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# ON THE HIGH RESOLUTION HeI PHOTOELECTRON SPECTRUM OF THE $C_2D_4^+$ ($\tilde{X}\ ^2B_3$) GROUND STATE

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ABSTRACT

The HeI (584A) photoelectron spectrum of $C_2D_4^+$ in its ground electronic state has been measured with a supersonic molecular beam. The improved resolution permits new vibrational fine structure to be observed and assigned. The disputed interpretation of $\nu_2$ and $\nu_3$ vibrations in $C_2H_4^+$ ground state and the abnormal isotopic shift from $C_2H_4^+$ to $C_2D_4^+$ are explained by comparing the experimental results with a Franck-Condon factor calculation and a recent ab initio calculation. The torsional vibration ($\nu_4$) is observed to be coupled significantly with the C=C stretching vibration ($\nu_2$).

## I. INTRODUCTION

The HeI (584Å) photoelectron (PE) spectrum of ethylene has been investigated by a number of authors.[1-7] Recently, several authors have discussed the $C_2H_4^+$ ($\tilde{X}\ ^2B_3$) ground state PE spectrum, which shows vibrational fine structure involved with excitation of the C=C stretching mode ($\nu_2$), the $CH_2$ angle bending mode ($\nu_3$), and the torsional vibrational mode ($\nu_4$). Traditionally, the interpretation of this state was based on the analogy between the PE spectrum and the 1744Å Rydberg spectrum of $C_2H_4$, with the exception that the $\nu_3$ mode is not active in the Rydberg transition.[8] In a recent study, Pollard et al.[7] reported a high quality HeI PE spectrum of ethylene by using a supersonic molecular beam. They assigned the major vibrational progression in the $C_2H_4^+$ ground state as the $\nu_2$ mode, based on the Franck-Condon principle and the traditional assignment. From their spectrum, they obtained the $\nu_2$ and $\nu_3$ vibrational frequencies as 1264 $cm^{-1}$ and 1494 $cm^{-1}$ respectively.

Cvitas, Gusten, and Klasinc[5] studied the ground state PE spectrum of $C_2D_4^+$ and obtained $\nu_2$ and $\nu_3$ as 1340 $cm^{-1}$ and 1050 $cm^{-1}$ respectively. Thus the ordering of the $\nu_2$ and $\nu_3$ vibrational frequencies appears to be reversed from $C_2H_4^+$ to $C_2D_4^+$. Cvitas et al.[5] explained this by invoking a Fermi resonance between $\nu_2$ and $\nu_3$ in $C_2H_4^+$, as Brundle and Brown[3] proposed. However, McDiarmid[9] questioned the traditional assignment for $\nu_2$ and $\nu_3$ in the $C_2H_4^+$ ground state PE spectrum on the basis of the noncrossing rule and Rayleigh's rule. She proposed to interchange the $\nu_2$ and $\nu_3$ assignments based on the evidence from studies of the first photoelectron bands of the $C_2H_nD_{4-n}$ series of isotopic molecules by Cvitas et al.[5] and from studies of 3s, 3p, 3d, 3d', 4d' and 5s Rydberg

spectra of these isotopic molecules.[10] Pollard and Trevor[11] expressed doubts about the assignment of one quantum of $\nu_3$ vibration ($3_0^1$, 1050 $cm^{-1}$) in the $C_2D_4^+$ PE spectrum by Cvitas et al.,[5] since the peak was very weak and the $\nu_3$ value was unexpected. They felt that it would be premature to interchange the traditional assignment of $\nu_2$ and $\nu_3$ in the absence of a high quality measurement or a definitive theoretical prediction of the $C_2D_4^+$ vibrational frequencies. As a consequence of this controversy, Somasundram and Handy[12] performed an ab initio calculation on the $\nu_2$ and $\nu_3$ vibrations in the ground state of ethylene ion. They predicted that the major vibrational progressions differed, being $\nu_3$ for $C_2H_4^+$, but $\nu_2$ for $C_2D_4^+$. Moreover, an earlier study of Franck-Condon factors by Botter and Carlier[13,14] on the $\nu_2$ and $\nu_3$ transitions in the ground states of $C_2H_4^+$ and $C_2D_4^+$ also suggested that interchanging the traditional assignment explained better the experimental results. Therefore, it is clear that an improved PE spectrum of $C_2D_4^+$ is needed to finally resolve the disagreement and remove all doubt about the $\nu_3$ assignment of $C_2D_4^+$. It can also serve as a confirmation of the recent ab initio calculation.[12]

