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### Authors

Boo, D.W.  
Lee, Yuan T.

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D.W. Boo and Y.T. Lee

May 1993



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INFRARED SPECTRA OF  $\text{CH}_5^+$  CORE IN  $\text{CH}_5^+(\text{H}_2)$

Doo Wan Boo and Yuan T. Lee

*Chemical Sciences Division  
Lawrence Berkeley Laboratory,*

*and*

*Department of Chemistry  
University of California  
Berkeley, California 94720, USA*

May 1993

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# INFRARED SPECTRA OF CH<sub>5</sub><sup>+</sup> CORE IN CH<sub>5</sub><sup>+</sup>(H<sub>2</sub>)

Doo Wan Boo and Yuan T. Lee

Department of Chemistry, University of California, Berkeley, California 94720, and  
Chemical Sciences Division, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley,  
California 94720, USA

## ABSTRACT

The infrared spectra of the CH<sub>5</sub><sup>+</sup> core in CH<sub>5</sub><sup>+</sup>(H<sub>2</sub>) are presented. These spectra are the first spectroscopic results for the CH<sub>5</sub><sup>+</sup> related systems. The C-H stretching bands of the CH<sub>5</sub><sup>+</sup> core were observed as one broad feature with shoulders, centered at 2966 cm<sup>-1</sup>. The predicted C-H stretching frequencies for the minimum energy structure containing CH<sub>5</sub><sup>+</sup> with eclipsed C<sub>s</sub> symmetry match quite well to those of the observed features after appropriate scaling. Possible reasons for the band broadening are also discussed.

## 1. Introduction

$\text{CH}_5^+$  and other protonated alkanes play important roles as intermediates in electrophilic reactions. The carbonium ions have been known to form a triangular three center-two electron bond where single bonds act as  $\sigma$ -donors.<sup>1</sup>  $\text{CH}_5^+$  is the simplest carbonium ion and serves as the prototype for the entire family of nonclassical carbonium ions.

Several theoretical calculations on the structures of  $\text{CH}_5^+$  suggested that the  $C_s$  symmetry structures, which can be regarded as complexes between  $\text{CH}_3^+$  and  $\text{H}_2$ , were lowest in energy.<sup>2,3</sup> However, when electron correlation was extensively taken into account with large and polarized basis sets and when the zero point energies were corrected, the  $C_s$ ,  $C_{2v}$  and  $C_{4v}$  symmetry structures were close in energy with the  $C_s$  and  $C_{2v}$  symmetry structures being nearly identical in energy.<sup>4,5</sup> The five hydrogens are predicted to scramble around the carbon atom, so that significant spectral congestion is expected in the infrared spectrum of  $\text{CH}_5^+$ .

Hiraoka *et al.* measured  $\Delta H^\circ_{n-1,n}$  and  $\Delta S^\circ_{n-1,n}$  for the clustering reactions  $\text{CH}_5^+(\text{CH}_4)_{n-1} + \text{CH}_4 = \text{CH}_5^+(\text{CH}_4)_n$  for  $n=1-9$  using a pulsed electron beam mass spectrometer.<sup>6,7</sup> The results show an irregular decrease in the value  $-\Delta H^\circ_{n-1,n}$  and  $-\Delta S^\circ_{n-1,n}$  between  $n=2$  and  $3$ , suggesting a  $C_s$  symmetry structure for  $\text{CH}_5^+$  with a three center-two electron bond, since the two acidic H atoms of the three center-two electron bond would give the most favorable sites for the first two  $\text{CH}_4$  ligands. However, this result only suggests the  $C_s$  structure for the core ion  $\text{CH}_5^+$  of  $\text{CH}_5^+(\text{CH}_4)_n$ , but it doesn't

provide any information on free  $\text{CH}_5^+$ , because a strong interaction with  $\text{CH}_4$  could deform the structure of free  $\text{CH}_5^+$  ( $\Delta H_{0,1}^\circ = 6.87$  kcal/mole). In order to get more reliable information on the structure of  $\text{CH}_5^+$ , Hiraoka *et al.* measured  $\Delta H_{n-1,n}^\circ$  and  $\Delta S_{n-1,n}^\circ$  for the cluster ions  $\text{CH}_5^+(\text{H}_2)_n$  ( $n=1-4$ ), which were expected to have much weaker interactions between  $\text{CH}_5^+$  and  $\text{H}_2$ .<sup>8</sup> Unlike the case for  $\text{CH}_5^+(\text{CH}_4)_n$ , a gradual decrease of  $\Delta H_{n-1,n}^\circ$  with  $n$  was observed for  $\text{CH}_5^+(\text{H}_2)_n$ , though a large gap in the van't Hoff plots was still seen between  $n=2$  and 3. Based upon these observations they proposed that  $\text{CH}_5^+$  core still has  $C_s$  structure, but the positive charge is more delocalized in  $\text{CH}_5^+$  when  $\text{CH}_5^+$  is complexed by  $\text{H}_2$ .

