

OVERTONE SPECTRA OF 1,2-DICHLORO- AND DIBROMO-ETHANES IN THE NEAR INFRARED REGION

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The vibrational overtone spectra of the liquid phase 1,2-dichloroethane and 1,2-dibromoethane in the spectral regions of the CH stretching local mode overtones corresponding to $\Delta\nu_{\text{CH}} = 2$ to $\Delta\nu_{\text{CH}} = 5$ are reported. The observed spectral features are assigned using the local mode model. Local mode frequencies ω_{CH} and diagonal local mode anharmonicities X_{CH} are obtained from an analysis of the spectra. The local–local combinations observed are interpreted on the basis of a coupled CH oscillator model hamiltonian. Local–normal combinations show complex structures and their possible assignments are given.

1. Introduction

The local mode (LM) model is usually used for the description of the vibrational overtone spectra of polyatomic molecules containing X–H (X = C, N, O) oscillators [1–3]. This model, introduced by Henry and Siebrand [4], treats a molecule as a set of loosely coupled anharmonic oscillators localized on individual X–H bonds. Experimentally, overtone spectra have been obtained for a wide variety of hydrogen-containing molecules like aromatics [5], alkanes [6–8] and haloalkanes [9–11]. In all these cases, the spectra are correctly interpreted by the local mode model. Overtone spectra have been used for conformational analyses [10,12] and for the study of non-equivalent CH groups [13]. Mass effects on the applicability of the LM description [9] and the effect of symmetry in the LM picture [11] are also studied from the overtone spectra of the dihalomethanes. Using a model hamiltonian containing a local mode CH anharmonicity constant and coupling parameters between CH oscillators, Mortensen et al. [11] calculated the overtone spectra of the dihalomethanes. The observed splitting between symmetric and antisymmetric states have been correctly explained by this model hamiltonian.

In the present paper we report the overtone spectra of 1,2-dichloroethane and 1,2-dibromo-

ethane in the near infrared region ($\Delta\nu_{\text{CH}} = 2, 3, 4$ and 5). Pure local mode overtones, local–local combinations and local–normal combinations are observed in the spectra. It has been found that the observed overtone spectra of these compounds are in close agreement with the calculated spectra obtained from the model hamiltonian given by Mortensen et al. [11]. Possible assignments of local–normal combinations are also given.

2. Experimental

High purity (99.5%) 1,2-dichloroethane (Sisco Research Laboratories, India) and high purity (99.0%) 1,2-dibromoethane (Merck, Germany) are used in this investigation. Except in the $\Delta\nu_{\text{CH}} = 2$ region, spectra are recorded from pure liquids. In the $\Delta\nu_{\text{CH}} = 2$ region, samples are dissolved in high purity (99.8%) carbon tetrachloride (Sisco Research Laboratories, India) to avoid saturation absorbance signals. All spectra are recorded on Hitachi Model 330 UV-VIS-NIR spectrophotometer operated in the NIR mode with a tungsten lamp as the analyzing light. The spectra are recorded at 28°C using a cell of path length 1 cm. The overtone spectra from $\Delta\nu_{\text{CH}} = 2$ to $\Delta\nu_{\text{CH}} = 5$ are shown in figs. 1–6. The spectra show pure local mode overtones, local–local and local–

