sub>3/2</sub></sup> 4d               | 9.678  | 78,058               | 0-0                               |                |
|  | [9.737] <sup>a</sup>                           | 78,534               | v <sub>6</sub>                    |                |
|  | 9.784  | 78,913               | v <sub>4</sub>                    |                |
|  | 9.812  | 79,139               | v <sub>5</sub> + v <sub>6</sub>   |                |
|  | 9.834  | 79,316               | 2v <sub>5</sub>                   |                |
|  | 9.845  | 79,405               | v <sub>4</sub> + v <sub>6</sub>   |                |
|  | 9.867  | 79,583               | v <sub>4</sub> + v <sub>5</sub>   |                |
|  | 9.878  | 79,671               | 2v <sub>4</sub>                   |                |
|  | <sup>(2)E<sub>3/2</sub></sup> 7sa <sub>1</sub> | 9.699                | 78,228                            | 0-0            |
| [9.784] <sup>a</sup>                           |  | 78,913               | v <sub>5</sub>                    |                |
| [9.796] <sup>a</sup>                           |  | 79,010               | v <sub>4</sub>                    |                |
| <sup>(2)E<sub>3/2</sub></sup> 5f               | 9.716  | 78,365               | 0-0                               |                |
|  | [9.784] <sup>a</sup>                           | 78,913               | v <sub>6</sub>                    |                |
|  | [9.796] <sup>a</sup>                           | 79,010               | v <sub>5</sub>                    |                |
|  | [9.812] <sup>a</sup>                           | 79,139               | v <sub>4</sub>                    |                |

(continued on next page)

**Table 4** (continued)

| Rydberg  | This work            |                  |  | Assignment                      |
|--|----------------------|------------------|--|---------------------------------|
|  | eV                   | cm <sup>-1</sup> |  |                                 |
| <sup>(2)E<sub>1/2</sub></sup> 6pa <sub>1</sub> | 9.726                | 78,445           |  | 0-0                             |
|  | [9.784] <sup>a</sup> | 78,913           |  | v <sub>6</sub>                  |
|  | 9.812                | 79,139           |  | v <sub>5</sub>                  |
|  | [9.834] <sup>a</sup> | 79,316           |  | v <sub>4</sub>                  |
|  | 9.867                | 79,583           |  | v <sub>5</sub> + v <sub>6</sub> |
| <sup>(2)E<sub>1/2</sub></sup> 6pe              | 9.770                | 78,800           |  | 0-0                             |
|  | [9.834] <sup>a</sup> | 79,316           |  | v <sub>6</sub>                  |
|  | [9.845] <sup>a</sup> | 79,405           |  | v <sub>5</sub>                  |
|  | [9.878] <sup>a</sup> | 79,671           |  | v <sub>4</sub>                  |
|  | 9.920                | 80,010           |  | v <sub>5</sub> + v <sub>6</sub> |
|  | 9.933                | 80,115           |  | 2v <sub>5</sub>                 |
|  | 9.952                | 80,268           |  | v <sub>4</sub> + v <sub>5</sub> |
|  |                      |                  |  |                                 |
| <sup>(2)E<sub>3/2</sub></sup> 7pa <sub>1</sub> | 9.867                | 79,583           |  | 0-0                             |
|  | [9.920] <sup>a</sup> | 80,010           |  | v <sub>6</sub>                  |
|  | [9.952] <sup>a</sup> | 80,268           |  | v <sub>5</sub>                  |
|  | 9.983                | 80,518           |  | 2v <sub>6</sub>                 |
| <sup>(2)E<sub>3/2</sub></sup> 7pe              | 9.878                | 79,671           |  | 0-0                             |
|  | [9.952] <sup>a</sup> | 80,268           |  | v <sub>5</sub>                  |
|  | [9.983] <sup>a</sup> | 80,518           |  | v <sub>4</sub>                  |
| <sup>(2)E<sub>1/2</sub></sup> 4d               | 9.996                | 80,623           |  | 0-0                             |
|  | 10.058               | 81,123           |  | v <sub>6</sub>                  |
|  | 10.071               | 81,228           |  | v <sub>5</sub>                  |
|  | 10.097               | 81,438           |  | v <sub>4</sub>                  |
|  | 10.132               | 81,720           |  | 2v <sub>6</sub>                 |
|  | 10.147               | 81,841           |  | v <sub>5</sub> + v <sub>6</sub> |
|  | 10.157               | 81,922           |  | 2v <sub>5</sub>                 |

<sup>a</sup> Data in brackets have different possible assignments or their intensity has different contributions. <sup>b</sup> n.a. = not assigned: see text.

