

## Experimental Determination of the $\nu_5$ Cis-Bending Vibrational Frequency and Renner-Teller Structure in Ground State ( $X^2\Pi_u$ ) $C_2H_2^+$ Using Laser Induced Reactions

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(Received 8 July 2004; published 22 February 2005)

The spectrum of the  $\nu_5$  cis-bending vibration of ground state ( $X^2\Pi_u$ )  $C_2H_2^+$  has been recorded applying the method of laser induced reactions in a low-temperature 22-pole ion trap. It is obtained by counting the number of products of the reaction  $C_2H_2^+ (\nu_5 = 1) + H_2 \rightarrow C_2H_3^+ + H$  as a function of the laser wavelength. The vibronic transitions  $\Delta$ - $\Pi$  and  $\Sigma$ - $\Pi$  with their corresponding spin-orbit and Renner-Teller substructure have been observed. Using a perturbative analysis, the vibrational frequency has been determined to  $\omega_5 = (710 \pm 4) \text{ cm}^{-1}$  and the Renner-Teller parameter  $\epsilon_5$  is on the order of  $3 \times 10^{-2}$ .

DOI: 10.1103/PhysRevLett.94.073001

PACS numbers: 33.20.Ea, 33.20.Vq, 33.20.Tp, 33.20.Wr

The Renner-Teller effect [1] in linear polyatomic molecules is a classical example of a breakdown of the Born-Oppenheimer approximation for the description of the electronic, vibronic, and rotational structure of a molecule. The coupling of the electronic and the vibrational angular momentum results in the lifting of the degeneracy of the electronic state with nonzero angular momentum ( $\Pi$ ,  $\Delta$ , ...). In general, this effect leads to an irregular vibrational structure and subsequently to complicated electronic spectra. The acetylene cation,  $C_2H_2^+$ , with its linear ( $X^2\Pi_u$ ) ground state is the prototype for a tetraatomic molecule exhibiting the Renner-Teller effect. It has been subject to many experimental and theoretical studies, but to date no reliable experimental value for the  $\nu_5$  cis-bending vibrational frequency has been reported.

Conventional HeI photoelectron spectra (PES) from ground state neutral  $C_2H_2$  have been used to examine the Renner-Teller structure of the ion [2,3]. Despite the poor resolution of these early experiments Reutt *et al.* found a feature  $837 \text{ cm}^{-1}$  above the ionization threshold, which became the recommended value in J. Phys. Chem. Ref. Data [4] for the cis-bending vibration ( $\nu_5 = 1$ ). Several studies used various resonantly enhanced multiphoton ionization (REMPI) schemes to resonantly excite the Rydberg state converging to the ionic ground state of  $C_2H_2^+$  [5–7]. As both ground states of  $C_2H_2$  and  $C_2H_2^+$  are linear with slightly different bond lengths, only very weak progressions in the bending vibrations have been observed. Resonant excitation of the state  $\tilde{A}^1A_u$  with *trans*-bend geometry led to the observation of the *trans*-bending vibration ( $\nu_4 = 1$ ) of  $C_2H_2^+$  [6]. In a two-color double-resonance laser experiment Pratt *et al.* refined their studies on the *trans*-bending vibrations via the  $\tilde{A}^1A_u$  state using zero electron kinetic energy photo electron spectroscopy [8]. In contrast to their earlier work, three Renner-Teller components for the *trans*-bending vibration at  $^2\Sigma^- =$

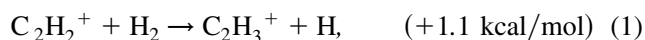
$485 \text{ cm}^{-1}$ ,  $^2\Sigma^+ = 903 \text{ cm}^{-1}$ , and  $^2\Delta = 668 \text{ cm}^{-1}$  were found, with spin-orbit splitting and rotational constants similar to the ground state, i.e.,  $A \approx -30 \text{ cm}^{-1}$  and  $B \approx 1.1 \text{ cm}^{-1}$ . Using the theoretical approach of Petelin and Kiselev [9] a frequency of  $\omega_4 = 694 \text{ cm}^{-1}$  and a Renner-Teller parameter of  $\epsilon_4 = 0.30$  were obtained for the *trans*-bending mode. An additional weak feature at  $748 \text{ cm}^{-1}$  was detected and tentatively assigned to the  $^2\Sigma^-$  component of the cis-bending vibration ( $\nu_5 = 1$ ) based on the assumption that the  $837 \text{ cm}^{-1}$  feature detected by Reutt *et al.* [2] represents the  $^2\Sigma^+$  component. As a consequence of this large splitting the Renner-Teller parameter,  $\epsilon_5$ , would be quite large. It remains uncertain why each experiment misses just the other component.