Table 1
Vibrational peak assignments for the dihaloethanes

| CH ₂ Cl-CH ₂ Cl | | CH ₂ Br-CH ₂ Br | |
|---------------------------------------|--|---------------------------------------|---|
| peak position (cm ⁻¹) | assignment | peak position (cm ⁻¹) | assignment |
| 5764 | 10> ± + 2ν ₂ ['] , 2ν ₁₅ ['] (C) | 5841 | 10> ± + 2ν ₂ , 2ν ₂ ['] , 2ν ₁₅ , 2ν ₁₅ ['] (C) |
| 5814 | 20> ± | 5893 | 20> ± |
| 5874 | 10> ± + 2ν ₂ , 2ν ₁₅ (C) | 6028 | 11> |
| 5988 | ? | 6477 | 20> ± + ν ₁₇ , ν ₁₇ ['] |
| 6803 | 20> ± + ν ₁₃ | 6575 | 20> ± + (ν ₃ - ν ₁₇) |
| 6944 | 20> ± + ν ₈ | 6640 | 20> ± + ν ₉ |
| 6993 | 20> ± + ν ₈ ['] | 6557 | 20> ± + ν ₉ ['] |
| 7105 | 20> ± + ν ₃ , ν ₁₆ ['] | 6826 | 20> ± + ν ₁₃ |
| 7143 | 20> ± + ν ₈ ['] + ν ₁₀ ['] | 6911 | 20> ± + ν ₄ , ν ₄ ['] |
| 7233 | 20> ± + ν ₂ ['] + ν ₁₅ ['] | 6969 | 20> ± + ν ₈ |
| 7313 | 20> ± + 2ν ₅ | 7062 | 20> ± + ν ₈ ['] |
| 7360 | 20> ± + ν ₁₃ ['] + ν ₁₇ ['] | 7128 | 20> ± + ν ₃ , ν ₁₆ |
| 7414 | 20> ± + ν ₅ ['] + ν ₉ ['] | 7215 | 20> ± + 2ν ₅ |
| 8574 | 30> ± | 7321 | 20> ± + ν ₂ , ν ₁₅ , ν ₂ ['] , ν ₁₅ ['] |
| 8734 | 21> + | 7429 | ? |
| 8818 | 21> - | 8576 | 20> ± + 2ν ₂ ['] , 2ν ₁₅ ['] (C) |
| 8869 | ? | 8628 | 30> ± |
| 9547 | 30> ± + ν ₁₃ | 8803 | 20> ± + 2ν ₂ , 2ν ₁₅ (C) |
| 9685 | 30> ± + ν ₈ | 8873 | 21> + |
| 9756 | 30> ± + ν ₈ ['] | 8937 | 21> - |
| 9852 | 30> ± + ν ₃ , ν ₁₆ ['] | 9294 | 30> ± + (ν ₃ - ν ₁₇) |
| 9901 | 30> ± + ν ₈ ['] + ν ₁₀ ['] | 9363 | 30> ± + ν ₉ |
| 11220 | 40> ± | 9488 | 30> ± + ν ₉ ['] |
| 13746 | 50> ± | 9551 | 30> ± + ν ₁₃ |
| | | 9653 | 30> ± + ν ₄ , ν ₄ ['] |
| | | 9699 | 30> ± + ν ₈ |
| | | 9804 | 30> ± + ν ₈ ['] |
| | | 9862 | 30> ± + ν ₃ , ν ₁₆ ['] |
| | | 10020 | 30> ± + ν ₂ , ν ₁₅ , ν ₂ ['] , ν ₁₅ ['] |
| | | 10162 | ? |
| | | 10288 | ? |
| | | 10616 | ? |
| | | 11223 | 40> ± |
| | | 13699 | 50> ± |

mal combinations. The peak positions of the bands are given in table 1. Each spectrum is recorded at least five times for determining the average value of the peak positions. The uncertainties in the peak positions are typically ± 5 cm⁻¹ in the $\Delta\nu_{\text{CH}} = 2$ and 3 regions and ± 10 cm⁻¹ in the $\Delta\nu_{\text{CH}} = 4$ and 5 regions.

3. Results and discussion

3.1. Pure local mode overtones and local-local combinations

The vibrational overtone spectra of the 1,2-dihaloethanes are analyzed using local mode picture and kinetic and potential energy coupling between CH oscillators attached to a common carbon atom. For interpreting the overtone excitation spectra of the 1,2-dihaloethanes, the molecular configuration

