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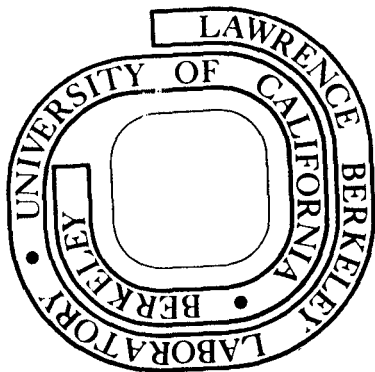
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Resonant multiphoton dissociation and mechanism of excitation
for ethyl chloride

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Multiphoton dissociation (MPD) of ethyl chloride was studied using a tunable 3.3 μ laser to excite CH stretches. Resonances in MPD yields vs frequency match the position and shape of peaks in the fundamental, as narrow as 0.4 cm^{-1} , and first and second overtone absorption spectra. Transitions through the discrete levels are all at or nearly resonant. Anharmonicity is compensated by the presence of five CH stretch modes. The lowest quasicontinuous level is $v = 3$.

The many recent experimental and theoretical studies of collisionless multiphoton dissociation by CO_2 lasers have established a good semi-quantitative understanding of MPD for SF_6 and similar molecules.^{1 - 5} The excitation of hydrogen stretching modes provides a qualitatively different situation. The anharmonicity is much larger; the quantum is a much larger fraction of the dissociation energy; the modes may be relatively weakly coupled to lower frequency vibrations. Qualitatively new phenomena in MPD result.

Typical MPD spectra recorded with CO_2 lasers exhibit widths which are greater than entire fundamental vibration-rotation bands and red shifts which are comparable to P-branch half-widths. In the case of C_2H_4 for which multiphoton absorption spectra have been recorded at high resolution, the resonances at MPD intensities were $10 - 20 \text{ cm}^{-1}$ broad, much broader than for the linear absorption spectrum.⁶ A peak 10 cm^{-1} wide has been reported for cyclopropane at the 3102 cm^{-1} Q-branch.⁷ Here we find for the first time sharp resonances in high resolution yield spectra. Since these resonances match those found in ordinary absorption spectra, the optimum selectivity and laser frequency for isotope enrichment and chemical purification may be predicted from these spectra.

In these experiments MPD of ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$
 $\rightarrow \text{C}_2\text{H}_4 + \text{HCl}$, is studied. Only seven photons $\nu \geq 2900 \text{ cm}^{-1}$
are needed to overcome the $58 \pm 2 \text{ kcal/mole}$ activation energy.⁸
A Nd:YAG laser pumped LiNbO_3 optical parametric oscillator⁹

(OPO) provided the photolysis pulses. With an etalon in the OPO cavity the 3.3μ pulse had a FWHM of $0.15 \pm 0.03 \text{ cm}^{-1}$ and is 10 ns between half power points. With a $3/4 \text{ m}$ SPEX monochromator and a simple spectrophone cell containing 2 torr $\text{C}_2\text{H}_5\text{Cl}$ the laser frequency was determined relative to sharp features in the linear absorption spectrum to $\pm 0.1 \text{ cm}^{-1}$. The energy of the laser pulse is monitored continuously, and the frequency occasionally, during photolysis. The 3.3μ beam is focused by a 5 cm focal length CaF_2 lens to a spot size of 0.6 mm FWHM. The beam diameter is less than 0.9 mm over a distance of 7.5 mm. A 14 mm thick glass cell with parallel NaCl windows attached by Torrseal epoxy is placed at Brewster's angle in the beam focus. For the data shown pulse energies ranged between $E_p = 2.7$ and 3.5 mJ. In this energy range dissociation yield is proportional to $(E_p)^{3.5}$. At 3.5 mJ the peak intensity in the center of the focus is 120 MW/cm^2 . The effective photolysis volume at the focus is $1.6 \times 10^{-3} \text{ cm}^3$. Between 3000 and 7200 pulses were used for each photolysis. The photolysis products are analyzed with a flame ionization gas chromatograph (Varian Model 3700) with picogram sensitivity. Ethylene is the only hydrocarbon observed as a product; thus simple HCl elimination is the only reaction. Flame ionization is not sensitive to HCl. The relative dissociation yield $W_d(\nu)$ is given by the total area beneath the gas chromatograph peak, normalized by gas pressure (1.65 to 1.72 torr), number of pulses and $(E_p)^{3.5}$.