Another interesting experiment was carried out on the collision induced intramolecular randomization of hydrogen and deuterium atoms in  $\text{CH}_4\text{D}^+$  and  $\text{CD}_4\text{H}^+$  formed by the primary collisions of  $\text{CH}_4$  (or  $\text{CD}_4$ ) with  $\text{CD}_4^{+\bullet}$  (or  $\text{CH}_4^{+\bullet}$ ).<sup>9</sup> If there is no intramolecular randomization, D in  $\text{CH}_4\text{D}^+$  and H in  $\text{CD}_4\text{H}^+$  will be involved in the charge center of the respective molecules. The product ion ratio  $[\text{NH}_4^+]/[\text{NH}_3\text{D}^+]$  associated with the proton/deuteron transfer reaction of  $\text{CH}_4\text{D}^+$  and  $\text{CD}_4\text{H}^+$  with  $\text{NH}_3$  was measured as a function of the average number of the primary collisions. The results suggested that no randomization of hydrogen and deuterium atoms takes place in  $\text{CH}_4\text{D}^+$  and  $\text{CD}_4\text{H}^+$  formed in the limit of zero collisions, but randomization starts to occur and the distribution of hydrogen and deuterium atoms in  $\text{CH}_4\text{D}^+$  and  $\text{CD}_4\text{H}^+$  becomes statistical as the average number of collisions is increased. The product ion ratio of 1 in the zero collision limit suggested a stable  $C_s$  structure for  $\text{CH}_5^+$  which has two hydrogens participating a three center-two electron bond.

The experimental results consistently suggest a  $C_s$  minimum energy structure for  $CH_5^+$  with some potential barrier for hydrogen scrambling. However, unless there is an unusual isotope effect, these results contradict the recent *ab initio* results<sup>45</sup> which predict complete hydrogen scrambling. Also, it is still unknown which of two  $C_s$  structures (eclipsed or staggered) is the minimum energy structure from the experimental results. In order to resolve the current disagreement between experiment and theory and to fully determine the structure of  $CH_5^+$ , it is necessary to carry out spectroscopic measurements on  $CH_5^+$  and its ion complexes which will provide direct information on the structure as well as the intra- and intermolecular dynamics of  $CH_5^+$ .

In our laboratory, we have been studying  $CH_5^+$  and its ion complexes,  $CH_5^+(X)_n$  ( $X = H_2, CH_4$ , etc;  $n=1,2,\dots$ ) using infrared absorption spectroscopy based upon vibrational predissociation. This technique has the advantage of zero background and high detection sensitivity, which is crucial for the study of weakly bound ion complexes which cannot be generated in large numbers. As the first step in the spectroscopic study of  $CH_5^+$  and its ion complexes, we present here the first infrared spectra of the  $CH_5^+$  core in  $CH_5^+(H_2)$ . Since no spectroscopic measurements for free  $CH_5^+$  have been yet successfully carried out, it seems to be very timely to report the infrared spectrum of  $CH_5^+$  in  $CH_5^+(H_2)$  where the structure and the vibrational frequencies of the  $CH_5^+$  group are expected to be similar to those of free  $CH_5^+$ . This system has a low binding energy ( $\Delta H^\circ=1.88$  kcal/mole), so the photon absorption of the  $CH_5^+$  group is readily detected by monitoring the daughter ion  $CH_5^+$  formed by vibrational predissociation of  $CH_5^+(H_2)$ .

## 2. Experimental

The experimental apparatus used in this work has been described previously.<sup>10,11</sup> Briefly, the  $\text{CH}_5^+(\text{H}_2)$  ions were produced from a high pressure corona discharge source and subsequent supersonic expansion through a 75  $\mu\text{m}$  nozzle. The corona discharge was maintained in 100-150 torr of gas with UHP  $\text{H}_2$  and UHP  $\text{CH}_4$  in a 2000 : 1 ratio, flowing past a 1.0 kV potential from the discharge tip of the needle to the source body maintained at approximately 350 V above ground. The discharge current under these conditions was around 20  $\mu\text{A}$ . The source was maintained at approximately  $-40^\circ\text{C}$  by contact with a liquefied gas reservoir. Typical pressures in the source chamber were around  $2 \times 10^{-4}$  torr during the experiment. To prevent the acceleration of ions in the higher pressure region which causes internal excitation and dissociation of the ion clusters via collisions with the background gas, the potential of the skimmer was maintained within 1 V of that of the source body.