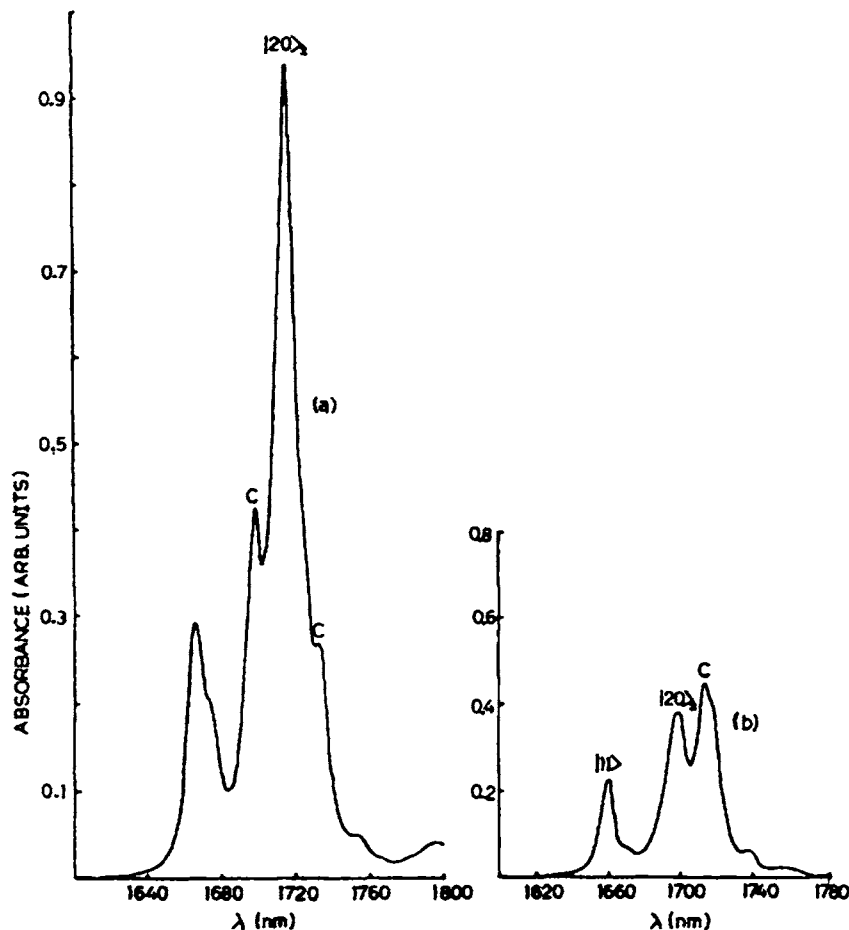


Fig. 1. Overtone spectrum of (a) 1,2-dichloroethane and (b) 1,2-dibromoethane in the $\Delta\nu_{\text{CH}} = 2$ region. Compounds dissolved in carbon tetrachloride. Reference - carbon tetrachloride.

can be regarded as two dynamically independent CH_2X ($\text{X} = \text{Cl}, \text{Br}$) fragments. Such an approach has been adopted for the normal mode analysis of all the dihaloethanes [14]. The assumption is again justified by the successful local mode analysis of the overtone spectrum of neopentane [15] where the CH_3 groups are assumed to be independent. Under this assumption, the mode of analyzing the overtone spectrum will be the same as in the case of the dihalomethanes [11]. The model hamiltonian which contains the kinetic and potential energy coupling parameters γ and ϕ and the relations connecting them to the Wilson G and F matrices are the same as reported by Mortensen et al. [11].

The operators a^+ and a in the hamiltonian perform the coupling between the CH oscillators and they have the raising and lowering properties in the harmonic oscillator limit. In the absence of coupling, the hamiltonian given in ref. [11] reduces to pure local mode hamiltonian in which states $|v0\rangle$ and $|0v\rangle$ are degenerate. The spectroscopic energies are then given by

$$\Delta E(v, 0) = \omega [v - x(v^2 + v)].$$

To obtain the structural aspects of the pure mode overtones and the local-local combinations, one has to diagonalize the full hamiltonian which contains the coupling terms. Then the symmetric and antisymmetric states of the type $|v0\rangle$

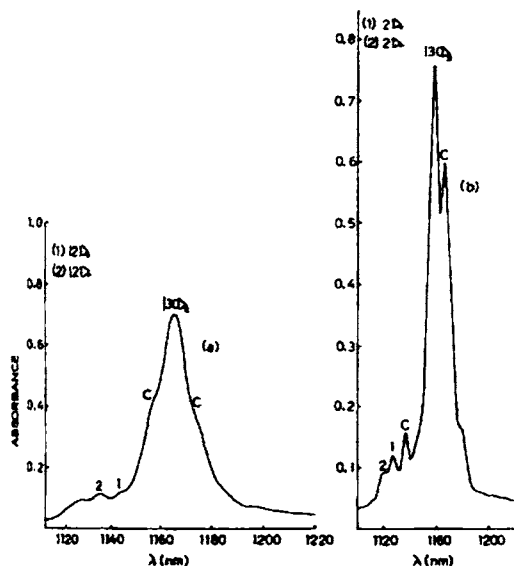


Fig. 2. Overtone spectrum of (a) 1,2-dichloroethane and (b) 1,2-dibromoethane in the $\Delta\nu_{\text{CH}} = 3$ region. Pure liquids. Reference - air.