Based on the known convergence limits resulting from photoelectron spectroscopy experiments [9] effective principal quantum numbers have been allocated to each vibronic transition. These have been determined earlier for the 0-0 Rydberg transitions [4]. As shown in Table 3, column 4, the calculated effective principal quantum numbers using these data are nearly constant over one electronic state. The variations are mostly of the order of a few thousandth. Most of the lines have been assigned by this method. A few features couldn't be classified and are noticed by n.a. (not assigned) in Table 3. A possible assignment could be Rydberg transitions in Br<sub>2</sub> produced by photolysis of CH<sub>3</sub>Br. Venkateswarlu [23] observed very strong absorptions in Br<sub>2</sub> in 66,227-66,559 cm<sup>-1</sup> region.

With the help of this hypothesis, we are able to interpret nearly all structures by the excitation of only three vibrational modes as defined in Section 4, i.e., v<sub>4</sub>, v<sub>5</sub> and v<sub>6</sub>. Averaging over about 40 energy intervals available for each vibrational mode and listed in Table 4, the energies of  $hc\omega_6 = 71 \pm 4$  meV ( $572 \pm 32$  cm<sup>-1</sup>),  $hc\omega_5 = 107 \pm 6$  meV ( $863 \pm 48$  cm<sup>-1</sup>) and  $hc\omega_4 = 146 \pm 6$  meV ( $1178 \pm 48$  cm<sup>-1</sup>) are obtained. These values are in very good agreement with those deduced from the data related to the 5s<sub>a1</sub> Rydberg series only. Furthermore, the three wavenumbers determined in this work can be compared with those obtained from the infrared spectrum of CH<sub>3</sub>Br<sup>+</sup> trapped in a neon matrix [8]: 550 cm<sup>-1</sup> for C-Br stretching, 815 cm<sup>-1</sup> for CH<sub>3</sub> rocking and 1297 cm<sup>-1</sup> for CH<sub>3</sub> umbrella modes. The discrepancy of about 100 cm<sup>-1</sup> for  $\omega_4$  could be ascribed to the steric hindrance experienced by vibrational motions in a neon matrix. The barrier associated with the umbrella mode is probably the most sensitive to this phenomenon. It is therefore not surprising that the associated force constant and wavenumber be larger in a matrix.

Table 4 displays the energy positions and assignments of the structures observed in CD<sub>3</sub>Br above 8.2 eV photon energy. Tentative assignments are listed in column 4. As already mentioned for CH<sub>3</sub>Br, a few lines are not assigned (n.a.). Also in the present case they could be assigned to Rydberg transitions in Br<sub>2</sub> [23].

Assignments were attempted and essentially based on the invariability of energy intervals between lines, within about 5-10 meV (i.e., about twice the error limit). The average over about 60-70 observations of each vibrational mode leads to values of  $hc\omega_6 = 62 \pm 4$  meV ( $500 \pm 32$  cm<sup>-1</sup>),  $hc\omega_5 = 82 \pm 4$  meV ( $661 \pm 32$  cm<sup>-1</sup>) and  $hc\omega_4 = 104 \pm 3$  meV ( $839 \pm 24$  cm<sup>-1</sup>). These values compare favorably with those determined from the 2e → 5s<sub>a1</sub> transitions. Additionally, these data are comparable with those provided by the infrared spectrum of CD<sub>3</sub>Br<sup>+</sup> [8] where only the CD<sub>3</sub> rocking at 660 cm<sup>-1</sup> and the CD<sub>3</sub> umbrella mode at 948 cm<sup>-1</sup> have been reported.