Theory is in much better shape in determining the vibrational structure of a tetraatomic Renner-Teller molecule. Most of the experimental analysis has been based on the perturbational approach derived by Petelin and Kiselev [9]. Multiconfiguration *ab initio* methods have been employed by Lee *et al.* [10] to obtain frequencies for all vibrational modes of  $C_2H_2^+$ . *Ab initio* investigations of the Renner-Teller effect beyond the Born-Oppenheimer and the harmonic approximations have been carried out over the years by Perić and Peyerimhoff [11,12]. Their variational approach has been refined to allow for the explicit treatment of the spin-orbit coupling which is present in the case of the  $X^2\Pi_u$  ground state of the acetylene cation [13]. These calculations predict  $\omega_5 = 724.2 \text{ cm}^{-1}$  and  $\epsilon_5 = 0.013$  (potentially even  $\epsilon_5 \approx 0$ ), while they predict also  $\omega_4 = 704.5 \text{ cm}^{-1}$  and  $\epsilon_4 = 0.306$  fitting reasonably well the experimental value for the frequency of the *trans*-bend vibration  $\omega_4 = 694 \text{ cm}^{-1}$  [8] and even better the Renner-Teller parameters ranging from  $\epsilon_4 = 0.30$  [8] to  $\epsilon_4 = 0.318$  [7]. Recently, a second order perturbational approach with explicit treatment of the vibronic and spin-orbit coupling has been published [14]. These results compare very

well with the variational approach and demonstrate that the approximate analytical equations can be applied to model experimental data.

As pointed out by Lee *et al.* in 1987 [10], the acetylene radical cation is a promising candidate to become the first odd-electron molecular ion of more than three atoms to be observed via high-resolution infrared spectroscopic techniques. These high-resolution spectra became available for the asymmetric C-H stretching vibration ( $\nu_3$ ) of the acetylene ion  $C_2H_2^+$  by using a difference frequency laser spectrometer probing an ac glow discharge [15,16]. Jagod *et al.* [16] derived high accuracy values of the vibrational frequency, the rotational and spin-orbit constants of the vibronic ground and excited state. However, no spectra are available for the other IR active mode, the  $\nu_5$  *cis*-bending vibration.

The experiment reported here has been set up to obtain first ro-vibrational spectra in the range of the bending vibrations between 600 and 950  $cm^{-1}$ . In previous work [17,18] a method called laser induced reaction, LIR, has been used to obtain spectra of molecular ions. In this method a cloud of typically 1000 cold ions, here  $C_2H_2^+$ , is stored in a variable temperature 22-pole ion trap and subject to (i) neutral reactant partners (here  $H_2$  of known number density) and (ii) the field of an IR laser. Ions and neutrals undergo inelastic and reactive collisions. In case of a reaction which is endothermic or hindered by a barrier as in the present case for



practically no reaction products are formed at low temperatures provided that other “open” reaction channels like



are also very slow [18,19]. However, if the parent ion is vibrationally excited after absorption of a laser photon, it may undergo reaction, in this case reaction (1). In our previous work the asymmetric  $\nu_3$  stretching vibration has been excited and the number of  $C_2H_3^+$  reaction products has been recorded as a function of the laser frequency [18]. The rotationally resolved spectrum was found to be in very good agreement with the former conventional study by Jagod *et al.* [16]. The main advantages of this kind of action spectroscopy are (i) its very high sensitivity, since spectra can be obtained with only about 1000 stored parent ions and (ii) the absence of interferences with the absorption of other species because of the mass selection of the parent ions. Special attention should be paid when comparing the intensities of these spectra to conventional absorption spectroscopy since the reactive collision with rate coefficient  $k_1^*$ , where the star denotes the reaction of the excited species in reaction (1), is an integral part of the detection scheme. It has been shown in the quantitative analysis in [18] that this feature of LIR can be used to

determine state-selective rate coefficients for the ion-molecule reactions under consideration.