After the skimmer, the ion beam entered a second differential pumping region containing collimating and focusing lenses. The pressure in this region was typically an order of magnitude lower than that of the source region. The beam was directed into a  $60^\circ$  sector magnet mass analyzer through a third differentially pumped region maintained at  $10^{-8}$  torr.

The mass-selected beam was then bent  $90^\circ$  in a dc quadrupole field, decelerated to less than 0.5 eV, and focused into a rf octapole ion trap through an entrance aperture lens. The ions were usually trapped here for  $\sim 1.5$  msec before IR irradiation. Usually

100 ions were trapped per cycle, which is not enough to allow direct measurement of photon absorption.

The trapped, mass-selected clusters were then vibrationally excited by a pulsed, tunable infrared laser. A Quanta-Ray IR WEX was used as a tunable infrared light source. The infrared wavelength was generated in a  $\text{LiNbO}_3$  crystal that takes the difference frequency between a Lambda Physics pulsed dye laser (Model FL3002E) and the  $1.06 \mu\text{m}$  fundamental of a Continuum Nd-YAG laser. The IR resolution was  $0.2 \text{ cm}^{-1}$ . The pulse duration was 6 nsec with a 20 Hz repetition rate, and the laser power was 0.5–2 mJ/pulse in the  $2650\text{--}4200 \text{ cm}^{-1}$  region.

If the ions absorb one or more IR photon(s) in the usual tuning range of  $2650\text{--}4200 \text{ cm}^{-1}$ , the  $\text{CH}_5^+(\text{H}_2)$  ions vibrationally predissociate into  $\text{CH}_5^+$  and  $\text{H}_2$ . Roughly 0.5 msec after the laser pulse, the potential on the exit aperture was lowered to extract ions of all masses from the trap. These ions were filtered by a quadrupole mass spectrometer tuned to pass only the  $\text{CH}_5^+$  daughter ions. The observation of  $\text{CH}_5^+$  signal was a measure of the infrared absorption of  $\text{CH}_5^+(\text{H}_2)$ .

Daughter ions were counted with a Daly ion detector<sup>12</sup> for each laser shot. Background daughter ions resulting from the decay of metastable parent ions in the rf ion trap were monitored in a separate cycle with the laser off at each wavelength and subtracted from the laser on signal. The laser power was monitored at each data point, and spectra were normalized for the power of the tunable infrared laser assuming a simple linear power dependence. For a typical experiment, signals were averaged for about 2,000 laser shots at each wavelength in the  $2650\text{--}4200 \text{ cm}^{-1}$  region.

In this experiment, it was seen that the composition of ions in the beam was strongly dependent on the  $\text{H}_2/\text{CH}_4$  mixing ratio, the source temperature and the gas pressure behind the nozzle. The optimum conditions for generating the  $\text{CH}_5^+(\text{H}_2)$  ions were obtained at a  $\text{H}_2:\text{CH}_4$  ratio of 2000:1, a  $-40^\circ\text{C}$  source temperature and a 100-150 torr source pressure. Fig.1 shows the mass spectrum obtained under these conditions.

### 3. Results and discussion

Fig.2(a) and (b) show the observed infrared spectra of  $\text{CH}_5^+(\text{H}_2)$  for the frequency range of  $2700 - 3300 \text{ cm}^{-1}$ . The infrared spectra were obtained under two different source conditions referred to subsequently as cold and hot ion conditions. The cold ion conditions were obtained with relatively low discharge current, high source pressure, low source temperature and low potential difference between nozzle and skimmer, compared to those for the hot ion conditions. The spectra in fig.2(a) and (b) show one broad feature with shoulders, centered at  $2966 \text{ cm}^{-1}$ . The shoulder features are more prominent in the spectrum (a) for the cold ion conditions. By comparison to the *ab initio* results on  $\text{CH}_5^+(\text{H}_2)^{13}$ , this broad feature can be assigned to a mixture of three C-H stretching bands of the  $\text{CH}_5^+$  group, and possibly a combination band involving a  $\text{CH}_3$  degenerate bending/rocking mode ( $2156 \text{ cm}^{-1}$ ) and a  $\text{H}_2$  rocking mode ( $847 \text{ cm}^{-1}$ ). These are the infrared transitions predicted to have the highest intensities.