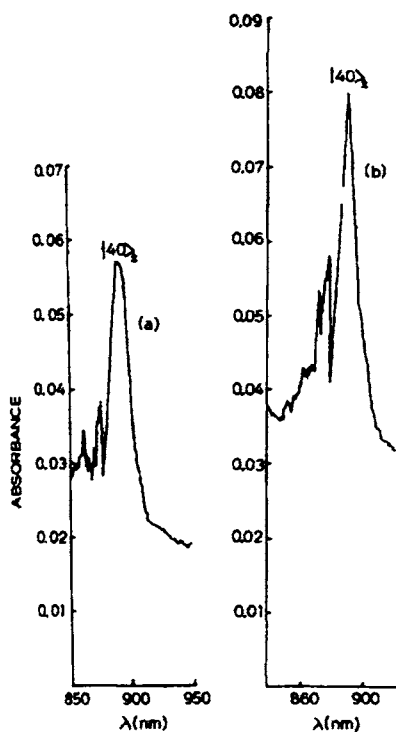


Fig. 3. Overtone spectrum of (a) 1,2-dichloroethane and (b) 1,2-dibromoethane in the $\Delta\nu_{\text{CH}} = 4$ region. Pure liquids. Reference - air.

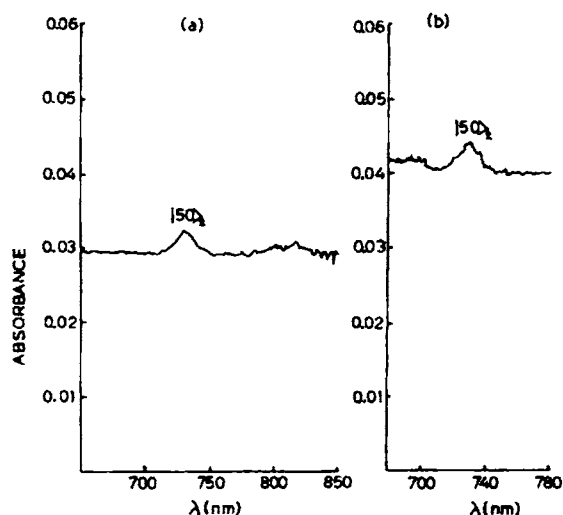


Fig. 4. Overtone spectrum of (a) 1,2-dichloroethane and (b) 1,2-dibromoethane in the $\Delta\nu_{\text{CH}} = 5$ region. Pure liquids. Reference - air.

$2^{-1/2}(|v0\rangle \pm |0v\rangle)$ are obtained where the degeneracy between $|v0\rangle$ and $|0v\rangle$ is lifted. The matrix elements of the coupling terms are calculated by Mortensen et al. [11] assuming harmonic oscillator basis functions. We have followed the same method in our analysis of the spectra of the 1,2-dihaloethanes. From the Birge-Sponer plot of $\Delta E(v, 0)/v$ versus v , the local mode parameters ω and x are obtained, where $\Delta E(v, 0)$ is the average of the $\Delta E(v, 0)_+$ and $\Delta E(v, 0)_-$ transition energies. We computed these parameters by a least-squares fit. The local mode parameters of the two dihaloethanes are given in table 2. At room temperature $\approx 80\%$ of 1,2-dichloro- and dibromoethane molecules exist in trans conformation [16]. Overtone spectroscopy, when used for conformational analyses of the haloethanes [10], shows that the peak positions for trans conformers obtained by deconvolution of the spectra deviate very little from the observed peak positions. Thus we took the average of trans A_g and trans B_u CH stretch frequencies as the value of the transition energy for $|10\rangle_+$ and the average of trans A_u and trans B_g CH stretch frequencies as the value of the transition energy for $|10\rangle_-$. The fundamental CH stretching frequencies of 1,2-dichloroethane and