## II. EXPERIMENTAL

The first band of the $C_2D_4^+$ PE spectrum was taken on a molecular beam photoelectron spectrometer which has been described in detail before.[15] In brief, a 10% $C_2D_4$ mixture with He was expanded through a 100μ nozzle and was skimmed by a 0.9 mm diameter conical skimmer. The photon beam crossed the skimmed molecular beam at 90°. The analyzer was an electrostatic hemispherical type with position-sensitive multi-channel detection. The entrance to the analyzer was perpendicular to both the molecular beam and the photon beam. The resolution of the spectrometer with which the $C_2D_4^+$ spectrum was taken was 13 meV, as measured for $Ar^+$ $^2P_{3/2}$. The $C_2D_4$ sample was supplied by Cambridge Isotope Lab. It had a minimum purity of 99% and was used without further purification.

## III. RESULTS AND DISCUSSION

The ground state PE spectrum of $C_2D_4^+$ with its vibrational assignment is shown in Figure 1. Rotational cooling in the present experiment enables all the vibrational fine structure to be more clearly defined and longer vibrational progressions to be evident than in previous experiments. The general features of the spectrum are regular, with the repetition of a group of four peaks. As assigned previously,[1-3,5] the principal vibrational progression is $\nu_2$ (C=C stretching), which forms the leading peak in each group of four peaks with 2 and 4 quanta of $\nu_4$. We observe $\nu_2$ up to 5 quanta. One quantum of $\nu_3$ excitation is clearly shown in the current spectrum, as the fourth peak in each group. Each 0n00 peak, in the notation of Figure 1, overlaps with a 0(n-1)12 peak. The mean positions of the peaks were determined by a global fitting procedure using gaussian lineshape functions. The overlapping of the 0n00 peak with the 0(n-1)12 peak is the major cause of uncertainty in the fitting procedure. The observed splittings and uncertainties are listed in Table I. The values for the $\nu_2$, $2\nu_4$, and $4\nu_4$ excitations compare well with the results of Stockbauer and Inghram from a threshold PE spectrum[16] and are better determined than in Cvitas et al's paper.[5] The $\nu_3$ value agrees with Stockbauer's result, but disagrees with Cvitas's value. Cvitas's $\nu_3$ value (1050 $cm^{-1}$) seems too high and might be mislocated in the spectrum due to its poor statistics. This is what makes it doubtful about their $\nu_3$ assignment. As shown in Table I, our fundamental $\nu_3$ value is 961(8) $cm^{-1}$, which is in reasonable agreement with Somasundram and Handy's ab initio calculation when scaled to neutral $C_2D_4$ (979 $cm^{-1}$).[12]

Least-squares fitting to $\Delta G(v_2+1/2)$ vs $(v_2+1/2)$ for $v_3 = 0$ yields the following spectroscopic constants: $\omega_e = 1332 \pm 8$ cm$^{-1}$, $\omega_e\chi_e = 5 \pm 4$ cm$^{-1}$. On the high energy side of peak 2 and 4 in each group, there are very weak shoulders present. These are assigned as odd quanta of $\nu_4$, $3\nu_4$ and $5\nu_4$, which are vibronically forbidden transitions. These are also observed in the Rydberg transitions.[10] Pollard et al.[7] observed $3\nu_4$ in the $C_2H_4^+$ spectrum.

One interesting observation from Table I is that the values for $2\nu_4$ and $4\nu_4$ seem to increase with $\nu_2$ vibrational excitation. The values for $2\nu_4$ are plotted in Figure 2 as a function of $\nu_2$ vibrational quantum number, $v_2$. It shows that the $2\nu_4$ value increases monotonically with the excitation of $\nu_2$. It indicates the same trend in $C_2H_4^+$ if the $\nu_2$ and $\nu_3$ are interchanged in Pollard et al's paper.[7] This suggests that the C=C stretching vibration ($\nu_2$) is coupled to the torsional vibration ($\nu_4$). No calculation has been done to predict this behavior. It would involve quantizing the torsional potential with the $\nu_2$ normal coordinate as a parameter. All the torsional potentials obtained so far including Rydberg states are for $v_2 = 0$.[7,8,17,18,19]