The comparison of the data related to both molecules with the ab initio calculated values remains fairly good. A stronger argument favouring the present values is the isotopic shift measured by the ratio  $p$ . As mentioned earlier its value was  $\rho_6 = 1.11$ ,  $\rho_5 = 1.29$  and  $\rho_4 = 1.41$  as determined from the  $5s_a$  transition. With all the available data these ratios become  $\rho_6 = 1.15 \pm 0.14$ ,  $\rho_5 = 1.31 \pm 0.14$  and  $\rho_6 = 1.39 \pm 0.10$ . The predicted ab initio values are, respectively, 1.04, 1.34 and 1.36, as already mentioned.

As already stressed, the comparison of the assignments made in this work and in previous papers [5,6] essentially differ by the assignment of the  $2670 \text{ cm}^{-1}$  interval [6] and  $2685 \text{ cm}^{-1}$  wavenumber [5] to the  $\nu_2$  C-H symmetric stretching vibration. In the present work an average energy interval of  $\Delta(hc\omega) = 0.323 \pm 0.009 \text{ eV}$  ( $2605 \pm 72 \text{ cm}^{-1}$ ) has been measured and assigned to  $3\nu_5$  or  $3 \times 0.108 \text{ eV}$  ( $2613 \text{ cm}^{-1}$ ), in very good agreement with the value proposed in this work for the fundamental wavenumber of the  $\nu_5$  CH<sub>3</sub> rocking vibration. In CD<sub>3</sub>Br an energy interval  $\Delta(hc\omega) = 0.249 \pm 0.004 \text{ meV}$  ( $2008 \pm 32 \text{ cm}^{-1}$ ) has consistently been assigned to  $3\nu_5$  or  $3 \times 0.083 \text{ eV}$  ( $2007 \text{ cm}^{-1}$ ), i.e., the CD<sub>3</sub> rocking vibration. Intensity arguments are difficult to invoke because peaks often overlap or are buried in stronger transitions. The situation is even worse at higher energies.

As shown in Section 4, the wavenumber associated with all the vibrational normal modes have been predicted by ab initio calculations. Despite the limitations of the method used when applied to molecules containing a heavy atom like Br, they show to be reliable for the prediction of all the fundamental vibrational wave-numbers of the neutral ground state. Discrepancies between the best experimental [20] and theoretical values of +4% for low  $\omega$  values and -3% for the highest  $\omega$  values are observed in CH<sub>3</sub>Br. These are smaller, i.e., about 2% or less, for CD<sub>3</sub>Br. For the CH<sub>3</sub>Br<sup>+</sup> cation the calculations proved to be useful for the three lowest wavenumbers. In the case of the  $\nu_2$  vibrational normal mode the predicted wavenumber is  $\omega_2 = 2953 \text{ cm}^{-1}$ . This value is much higher, and outside the allowed error limits, than the proposed experimental value [5,6]. Lugez et al. [8] using the MP2 calculations determined  $\omega_2 = 2912$  and  $3056 \text{ cm}^{-1}$  using QCISD. In their infrared spectrum of CH<sub>3</sub>Br<sup>+</sup> cation trapped in a neon matrix [8] these authors consistently assigned the feature observed at  $2909.5 \text{ cm}^{-1}$  to the  $\nu_2$  C-H symmetric stretching vibration. Furthermore, no signal at about  $2600 \text{ cm}^{-1}$  has been observed in this spectrum. All these arguments seem to converge to support the present interpretation.

### 5.3. The CH<sub>3</sub>Br<sup>+</sup>( $\tilde{\chi}^2E$ ) photoelectron band [9]

The analysis of the vibrational structure of the Rydberg series in the vacuum UV photoabsorption spectrum of CH<sub>3</sub>Br and CD<sub>3</sub>Br allows us to reconsider the high resolution  $\tilde{\chi}^2E$  photoelectron band of CH<sub>3</sub>Br<sup>+</sup> and to compare the assignments proposed in [9].

Table 5 summarizes the measurements (column 1) and their analysis (column 2) presented by Karlsson et al. [9]. In the third column, we listed our assignments based on the Rydberg series analyses. For the  $^2E_{3/2}$  component both works agree fairly well: CBr-stretching, CH<sub>3</sub>-rocking and CH<sub>3</sub>-umbrella mode, overtones and combinations are observed. However, the CH-symmetric and antisymmetric stretching have not been observed in the present work.