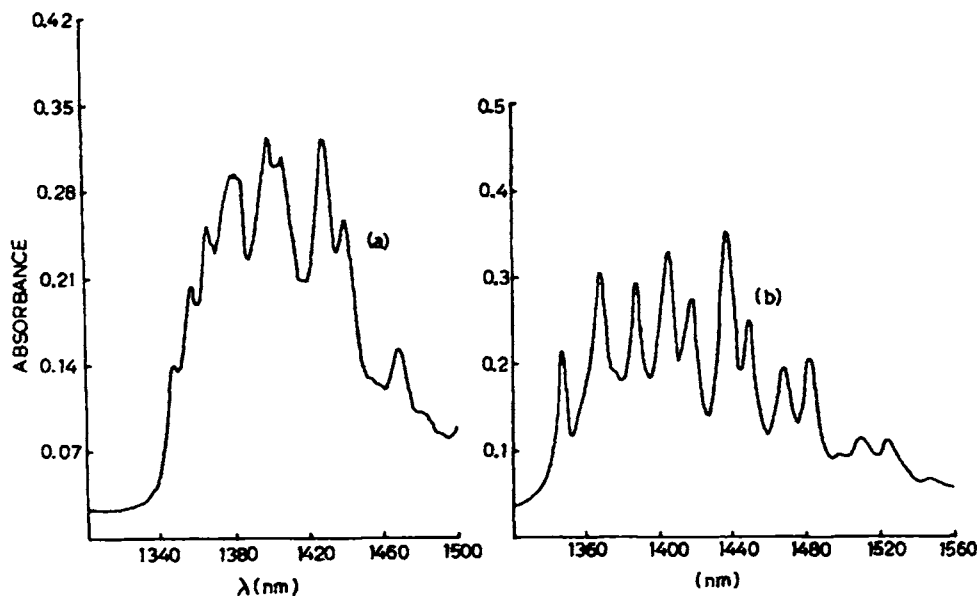


Fig. 5. Local-normal combination structure of (a) 1,2-dichloroethane and (b) 1,2-dibromoethane involving $\Delta\nu_{\text{CH}} = 2$ plus low-frequency quantum. Pure liquids. Reference - air.

1,2-dibromoethane are taken from the work of Nakagawa and Mizushima [17] and Tanabe et al. [18] respectively. This gave $\Delta E(10)_+ = 2960 \text{ cm}^{-1}$ and $\Delta E(10)_- = 3005 \text{ cm}^{-1}$ for 1,2-dichloroethane

and $\Delta E(10)_+ = 2971 \text{ cm}^{-1}$ and $\Delta E(10)_- = 30 \text{ cm}^{-1}$ for 1,2-dibromoethane. The splitting between $|10\rangle_+$ and $|10\rangle_-$ transitions is $2(\gamma - \nu_{\text{CH}})$ [11] giving values of 0.0073 and 0.0082 for ($\gamma - \nu_{\text{CH}}$)

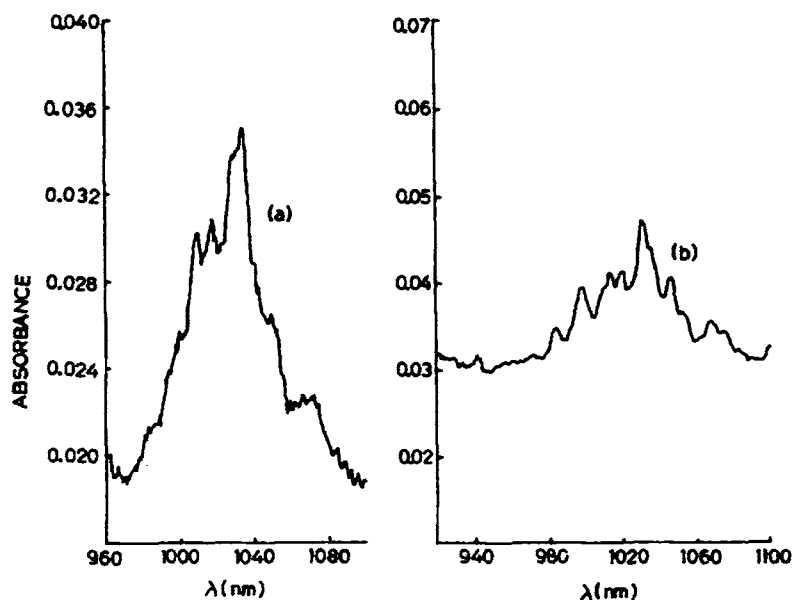


Fig. 6. Local-normal combination structure of (a) 1,2-dichloroethane and (b) 1,2-dibromoethane involving $\Delta\nu_{\text{CH}} = 3$ plus low-frequency quantum. Pure liquids. Reference - air.

for 1,2-dichloroethane and 1,2-dibromoethane respectively. All the parameters necessary for calculating the overtone spectrum are now available and the diagonalization of the hamiltonian matrices [11] gives the entire overtone spectrum of the two molecules.