To study the *cis*-bending mode of  $C_2H_2^+$  via reaction (1) we combined the trapping experiment with the wide range tuning capabilities of the free electron laser FELIX [20]. The  $C_2H_2^+$  ions were produced by electron bombardment of acetylene gas highly diluted in hydrogen (ratio 1:100). Electrons with low kinetic energies ( $<17$  eV) were utilized to avoid internal excitation or fragmentation of the ions. Trapping the ions in an external rf storage ion source [21] allowed to keep the pressure of the gas mixture in the source below  $10^{-5}$  mbar. Furthermore, vibrationally excited (“hot”)  $C_2H_2^+$  ions were quenched by reaction (1) taking place inside the source. Nonreactive collisions with  $H_2$  cooled the acetylene cations to the source temperature of 350 K. After extraction of the ions by a pulsed electrode, they were mass selected by a quadrupole mass spectrometer and injected into the 22-pole ion trap where they were finally cooled to the desired low temperature by a short intense He pulse ( $\sim 10$  ms). In the 22-pole trap the ions were stored 4 s at an ambient temperature of 90 K and a  $H_2$  target gas number density of  $1.2 \times 10^{11} \text{ cm}^{-3}$ . The stored ion ensemble was exposed to 40 laser shots of the tunable IR laser light of FELIX. After this storage period the number of  $C_2H_3^+$  products of reaction (1) were counted and the laser was tuned to the next frequency. For improving the S/N ratio, the scan was repeated 10 times.

FELIX was operated at its maximum repetition rate of 10 Hz. The laser pulses have a typical length of 7  $\mu s$  with a ps microstructure and an energy of around 30 mJ, giving a cw equivalent power in the range of 300 mW at the user station. The resolution of FELIX is bandwidth limited and was chosen to be on the order of 0.6% FWHM; i.e., the typical bandwidth in our experiment was  $\Delta\omega = 3\text{--}4 \text{ cm}^{-1}$  (FWHM). At the user station, the IR radiation has been coupled out of the vacuum IR beam line via a ZnSe window, steered through the axially transparent 22-pole trapping machine via a set of gold coated mirrors and with ZnSe windows both at the detector (in) and the ion-source side (out). Laser power measurements have been carried out in front of the entrance window. The unblocked passage of the IR beam through the machine has been checked by the transmission of a He-Ne laser beam coaxially to the IR beam and by monitoring the outcoupled IR beam using a pyroelectric detector. Synchronization of the laser pulses of FELIX and the ion pulses of the 22-pole trapping machine was not necessary due to the long ion trapping time of 4 s and the high laser repetition rate.

The solid line in Fig. 1 shows the LIR spectrum recorded in the range from 600 to 950  $cm^{-1}$ . The signal extends from around 670  $cm^{-1}$  to 770  $cm^{-1}$  with a main peak at 710  $cm^{-1}$  and distinct substructure with peaks at 694  $cm^{-1}$ , 719  $cm^{-1}$ , and 743  $cm^{-1}$  ( $\pm 1 \text{ cm}^{-1}$ ). There is no intensity observed outside this range; in particular, no signal is recorded at the originally proposed position of the

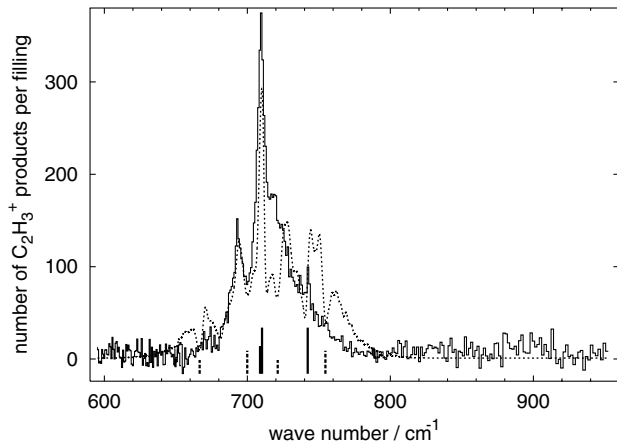


FIG. 1. The number of  $C_2H_3^+$  product ions of reaction (1) is shown as a function of the FELIX laser frequency (solid line). The spectrum has been normalized with respect to the measured laser intensity. Per storage cycle, around 2200  $C_2H_2^+$  parent ions have been trapped. For better statistics, ten iterations have been averaged for the central peak, but only four iterations in the featureless side parts. The frequency steps are about  $1\text{ cm}^{-1}$  corresponding to about four steps within the FELIX bandwidth in this frequency range. Because of hot  $C_2H_2^+$  parent ions coming from the source, there are about 340 background counts per storage cycle which have been subtracted. The dashed line shows the best fit spectrum. A Doppler-limited ro-vibrational spectrum of seven subbands at  $T = 90\text{ K}$  has been calculated and convoluted with a Gaussian laser profile of  $3\text{ cm}^{-1}$  half width (FWHM). The bars below show the band center positions of the four  $\Sigma$ - $\Pi$  (dashed) and three  $\Delta$ - $\Pi$  (solid) subbands. For the calculated line strengths, the thermal population and the degeneracy of the states have been taken into account.