H.F. Schaefer and coworkers recently carried out a high level *ab initio* calculation

on  $\text{CH}_5^+(\text{H}_2)$  at our request using various levels of theory.<sup>13</sup> They found that the minimum energy structure of  $\text{CH}_5^+(\text{H}_2)$  is of  $C_s$  symmetry with the  $\text{H}_2$  molecule bound to the H2 atom of  $\text{CH}_5^+$  with eclipsed  $C_s$  symmetry out of plane to the three center-two electron bond (H1-C-H2) as shown in fig.3. This structure will be notated in this paper by "o- $\text{H}_2/\text{H}_2(\text{e-}C_s\text{CH}_5^+)$ ": "o- $\text{H}_2$ " means the  $\text{H}_2$  molecule is out of plane to the H1-C-H2 plane, and " $\text{H}_2(\text{e-}C_s\text{CH}_5^+)$ " means the  $\text{H}_2$  molecule binds to the H2 atom of  $\text{CH}_5^+$  with eclipsed  $C_s$  symmetry. However, the energy difference between the minimum energy structure and the other structures such as i- $\text{H}_2/\text{H}_2(\text{e-}C_s\text{CH}_5^+)$ , o-(or i)- $\text{H}_2/\text{H}_1(\text{e-}C_s\text{CH}_5^+)$  were predicted to be less than 0.25 kcal/mole at TZ2P CISD(Q). The structures containing staggered- $C_s$  (s- $C_s$ ) or  $C_{2v}$   $\text{CH}_5^+$  were slightly higher in energy than those with eclipsed- $C_s$  (e- $C_s$ )  $\text{CH}_5^+$ . When the zero point energies are considered, the energy differences between the minimum energy structure and the structural isomers are much smaller still, so that most of these structures will be accessible for  $\text{CH}_5^+(\text{H}_2)$ , especially for internally hot ions. This may be the case for  $\text{CH}_5^+(\text{H}_2)$  ions produced by the gas discharge ion source which was employed in this work. The structural floppiness of  $\text{CH}_5^+(\text{H}_2)$  is also supported by the observation of the broad C-H stretching bands shown in fig.2. In addition, the broad feature becomes structureless as the internal energies of the ions increase as shown in fig.2(b).

According to the results of Schaefer *et al.*,<sup>13</sup> the five highest vibrational frequencies for  $\text{CH}_5^+(\text{H}_2)$  with the minimum energy structure are predicted to be 4323, 3243, 3156, 3050, and 2737  $\text{cm}^{-1}$  at TZ2P CCSD. These frequencies can be assigned to the H-H stretching mode of  $\text{H}_2$  in  $\text{CH}_5^+(\text{H}_2)$ , asymmetric  $\text{CH}_3$  stretching, symmetric  $\text{CH}_3$

stretching, symmetric  $\text{CH}_3$  breathing, and H-H stretching modes of  $\text{CH}_5^+$  in  $\text{CH}_5^+(\text{H}_2)$ , respectively. When these frequencies are scaled down by the ratio of the center of the observed feature ( $2966 \text{ cm}^{-1}$ ) to the predicted frequency of asymmetric  $\text{CH}_3$  stretching mode ( $3156 \text{ cm}^{-1}$ ), the corresponding scaled frequencies are 4063, 3048, 2966, 2866, and  $2572 \text{ cm}^{-1}$ , respectively. The three C-H stretching bands with the scaled frequencies are shown as a stick spectrum in fig.2(a). It is readily seen that the 3048 and  $2866 \text{ cm}^{-1}$  bands which are assigned to symmetric  $\text{CH}_3$  stretching and symmetric  $\text{CH}_3$  breathing modes, respectively, match quite well to the two shoulder features (marked with arrows) around the central peak. In addition, the scaled frequency of the H-H stretching mode ( $4063 \text{ cm}^{-1}$ ) also agrees well with the observed frequency ( $4077 \text{ cm}^{-1}$ ) which is not shown.\* On the other hand, the scaled frequency of the H-H stretching mode of  $\text{CH}_5^+$  in  $\text{CH}_5^+(\text{H}_2)$  is predicted to be  $2572 \text{ cm}^{-1}$ , which is outside the frequency range covered in this work. The H-H stretching mode is directly related to the three center-two electron bond of  $\text{CH}_5^+$ , so that it is expected to be very anharmonic and strongly coupled with other vibrational modes of  $\text{CH}_5^+$ . Since  $\text{CH}_5^+(\text{H}_2)$  is a weakly bound cluster ( $D^\circ(\text{CH}_5^+-\text{H}_2) = 1.08 \text{ kcal/mole}^{13}$ ), and the  $\text{CH}_3$  group of the core ion is not directly involved in the clustering, the frequencies of three C-H stretching bands of free  $\text{CH}_5^+$  are predicted to be similar to those of  $\text{CH}_5^+(\text{H}_2)$ . This prediction is also supported by the results of the *ab initio* calculation, as the calculated C-H stretching frequencies for  $\text{CH}_5^+(\text{H}_2)$  are only different from those of free  $\text{CH}_5^+$  by  $-10 \text{ cm}^{-1}$  at TZ2P CISD.<sup>13</sup> As

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\*The H-H stretching band will be reported elsewhere.