The calculated and observed values of the peak positions of the pure local mode and the local-local combinations are given in table 2. The calculated values are in good agreement with the observations. It is seen from the spectra that the pure local mode overtones show single peaks instead of two split peaks expected from theory. This is due to the fact that the coupling constant ($\gamma - \phi$) is small for the 1,2-dihaloethanes as compared to the dihalomethanes. The calculated spectra also show that the energy separations between symmetric and antisymmetric overtone states are small compared with those in the dihalomethanes. A similar situation occurs in the CH_2D_2 overtone spectrum reported recently by Perry et al. [19] where the $|60\rangle_{\pm}$ band is observed as a single peak. For the combination bands $|21\rangle_{+}$ and $|21\rangle_{-}$ of 1,2-dichloroethane, since their separation is large, two distinct peaks are observed and these peaks agree

well with the calculations. The $|11\rangle$ band is not observed in the spectrum of 1,2-dichloroethane and we strongly believe that this band is buried under the strong local-normal combination band observed as a shoulder to the $|20\rangle_{\pm}$ band. This is possible since the local-local combination bands have low intensities as observed in the cases of the $|21\rangle_{+}$ and $|21\rangle_{-}$ bands. For dibromoethane all the bands $|21\rangle_{+}$, $|21\rangle_{-}$ and $|11\rangle$ are observed which show, with the exception of $|21\rangle_{-}$, a good agreement with the calculations. The $|31\rangle_{+}$ and $|31\rangle_{-}$ bands are not observed for both the molecules due to the change of grating in that region. This problem could not be eliminated by a careful recording since the absorptivities involved are very small and the signal-to-noise ratio is poor.

3.2. Local-normal combinations

The bands indicated by "C" in the spectra are combination bands involving a pure CH local mode and two quanta of CH bending normal modes. Their assignments are given in table 1. The numbering of the normal modes is as given by Nakagawa and Mizushima [17]. The fundamental normal frequencies of 1,2-dichloroethane and 1,2-dibromoethane are from refs. [17] and [18] respectively. The bands appearing as shoulders to the $|30\rangle_{\pm}$ band of 1,2-dichloroethane are not given in table 1 due to the large uncertainties in peak positions. We believe that they are the counterparts of the bands appearing near the $|20\rangle_{\pm}$ overtone band. In the case of 1,2-dibromoethane the band appearing on the low-energy side of the $|20\rangle_{\pm}$ overtone band is a combination band involving two quanta of CH bending normal mode. This band (1712 nm) has larger intensity than the pure $|20\rangle_{\pm}$ overtone band (1697 nm). Such intensity stealing has been observed in many overtone spectra [10,20]. The corresponding combination band near the $|30\rangle_{\pm}$ pure overtone band is at 1166 nm. This band is less intense than the $|30\rangle_{\pm}$ pure overtone band. This is due to the detuning effect, that is, a decreased matching as we pass from the $|20\rangle_{\pm}$ to the $|30\rangle_{\pm}$ state. This type of combination band which involves two quanta of CH bending normal mode arises due to the coupling between CH stretching local mode and CH

Table 2

Observed and calculated local mode spectra of the 1,2-dihaloethanes. For 1,2-dichloroethane $\omega = 3067 \pm 4.3 \text{ cm}^{-1}$, $x = 0.0172 \pm 0.0007$ with correlation -0.999558 . for 1,2-dibromoethane $\omega = 3152.7 \pm 4.2 \text{ cm}^{-1}$, $x = 0.0219 \pm 0.0005$ with correlation -0.999874