Two hot-band transitions are also observed at the low ionization energy side of the spectrum. They are assigned to be $4_1^1$ and $4_1^3$. The splittings of these two features from the 0000 peak are 703 ± 10 cm$^{-1}$ and 223 ± 16 cm$^{-1}$. This is consistent with the temperature-dependence study in the 1744Å Rydberg spectrum by Merer and Schoonveld.[8] These hot-band transitions were also seen by Stockbauer and Inghram in the threshold PE spectrum.[16] Taking the $1\nu_4$ value of $C_2D_4$ (726 cm$^{-1}$),[20] we obtain the $1\nu_4$ and $3\nu_4$ values for $C_2D_4^+$ as 23 ± 10 cm$^{-1}$ and 503 ± 16 cm$^{-1}$

respectively. The uncertainties are only tentative, since the uncertainty for the $1\nu_4$ value of $C_2D_4$ is not known. However, these values are consistent with the calculation of Findley et al.[19] and with McDiarmid's values in the Rydberg spectra.[10] Chau[19] calculated the torsional energies in $C_2H_4^+$ and $C_2D_4^+$ ground states using a double well potential which is a harmonic potential perturbed by a small Gaussian function term. In Table II, a comparison is made between the experimental and calculated values. The agreement is excellent.

As McDiarmid has pointed out,[9] the question to be answered is, "why is the traditional assignment of $\nu_2$ and $\nu_3$ for $C_2H_4^+$ incorrect?". Somasundram and Handy's ab initio calculation suggests that indeed the traditional $\nu_2$ and $\nu_3$ assignment should be interchanged.[12] This makes the isotopic shift of $\nu_2$ and $\nu_3$ for going from $C_2H_4^+$ to $C_2D_4^+$ more reasonable. The noncrossing rule and Rayleigh's rule are satisfied. But, why are the intensities of $\nu_2$ and $\nu_3$ reversed from $C_2H_4^+$ to $C_2D_4^+$? Conventionally, the vibrational structure in a PE spectrum for a diatomic or quasi-diatomic molecule is predicted through the Frank-Condon principle; that is, it depends upon whether a bonding, a nonbonding or an antibonding electron is ejected. If the ejected electron is a bonding or an antibonding electron, the bond length of the molecule will be changed and an extensive vibrational structure should be expected. On the other hand, if the ejected electron is a nonbonding electron, no significant bond length change will occur, and accordingly, the vibrational structure will not be substantial. The ground state ethylene ion is formed by losing a C=C $\pi$ bonding electron. This led the early authors[1-5,7] to assign the stronger vibrational progression to $\nu_2$

(C=C stretching), and another weaker progression to $\nu_3$ ($CH_2$ angle bending). In $C_2D_4^+$, the intensities of the two progressions are reversed, and therefore so is the assignment. This made the isotopic shift of $\nu_2$ and $\nu_3$ from $C_2H_4^+$ to $C_2D_4^+$ abnormal. Brundle and Brown[3] and Cvitas et al.[5] postulated a Fermi resonance between $\nu_2$ and $\nu_3$ in $C_2H_4^+$ to explain this. Botter and Carlier[13,14] have calculated the Franck-Condon factors (FCF's) for the transition $\tilde{X}\ ^2B_3 \leftarrow \tilde{X}\ ^1A_{1g}$ in ethylene and deuterium ethylene in the harmonic approximation. They proposed that the traditional assignment of $\nu_2$ and $\nu_3$ in $C_2H_4^+$ should be interchanged in order to have the calculated FCF agree with the experiment.[5] Their basic consideration is that the normal mode of vibration can not generally be related to simple bond length or angle change in polyatomic molecules. That is, the quasi-diatomic approximation is not generally valid, especially when the equilibrium geometries of the initial and final states are different. This is exactly the case for ethylene. The neutral ethylene molecule in its ground state is planar ($D_{2h}$), but the ground state ethylene ion is nonplanar with its two $CH_2$ (or $CD_2$) twisted by ~25° to each other.[7,8,18] It turns out that there is a strong mixing of the C=C stretching and the $CH_2$ (or $CD_2$) bending internal coordinates in the two normal modes $\nu_2$ and $\nu_3$.[13,14] This mixing is quite different for $C_2H_4$ and $C_2D_4$. So the variation of C=C bond length can produce excitations in both $\nu_2$ and $\nu_3$, but the excitations are different in $C_2H_4^+$ and $C_2D_4^+$. The $CH_2$ (or $CD_2$) angle change ($\Delta\alpha$, where $\alpha$ is the half angle of $CH_2$) should also have a strong effect on the excitations of $\nu_2$ and $\nu_3$ in $C_2H_4^+$ and $C_2D_4^+$. In other words, the potential surfases for $C_2H_4^+$ and $C_2D_4^+$ are different because of the different mode mixing in the two