Owing to partial overlap, the comparison is more difficult for the  $^2E_{1/2}$  component. Overtones and/or combinations of C-H symmetric stretching and CH<sub>3</sub>-umbrella modes are identified by Karlsson et al. [9]. In the present work, the observations are mainly assigned to the CH<sub>3</sub>-rocking and umbrella vibrations.

**Table 5**-Analysis of the CH<sub>3</sub>Br<sup>+</sup>( $\tilde{\chi}^2E$ ) photoelectron band as measured (eV) by Karlsson et al. [9] and the alternative assignments derived from Rydberg series analysis

| Ionization energy [9] | Assignment [9]<br>(in C <sub>3v</sub> symmetry) | Assignment [this work]<br>(in C <sub>s</sub> symmetry) |
|-----------------------|---|--|
| 10.543                | ( $^2E_{3/2}$ )                                 | ( $^2E_{3/2}$ )  |
| 10.601 <sup>a</sup>   | $\nu_3(a_1)$                                    | $\nu_6(a')$  |
| 10.648                | $\nu_6(e)$                                      | $\nu_5(a')$  |
| 10.703                | $\nu_2(a_1)$                                    | $\nu_4(a')$  |
| 10.751                | $2\nu_6(a_1)$                                   | $2\nu_5/\nu_4 + \nu_6$                                 |
| 10.862                | ( $^2E_{1/2}$ )                                 | ( $^2E_{1/2}$ )/( $^2E_{3/2}$ ) $3\nu_5$               |
| 10.931                | ( $^2E_{3/2}$ ) $\nu_4(e)$                      | ( $^2E_{3/2}$ ) $2\nu_4 + \nu_5$                       |
| 11.021                | $\nu_2(a_1)$                                    | ( $^2E_{3/2}$ ) $\nu_4 + 3\nu_5/\nu_5 + \nu_6$         |
| 11.090                | ( $^2E_{3/2}$ ) $\nu_2 + \nu_4$                 | $2\nu_5 + \nu_6$                                       |
| 11.179                | $2\nu_2(a_1)$                                   | $2\nu_4(a')$   |
| 11.22                 | $\nu_1(a_1)$                                    | $3\nu_5(a')$   |
| 11.29                 | ( $^2E_{3/2}$ ) $2\nu_4(a_1)$                   | $3\nu_4(a')$   |

<sup>a</sup> The Rydberg series convergence limit is calculated to be 10.611 eV.

## 6. CONCLUSIONS

The abundant fine structure observed in the 6.9-10.2 eV photon energy range in the vacuum UV spectrum of CH<sub>3</sub>Br and CD<sub>3</sub>Br has been analyzed in terms of short vibrational progressions. To support the assignments, the geometry and all the vibrational wavenumbers of the neutral molecule and of the cation in their ground electronic states were calculated by ab initio quantum mechanical methods for CH<sub>3</sub>Br and CD<sub>3</sub>Br. The Jahn-Teller distortion upon ionization has also been considered and calculated. The fairly good agreement between experimental and predicted wavenumbers, as well as the isotope effect, allowed us to assign the observed progressions to three vibrational normal modes. These were identified as  $\nu_6$  ( $\omega_6 = 572 \pm 32 \text{ cm}^{-1}$ ) (C-Br stretching),  $\nu_5$  ( $\omega_5 = 863 \pm 48 \text{ cm}^{-1}$ ) (CH<sub>3</sub> rocking) and  $\nu_4$  ( $\omega_4 = 1178 \pm 48 \text{ cm}^{-1}$ ) (CH<sub>3</sub> umbrella). A discrepancy between previous works [5,6] and the present study is related to the assignment of  $\Delta(hc\omega) \approx 2670 \text{ cm}^{-1}$  to  $\nu_2$  or to  $3\nu_5$ . Several arguments are suggested converging to assign this energy to  $3\nu_5$ . Finally, alternative assignments are proposed for the interpretation of the CH<sub>3</sub>Br<sup>+</sup>( $\tilde{X}^2E$ ) photoelectron band.

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