| State | $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ | | $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$ | |
|--------------------|---|------------------------------------|---|------------------------------------|
| | observed (cm^{-1}) | calculated (cm^{-1}) | observed (cm^{-1}) | calculated (cm^{-1}) |
| $ 10\rangle_{+}$ | 2960 | 2960 | 2971 | 2971 |
| $ 10\rangle_{-}$ | 3005 | 3005 | 3022.5 | 3022.5 |
| $ 20\rangle_{+}$ | 5814 | 5801 | 5893 | 5874 |
| $ 20\rangle_{-}$ | 5814 | 5818 | 5893 | 5891 |
| $ 11\rangle$ | - | 5939 | 6028 | 6046 |
| $ 30\rangle_{+}$ | 8574 | 8559 | 8628 | 8621 |
| $ 30\rangle_{-}$ | 8574 | 8562 | 8628 | 8623 |
| $ 21\rangle_{+}$ | 8734 | 8743 | 8873 | 8863 |
| $ 21\rangle_{-}$ | 8818 | 8829 | 8937 | 8963 |
| $ 40\rangle_{\pm}$ | 11220 | 11206 | 11223 | 11223 |
| $ 31\rangle_{+}$ | - | 11495 | - | 11605 |
| $ 31\rangle_{-}$ | - | 11535 | - | 11650 |
| $ 22\rangle$ | - | 11676 | - | 11827 |
| $ 50\rangle_{\pm}$ | 13746 | 13746 | 13699 | 13686 |

bending normal modes. Such interactions play a key role in intramolecular energy decay from the excited CH local modes through non-linear resonances [21].

There are combination bands arising from excitation of a pure CH overtone along with one quantum of a low-frequency normal mode. These combination bands are shown in figs. 5 and 6 and their assignments are given in table 1. Comparison of the combination band structures of the 1,2-dichloroethane and 1,2-dibromoethane molecules has helped in the unambiguous assignments of the bands arising from the ν_{13} , ν_8 , ν'_8 and $2\nu_5$ normal modes. Other combination bands involving one quantum of a normal mode are given more than one assignment. This is due to the fact that there are several nearly equal normal frequencies for 1,2-dihaloethane molecules and one cannot assign with certainty which normal mode is involved in a particular combination band. In such cases, where more than one possible assignment is given, there can be contributions from more than one normal mode also.

For 1,2-dichloroethane the band at 1382.5 nm (7233 cm^{-1}) is not sharp. This is due to the contributions from combinations involving ν'_2 (gauche A $\delta\text{ CH}_2$) and ν'_{15} (gauche B $\delta\text{ CH}_2$). The band at 1358.75 nm (7360 cm^{-1}) is assigned to the excitation of two normal frequencies ν'_{13} (gauche B $\rho\text{ CH}_2$) and ν'_{17} (gauche B CCl stretch) along with $\Delta\nu_{\text{CH}} = 2$; since ν'_{13} and ν'_{17} are coupled [17]. Similarly, as there is a coupling between normal modes ν'_5 and ν'_6 [17], the band at 1348.75 nm (7414 cm^{-1}) is assigned as the excitation of ν'_5 (gauche A CCl stretch) and ν'_6 (gauche A $\rho\text{ CH}_2$) along with $\Delta\nu_{\text{CH}} = 2$. The local-normal combination band structure $\Delta\nu_{\text{CH}} = 3$ plus one low-frequency quantum shows correspondence with its counterpart $\Delta\nu_{\text{CH}} = 2$ plus one low-frequency quantum combination structure. Since these combination bands are very weak in intensity, the signal-to-noise ratio is very low and the determination of the peak positions becomes difficult. Thus we have assigned only five peaks from this structure and these five peaks have corresponding peaks in the $\Delta\nu_{\text{CH}} = 2$ plus one low-frequency quantum structure. For 1,2-dibromoethane also there are a number of combina-

tion bands involving one quantum of low-frequency normal vibrations. An examination of table 1 reveals that there are combination bands common to both molecules.

4. Conclusions

We have shown that the local mode picture model hamiltonian used for the 1,2-dihaloethanes can explain the overtone spectrum of the 1,2-dihalo- (chloro- and bromo-) ethanes in the NIR region. The splitting between symmetric and antisymmetric pure overtone states is very small and hence they are not observed. The $|11\rangle$, $|21\rangle$, and $|21\rangle_-$ local-local combination band positions are in good agreement with the calculations. Possible assignments of the local-normal combinations are also given. Almost all combinations involving one low-frequency quantum show additive relation between local and normal frequencies. The combination bands involving two quantum of CH bending mode show deviations from additive relations. This is due to mechanical coupling between the motions. However, one cannot very easily pick out bands arising from different mechanisms from a rich combination structure like in the 1,2-dihaloethanes. A high-resolution study of the gas-phase 1,2-dihaloethanes in the visible region using photoacoustic technique is being attempted and these investigations can yield more information about the overtone spectra.

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