molecules. Therefore, it is expected that the excitations will be different in the two molecules. Botter and Carlier calculated the FCF's of $\nu_2$ and $\nu_3$ in the ground states of $C_2H_4^+$ and $C_2D_4^+$ as a function of $\Delta\alpha$,[1,3,14] and found that the theoretical and experimental results agree best at about $\Delta\alpha = 1°$. The ratios of FCF's for $\nu_2$ and $\nu_3$ in $C_2H_4^+$ and $C_2D_4^+$ are listed in table II, together with experimental values. This result is also consistent with Somasundram and Handy's ab initio calculation,[12] which predicted that the $CH_2$ angle change ($\Delta\alpha$) to be ~1° and the principal vibration to be $\nu_3$. Both the FCF and ab initio calculations make it unnecessary to invoke a Fermi resonance between $\nu_2$ and $\nu_3$ in $C_2H_4^+$ to explain why the major vibration in $C_2H_4^+$ should be $\nu_3$, rather than $\nu_2$ as many earlier authors expected from a quasi-diatomic model.[1-5,7]

## IV. CONCLUSION

In conclusion, our high resolution PES study using a supersonic molecular beam for rotational cooling has uncovered additional vibrational fine structure in the ground state of $C_2D_4^+$. Clear assignments are made to all the observed features. The doubtful $\nu_3$ frequency from previous studies is corrected. The $\nu_2$ and $\nu_3$ values are consistent with Somasundram and Handy's recent ab initio calculation of harmonic frequencies[14] though their calculation gives slightly higher values than are measured. The disputed assignment of $\nu_2$ and $\nu_3$ in $C_2H_4^+$ is resolved by comparing the experimental results of $C_2H_4^+$ and $C_2D_4^+$ with Botter and Carlier's FCF calculation,[13,14] in addition to Somasundram and Handy's ab initio calculation. The significant coupling of C=C stretching vibration ($\nu_2$) with the torsional vibration ($\nu_4$) is observed in $C_2D_4^+$ for the first time.

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Table I. Vibrational frequencies in $cm^{-1}$ of the $C_2D_4^+$ ($\tilde{X}\ ^2B_3$) ground state.[a]

| | $v_2$ | $\Delta G(v_2+\frac{1}{2})$ | $\Delta G(v_3+\frac{1}{2})$ | $2\nu_4$ | $4\nu_4$ |
|---|---|---|---|---|---|
| $v_3=0$ | 0 | 1329(14)[b] | | 269(7) | 714(8) |
| | 1 | 1322(46)[b] | | 288(14) | 728(15) |
| | 2 | 1262(45)[b] | | 294(45) | 736(45) |
| | 3 | 1305(31)[b] | | 364(31) | 859(32) |
| | 4 | 1295(32)[b] | | 373(12) | 861(18) |
| | 5 | | | 399(22) | |
| $v_3=1$ | 0 | 1310(13) | 961(8) | 266(17) | |
| | 1 | 1286(17) | 941(17) | 292(39) | |
| | 2 | | 905(46) | | |

a. Error limits are given in the parentheses, which combines the uncertanities in the fitting procedure and the energy scale shift during scan (± 0.0005eV).

b. Values used in least-squares fitting.

Table II. Observed and calculated torsional energy levels in the $C_2H_4^+$ and $C_2D_4^+$ ($\tilde{X}\ ^2B_3$) ground states ($cm^{-1}$).

| $v_4$ | $C_2H_4^+$ | | $C_2D_4^+$ | |
|---|---|---|---|---|
| | Observed value[a] | Calculated value[b] | Observed value[c] | Calculated value[b] |
| 0 | 0 | 0 | 0 | 0 |
| 1 | | 100.8 | 23(10) | 35 |
| 2 | 438.4(0.5) | 438.4 | 269(7) | 267 |
| 3 | 766(3) | 769 | 503(16) | 451 |
| 4 | 1158(10) | 1158 | 7149(8) | 691 |

a. From reference 7. The error limits are given in the parentheses.

b. From reference 19.

c. This work. The error limits are given in the parentheses.