mentioned previously, the broad feature with shoulders could be assigned to a mixture of three C-H stretching bands of  $\text{CH}_5^+(\text{H}_2)$  containing e- $\text{C}_s$   $\text{CH}_5^+$ , but because of the absence of clearly resolved features, the contributions of C-H stretching bands of other structural isomers (i.e. s- $\text{C}_s$   $\text{CH}_5^+$  and  $\text{C}_{2v}$   $\text{CH}_5^+$ ) as well as some combination bands cannot be excluded. In order to clearly determine the contributions of the structural isomers of  $\text{CH}_5^+$  as well as the combination bands in the spectra, it would be necessary to cool the ions considerably and also to use a high resolution laser. In addition, the observation of the H-H stretching band of the three center-two electron bond in  $\text{CH}_5^+$  would be important for determining the relative stability of the  $\text{C}_s$  structure versus the  $\text{C}_{2v}$  structure.

The origin of the broad feature in the spectrum clearly needs to be addressed. Though the exact reason is still unknown, there are several possible explanations. First, there are likely to be some contributions from internally hot ions, evident from the observation that the shoulder features under the cold ion conditions almost disappear in the spectrum for the hot ion conditions (see fig.2(a) and 2(b)). One of the hot ion contributions may come from hot band transitions. For internally hot ions, the possible maximum internal energy would be the binding energy of  $\text{CH}_5^+(\text{H}_2)$  ( $D^0 = 1.08$  kcal/mole) since ions possessing higher internal energy would eventually dissociate while inside the octapole ion trap. Therefore, the vibrational modes which are involved in hot band transitions would be only those with frequencies lower than the binding energy ( $378 \text{ cm}^{-1}$ ). There are five such low frequency modes according the *ab initio* calculation<sup>13</sup>:  $\text{H}_2$  torsional twist ( $57 \text{ cm}^{-1}$ ),  $\text{H}_2\text{-H}_2$  twist ( $123 \text{ cm}^{-1}$ ),  $\text{H}_2\text{-H}_2$  wag ( $227 \text{ cm}^{-1}$ ),

H<sub>2</sub>-H<sub>2</sub> stretch (313 cm<sup>-1</sup>), and CH<sub>3</sub> torsional twist (336 cm<sup>-1</sup>). Among these five vibrational modes, the CH<sub>3</sub> torsional twist mode is expected to be strongly coupled to the C-H stretching modes. From the *ab initio* structure of CH<sub>5</sub><sup>+</sup>(H<sub>2</sub>) of fig.3, it is also seen that excitation of CH<sub>3</sub> torsional twist would change the interaction between the bonds C-H<sub>2</sub> and C-H<sub>3</sub>, inducing a change in the C-H<sub>3</sub> bond strength. Consequently, the C-H stretching bands are expected to have different absorption frequencies from the normal transition bands. On the other hand, if the ions are internally hot, it would be possible to form the isomers *i*-H<sub>2</sub>/H<sub>2</sub>(e-C<sub>s</sub>CH<sub>5</sub><sup>+</sup>), *o*,*i*-H<sub>2</sub>/H<sub>1</sub>(e-C<sub>s</sub>CH<sub>5</sub><sup>+</sup>), *o*,*i*-H<sub>2</sub>/H<sub>1</sub>(or H<sub>2</sub>)(s-C<sub>s</sub>CH<sub>5</sub><sup>+</sup>), and *o*,*i*-H<sub>2</sub>/H<sub>1</sub>(H<sub>2</sub>,or H<sub>3</sub>)(C<sub>2v</sub>CH<sub>5</sub><sup>+</sup>) (refer to the earlier discussion for the notation). Most of these structures are likely to have different absorption frequencies from those of the minimum energy structure. In both cases, the vibrational bands become broad and structureless.

Another contribution to the broad feature could come from large amplitude motions of the CH<sub>5</sub><sup>+</sup> group of CH<sub>5</sub><sup>+</sup>(H<sub>2</sub>). According to the *ab initio* calculation on the structures of free CH<sub>5</sub><sup>+</sup>, the energy differences between eclipsed C<sub>s</sub> (e-C<sub>s</sub>), staggered C<sub>s</sub> (s-C<sub>s</sub>), and C<sub>2v</sub> structures of free CH<sub>5</sub><sup>+</sup> were almost negligible when the zero point energies were corrected.<sup>4,5</sup> The s-C<sub>s</sub> and C<sub>2v</sub> structures could be considered as transition states along the large amplitude motions such as CH<sub>3</sub> torsional twist motion (almost a free internal rotation according to ref.14) and the bending motion of the C-H<sub>2</sub> bond in the ∠H<sub>1</sub>CH<sub>3</sub> plane, respectively (see fig.3 for the numbering of H atoms). The combination of both large amplitude motions can lead to exchange of any pair of H atoms in free CH<sub>5</sub><sup>+</sup>. All five H atoms of free CH<sub>5</sub><sup>+</sup> can be permuted and the ion can