*cis*-bending vibration around  $837\text{ cm}^{-1}$  [2,4]. The observed spectrum agrees reasonably well with the weak band at  $748\text{ cm}^{-1}$  by Pratt *et al.* [8]. Without further analysis we attribute this structure to the only IR active vibration in this frequency range, the  $\nu_5$  *cis*-bending vibration. The comparably narrow spectrum suggests that all vibronic components of the vibrational transition fall in this range, restricting the size of the Renner-Teller parameter,  $\epsilon_5$ . Assuming that some features lie even outside the broad spectral range covered in this experiment would lead to a very large Renner-Teller parameter ( $\epsilon_5 > 0.3$  using the perturbative analysis of [9,14]) in contradiction to the most advanced theoretical calculations [13].

In order to determine experimental values for the frequency of the  $\nu_5$  vibration and the Renner-Teller parameter,  $\epsilon_5$ , rotational spectra of the vibronic transitions involved have been calculated and compared to the experimental spectrum. The best fit result is shown as a dashed line in Fig. 1 using the values  $\omega_5 = 710\text{ cm}^{-1}$  and  $\epsilon_5 = 0.032$ . Only these two parameters were fitted while the spin-orbit constant  $A$  and the rotational constant  $B$  were fixed for all vibronic states at the ground state values taken from Jagod *et al.* [16]. Figure 2 shows the energy level

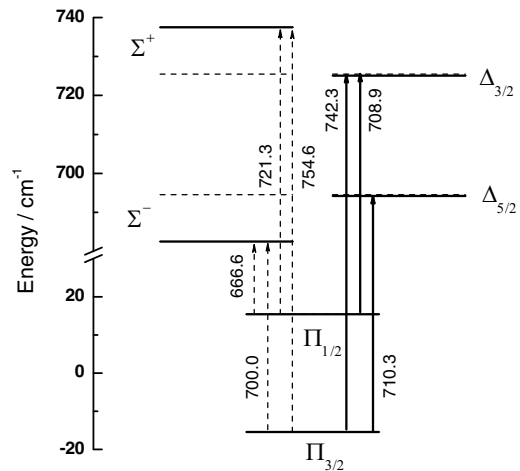


FIG. 2. Energy level diagram of the vibronic states for the vibrational ground ( $\Pi$ ) and the first excited states ( $\Sigma$ ,  $\Delta$ ). The splitting in two components arises from spin-orbit and vibronic (Renner-Teller) coupling. Levels for vanishing vibronic coupling ( $\epsilon_5 = 0$ ) appear as dashed lines while levels for the best fit simulation shown in Fig. 1 appear as solid lines. Observed transitions are shown as vertical arrows ( $\Sigma$ - $\Pi$ : dashed,  $\Delta$ - $\Pi$ : solid) with the corresponding transition wave number in  $\text{cm}^{-1}$ .

diagram for the vibrational ground and first excited state of a  ${}^2\Pi$  electronic state molecule. The term energies were calculated using the perturbative equations given by Perić and Peyerimhoff [14]. Seven vibronic transitions, four  $\Sigma$ - $\Pi$  (dashed lines in Figs. 1 and 2) and three  $\Delta$ - $\Pi$  (solid lines), arise from the level diagram shown in Fig. 2. The band origins are depicted by sticks in Fig. 1 whose lengths represent their intensities due to the population of the corresponding lower level at  $T = 90\text{ K}$  and due to the degeneracy of the corresponding levels. It turns out that the main spectral feature at  $710\text{ cm}^{-1}$  is related to the coincidence of two of the  $\Delta$ - $\Pi$  transitions which show strongly overlapping  $Q$  branches assuming equal rotational constants for all vibronic states. This main peak determines the actual position of the vibrational frequency of the *cis*-bending mode. In Fig. 2 the levels of the vibronic states for vanishing Renner-Teller effect are depicted by broken lines. For the small value of  $\epsilon_5 = 0.032$ , which we obtained from our best fit, the shifts of the  $\Pi$  and  $\Delta$  energy levels are almost zero whereas the positions of the  $\Sigma$  states change considerably. As a consequence, the frequencies of the  $\Delta$ - $\Pi$  transitions are very insensitive to the magnitude of the Renner-Teller effect and the vibrational frequency derived is rather well determined. From the strong and narrow  $710\text{ cm}^{-1}$  main peak it can be concluded that two of the  $\Delta$ - $\Pi$  transitions indeed coincide and that therefore the spin-orbit constants,  $A$ , for the  $\Pi$  and  $\Delta$  states, are equal or almost equal. Because of the limited resolution of this study,  $A$  has been assumed to be the same for all vibronic states involved. Because of this fact the third  $\Delta$ - $\Pi$  transition is located about  $30\text{ cm}^{-1}$  blue of the