An absolute calibration of the gas chromatograph combined with the effective focal volume estimate gives an approximate absolute yield scale.

MPD occurs throughout the entire spectral range for the five C—H stretching fundamentals, Fig. 1. The dissociation yield spectrum follows approximately the same shape as the ordinary linear absorption spectrum $A_{01}(\nu)$. The relative yields are somewhat enhanced at longer wavelengths. The peak yields near 2944 and 2977 cm^{-1} are about 2%. The band center frequency and band shape of the sharp peak in W_d at 2943.8 cm^{-1} match those of the fundamental Q-branch almost exactly. The W_d peak near 2913 cm^{-1} does not correspond to a peak of $A_{01}(\nu)$. However, it coincides with half the frequency of a strong, sharp Q-branch in the first overtone spectrum. When W_d is divided by $A_{01}(\nu)$, a good correlation with the overtone spectrum is found, Fig. 2. Finally, far in the red end of the spectrum where the yield is low, W_d/A_{01} shows a broader resonance, Fig. 3, which corresponds to one-third the frequency of the strong resonance in the second overtone spectrum. We believe that the structured MPD spectra observed here arise in a natural way from excitation of higher frequency fundamentals and from the spectral properties of $\text{C}_2\text{H}_5\text{Cl}$.

Ethyl chloride is nearly a prolate symmetric top ($\kappa = 0.904$) with 18 non-degenerate vibrational modes.¹⁰ The 5 C—H modes provide the dominant coupling between the radiation field and the molecule. The fundamental absorption spectrum in Fig. 1 gives the necessary information for the

$\nu_{\text{CH}} = 0 \rightarrow 1$ transition. Each vibrational band contains 9, 6 \perp and 3 \parallel , lines for most populated rotational states. The absorption cross section averaged over the 200 cm^{-1} CH stretching region is $6 \times 10^{-20} \text{ cm}^2$. In this range each rotational state has about $5 \times 9 = 45$ lines with an average effective cross section when coincident with the laser of $[6 \times 10^{-20} \text{ cm}^2 \times 200 \text{ cm}^{-1}] / [45 \Delta\nu_{\text{laser}}] \approx 1 \times 10^{-18} \text{ cm}^2$. P- and R-branches of strong parallel bands may have cross sections up to 10^{-17} cm^2 while Q-branches¹¹ are about one order of magnitude weaker. There are 15 overtone and combination levels, $\nu_{\text{CH}} = 2$. The overtone spectrum in Fig. 2 gives the positions of some levels, but does not show the more harmonic higher frequency levels and does not indicate relative intensities of the $\nu_{\text{CH}} = 1 \rightarrow 2$ spectra. All $\nu_{\text{CH}} = 1 \rightarrow 2$ transitions are symmetry allowed. For non-interacting harmonic oscillators only 5 transitions are allowed, addition of one quantum in one mode. Mixing of the C—H modes would spread the $\nu_{\text{CH}} = 1 \rightarrow 2$ oscillator strength among transitions to one or more of the remaining fifteen levels. The 35 $\nu_{\text{CH}} = 3$ levels are strongly mixed with each other and with the low frequency modes by anharmonic and Coriolis coupling (see below).¹² The absorption spectrum of a molecule in any of the $\nu_{\text{CH}} = 2$ states should exhibit smooth broad (tens of cm^{-1}) spectral features throughout the CH stretching region. Sharp Q-branches and other rotational structure in the linear absorption spectrum of $\nu = 1$ have widths limited by the

0.06 cm^{-1} FTIR resolution. This indicates that mixing of the C—H stretches with other vibrations is limited to interaction with a few discrete overtones, e.g. band near 2904 cm^{-1} .¹⁰ The widths of Q-branches for $\nu_{\text{CH}} = 2$ and 3 are much greater than expected from changes in rotational constants with vibrational quantum number and indicate a substantial broadening of the C—H levels by mixing with the 13 lower frequency modes. The total vibrational level densities near 6000 and 9000 cm^{-1} are about 70 and 1300 per cm^{-1} .¹³ Thus any frequency within a $\nu_{\text{CH}} = 1 \rightarrow 2$ or $\nu_{\text{CH}} = 2 \rightarrow 3$ Q-branch will resonantly excite molecules from lower to upper vibrational level for almost any rotational state. In summary, for $\text{C}_2\text{H}_5\text{Cl}$ the levels $\nu_{\text{CH}} = 0, 1$ and 2 are discrete or nearly discrete levels, and $\nu_{\text{CH}} = 3$ is the onset of the quasicontinuum.