access  $5! = 120$   $e-C_s$  potential minima. Similar large amplitude motions would be expected to occur for  $CH_5^+$  in  $CH_5^+(H_2)$ , although they would be slightly restricted because of the interaction between  $H_2$  and  $CH_5^+$ . The hydrogen scrambling will result in many splittings in each vibrational band of  $CH_5^+(H_2)$ . These tunnelling splittings would be reduced to some extent from nuclear spin considerations; nevertheless, one could expect the vibrational bands of ground state  $CH_5^+(H_2)$  to be significantly broadened.

A third possibility is lifetime broadening, which has been observed in the vibrational predissociation spectra of some van der waals clusters.<sup>15</sup> In order to clarify the origin of the band broadening, it is necessary to carry out a study of the internal energy dependence of the spectrum as well as lifetime measurements of the vibrationally excited ions.

#### 4. Conclusion

The first infrared spectra of  $CH_5^+(H_2)$  have been presented and analyzed. The C-H stretching bands of  $CH_5^+$  in  $CH_5^+(H_2)$  were observed as one broad feature with shoulders for cold ion conditions. The predicted C-H stretching frequencies for the *ab initio* minimum energy structure containing  $e-C_s$   $CH_5^+$  match quite well to those of the observed features after appropriate scaling. Possible reasons for the band broadening were also discussed. A clear extension of this work would be to carry out a systematic

study on the internal energy dependence of the spectrum for  $\text{CH}_5^+(\text{H}_2)$  using a high resolution laser. In addition, it would be important to observe the H-H stretching band of the three center-two electron bond in  $\text{CH}_5^+$  in order to clearly determine the stability of the  $\text{C}_s$  structures relative to the  $\text{C}_{2v}$  structure of  $\text{CH}_5^+$ .

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## FIGURE CAPTIONS

Fig.1 Mass spectrum showing the carbonium ion  $\text{CH}_5^+$  and the solvated carbonium ions  $\text{CH}_5^+(\text{H}_2)_n$  ( $n = 1,2,3$ ), etc. The mixing ratio  $\text{CH}_4:\text{H}_2$  was 1:2000, and the source pressure, the source temperature and the discharge current were 150 torr,  $-40^\circ \text{C}$  and  $20 \mu\text{A}$ , respectively.

Fig.2 IR spectra of C-H stretching bands of the  $\text{CH}_5^+$  group in  $\text{CH}_5^+(\text{H}_2)$  with (a) cold ion conditions and (b) hot ion conditions. The stick spectrum shown in (a) is a spectrum predicted by *ab initio* calculation for three C-H stretching modes of the  $\text{CH}_5^+$  group in  $\text{CH}_5^+(\text{H}_2)$  after appropriate scaling (see the text and ref.13). The dotted lines (...) indicate the segments of spectra which were combined to give the full spectra shown.

Fig.3 The minimum energy structure of  $\text{CH}_5^+(\text{H}_2)$  predicted by *ab initio* calculation at TZ2P CISD (see ref.13).