main peak. This is in rather good agreement with the peak observed at  $743\text{ cm}^{-1}$ .

Matters are different for the  $\Sigma$ - $\Pi$  transitions. These four transitions are rather variable in position when varying  $\epsilon_5$ . The situation is becoming more complicated due to the influence of the Renner-Teller effect on the rotational levels of a  $^2\Sigma$  state. A detailed description of the problem has been given by Herzberg [22]. This influence has been accounted for in the calculated rotational structure of the vibronic bands discussed above. In fact, the change of the effective rotational constant for the  $^2\Sigma$  vibronic states leads to faint and barely recognizable  $Q$  branches of the  $\Sigma$ - $\Pi$  transitions (dashed lines in Figs. 1 and 2), whereas  $\Delta$ - $\Pi$  bands show compact and most prominent  $Q$  branches. As a consequence, it is hard to determine an accurate value for the Renner-Teller parameter,  $\epsilon_5$ . Instead, the confined frequency range of the measured spectrum and the wing positions of the  $\Sigma$ - $\Pi$  transitions impose an upper limit on  $\epsilon_5$ . As can be seen from Fig. 1 the predicted wing intensities from the fit are considerably larger than the measured ones. We found  $\epsilon_5 < 0.037$  to be an appropriate upper bound for the magnitude of the Renner-Teller effect and  $\epsilon_5 = 0.032$  leads to the best fit. Better agreement with the experimental spectrum can readily be obtained by variation of more than the two parameters,  $\omega_5$  and  $\epsilon_5$ , discussed so far. However, in view of the limited resolution of the experiment this would not lead to an unambiguous determination of all parameters.

The results are discussed regardless of the fact that spectroscopy using LIR involves the collision between the excited ion and the neutral reaction partner as an integral part of the detection scheme. While this fact does not affect the spectral positions, the intensities, which are discussed above, might well be influenced. In particular, the intensity ratio of the  $\Delta$ - $\Pi$  and  $\Sigma$ - $\Pi$  transitions might be different from what is expected for a regular absorption experiment. This is an interesting aspect of LIR since the reactivity of the  $\Delta$  or  $\Sigma$  electronic components may be derived from dedicated experiments. The LIR spectrum clearly shows that both transitions  $\Delta$ - $\Pi$  and  $\Sigma$ - $\Pi$  are observed and further details of reaction dynamics in this system will be discussed in a forthcoming publication [23].

The present study is the third example for LIR spectroscopy of cold ions. For the first time new spectral features have been discovered for an important primary ion in plasmas and interstellar space. For such systems LIR appears to be an interesting complementary technique to high-resolution VUV and XUV ZEKE ionization spectroscopy. Very recently Rupper and Merkt studied the ground state of the acetylene ion in full rotational resolution [24]. Both techniques seem to be capable of determining the Renner-Teller effect of this molecule in great detail, pointing at deficiencies of the present limited theoretical de-

scription. Even larger potential is seen for LIR of ions which are produced in plasmas, in particular, for many protonated molecules, that cannot be studied by ionization techniques. One prominent example is  $\text{CH}_5^+$  of which first wide range spectra have been obtained also using the unique possibilities of FELIX.

We gratefully acknowledge the support by the *Stichting voor Fundamenteel Onderzoek der Materie* (FOM) in providing the required beam time on FELIX, the skillful assistance by the FELIX staff, as well as financial support from DFG [No. FOR 388 and No. GI 319/1-2 within the European Associated Laboratory for High Resolution Spectroscopy (LEA)]. O. A. thanks E. van Dishoeck for financial support through a NWO Spinoza Grant.

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