Table III. Ratios of the vibrational intensities of $\nu_2$ and $\nu_3$ in $C_2H_4^+$ and $C_2D_4^+$ ($\tilde{X}\ ^2B_3$) ground states.

| | FCF calculation[a] | Experimental | |
|---|---|---|---|
| $\frac{\nu_2}{\nu_3}$ ($C_2H_4^+$) | 0.45 | 0.55[b] | 0.54[d] |
| $\frac{\nu_2}{\nu_3}$ ($C_2D_4^+$) | 2.86 | 2.9[c] | 2.75[d] |

a. From reference 14.

b. Ratio obtained by reading off peak hights from reference 7.

c. This work.

d. From reference 5.

FIGURE CAPTION

Figure 1. The HeI (584A) photoelectron spectrum of $C_2D_4^+$ ($\tilde{X}\ ^2B_3$) ground state. The vibrational levels are labelled with the $\nu_1$, $\nu_2$, $\nu_3$, and $\nu_4$ vibrational quantum numbers. The symmetry of the state is assumed to be $D_2$.

Figure 2. The $2\nu_4$ values as a function of $\nu_2$ vibrational quantum numbers.

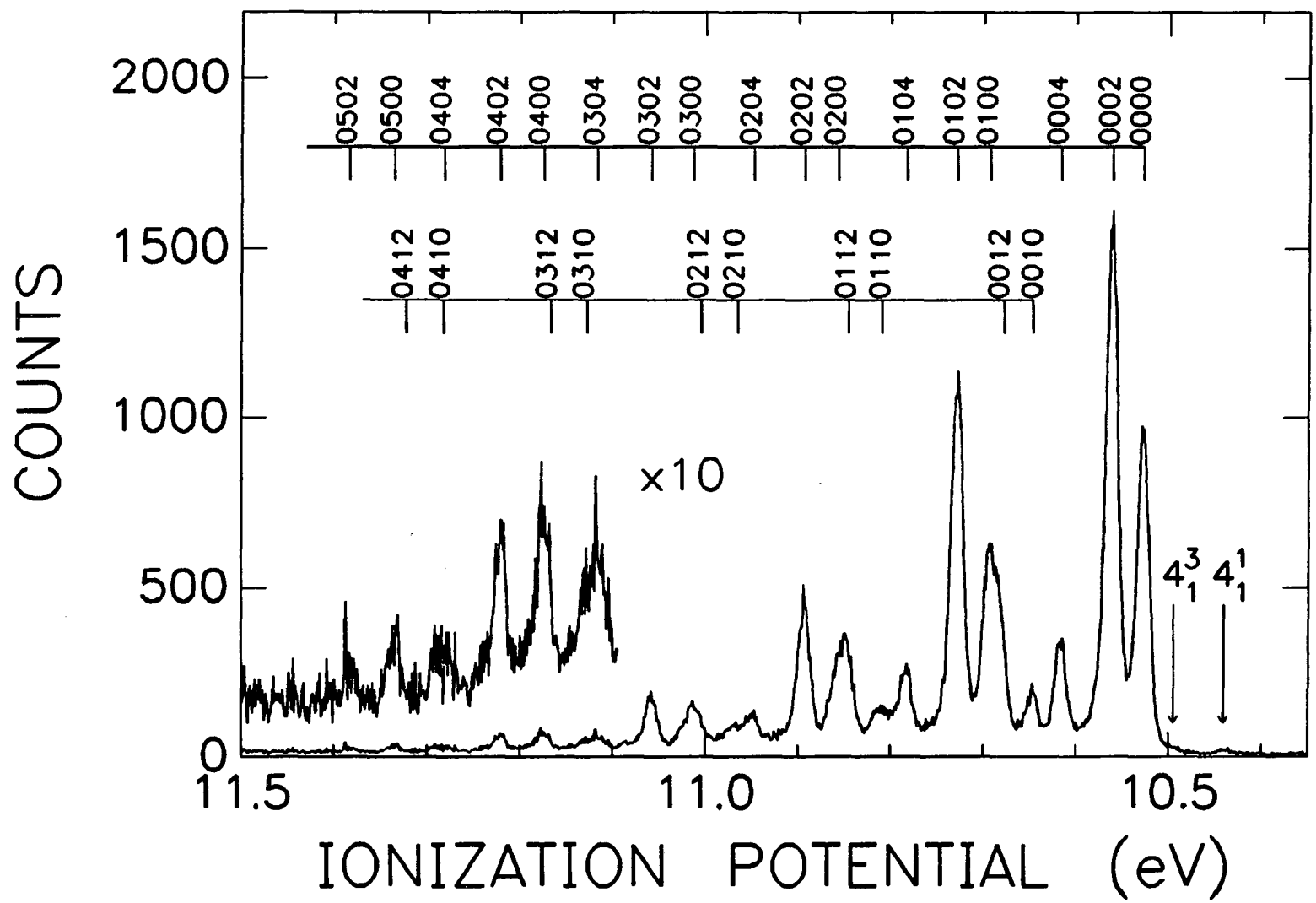


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Figure 1

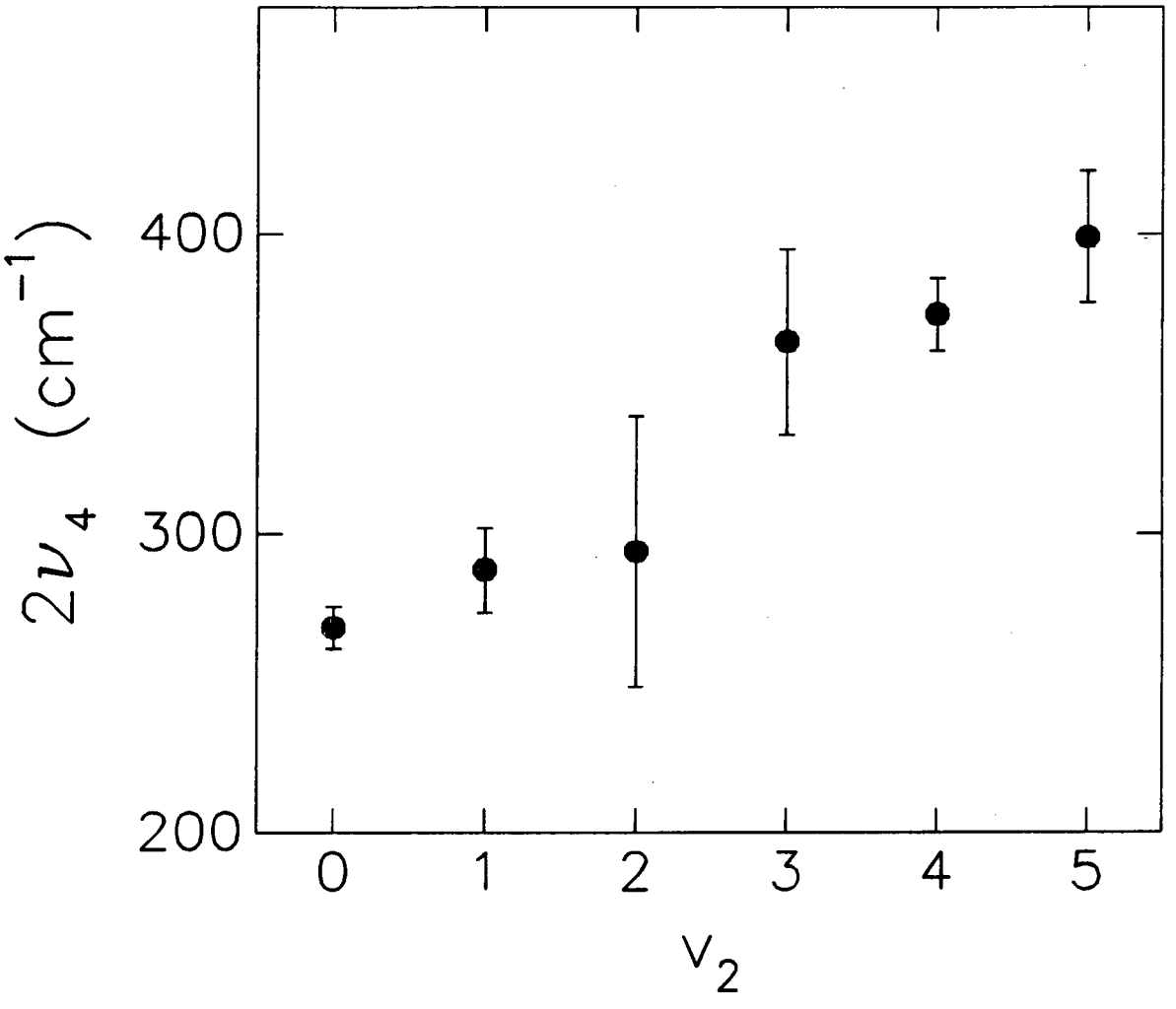


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Figure 2

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