# MASS SPECTRUM

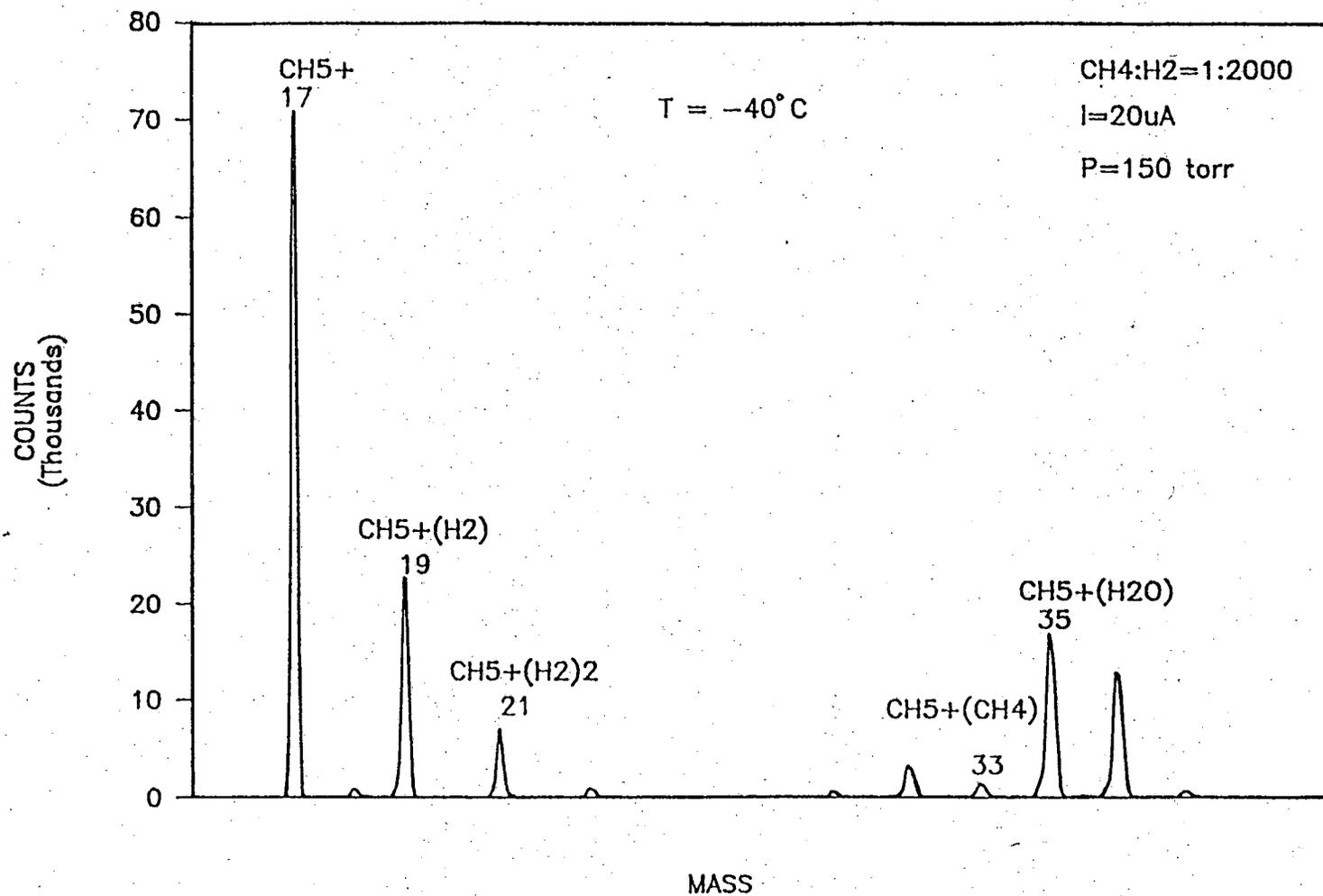


Figure 1

# C-H STRETCHING BAND

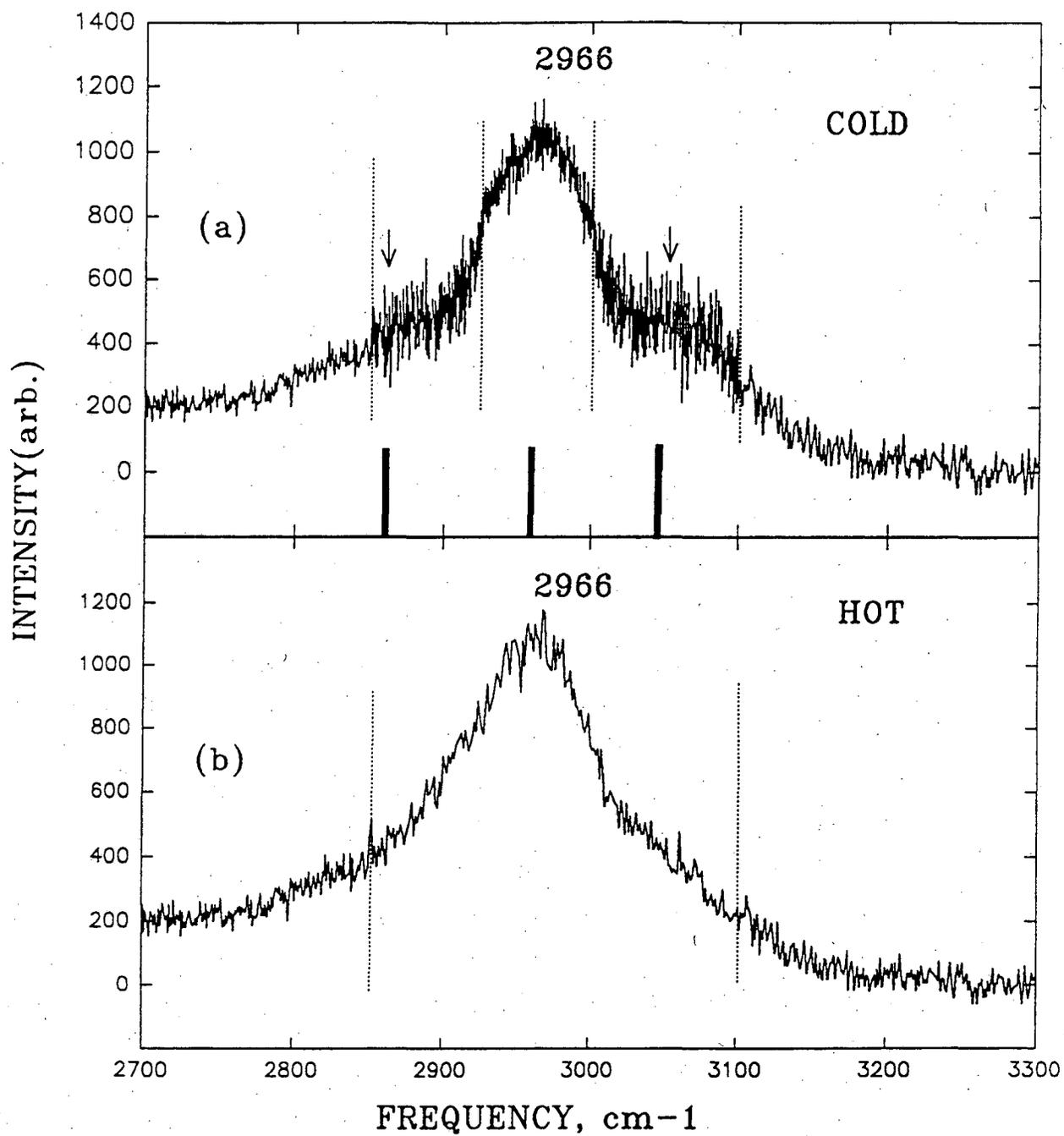
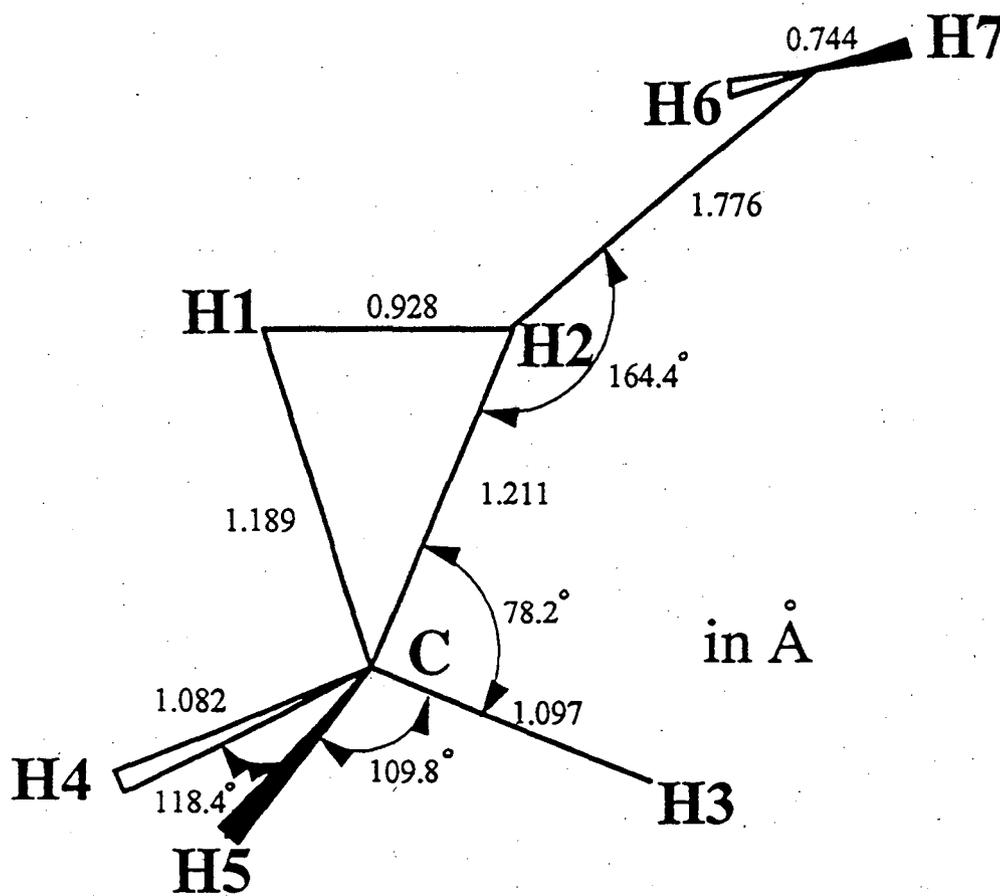


Fig. 2

# AB INITIO STRUCTURE



@TZ2P CISD

Fig. 3

LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
TECHNICAL INFORMATION DEPARTMENT  
BERKELEY, CALIFORNIA 94720