For dissociation to occur the molecule must absorb two photons at or near resonance to reach $\nu_{\text{CH}} = 2$. Then sequential absorption of 5 or more photons must excite the molecule to the continuum. Dissociation must then occur before collisions can remove excitation energy. The 10 ns pulse is short compared to the 80 ns between gas kinetic collisions. The Q-branch shape of the fundamental spectrum at 2943.8 cm^{-1} is reproduced within the combined laser width, $0.15 \pm 0.03 \text{ cm}^{-1}$, plus power broadening width, $< 0.1 \text{ cm}^{-1}$. Other spectral fine structure, such as the peak and valley near 2977 cm^{-1} are likewise reproduced. Thus only molecules in rotational states with a $\nu_{\text{CH}} = 0 \rightarrow 1$ transition in near resonance with

the laser are excited. Those transitions which are resonant are strongly saturated. At the center of the Q-branch the laser should excite approximately 1/4 of the molecules to $v_{CH} = 1$. For excitation to $v_{CH} = 2$ to occur the laser must be sufficiently resonant with $1 \rightarrow 2$ transitions of molecules in the rotational states which have been excited to $v_{CH} = 1$. Since the anharmonicity of C—H levels is larger than vibration rotation band widths, the usual compensation mechanisms^{2 - 4} cannot operate. The second photon may excite a higher frequency C—H mode than the first, e.g., the R-branch excitation near 2956 cm^{-1} in Fig. 1. The fraction of $v_{CH} = 1$ molecules which will reach $v = 2$ depends strongly on the mixing of $v_{CH} = 2$ levels among themselves and with other modes. The Q-branch at 5826 cm^{-1} in the $0 \rightarrow 2$ absorption spectrum guarantees that all molecules which are excited $0 \rightarrow 1$ at $5826/2 \text{ cm}^{-1}$ are resonant for $1 \rightarrow 2$. The importance of resonance on the $1 \rightarrow 2$ transition is clearly demonstrated by the strong enhancement in W_d at 2913 cm^{-1} . The 4 cm^{-1} breadth in the overtone spectrum of Fig. 2 suggests that $v = 2$ is broadened by that amount. Thus with parallel band R-branch widths of $\sim 13 \text{ cm}^{-1}$ a large fraction of all rotational states would be in resonance within the $\sim 4 \text{ cm}^{-1}$ width. The $v_{CH} = 3$ levels do not present a perfectly flat continuous absorption throughout the CH range. The three points at the right in Fig. 2 and the modest broad resonance in Fig. 3(b) indicate the importance of this structure in

the first level of the "quasicontinuum." Nonetheless all molecules which reach $\nu_{\text{CH}} = 2$ should exhibit significant cross sections for excitation to $\nu_{\text{CH}} = 3$.

The most interesting new feature experimentally and for practical application is the occurrence of sharp peaks in MPD yield (W_d and W_d/A_{01}) at frequencies given by ordinary absorption spectra. The MPD mechanism deduced from the experiments is a modification of the established model for SF_6^2 for the different spectral and structural properties of $\text{C}_2\text{H}_5\text{Cl}$. Anharmonicity is compensated by involving several C—H modes of different frequencies rather than by the splitting of degenerate modes to give a spread of frequencies. Study of molecules with fewer C—H modes should define limits to the class of molecules for which this compensation mechanism is useful.

The absorption and yield spectra presented are a direct experimental study of transitions among the discrete levels and from the discrete levels to the quasicontinuum. A more complete knowledge of the level structure and mode mixing for $\nu_{\text{CH}} = 2$ will permit a thorough quantitative test of the entire model.

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Figure 1. Relative dissociation yield, W_d , and linear absorption spectrum, A_{01} (Nicolet 7199 FTIR with 1 cm^{-1} resolution) vs frequency. All points (●) were measured at the peaks of absorption lines. Two points (▼) were taken in valleys. A sharp resonance (O) is shown enlarged with an absorption spectrum at 0.24 cm^{-1} resolution. Two points near 2977 cm^{-1} show sharp structure in a P-branch.

Figure 2. Relative dissociation yield, $W_d(\nu/2)$, divided by the absorbance, $A_{01}(\nu/2)$ at 0.24 cm^{-1} resolution, from () in Fig. 1. The first overtone absorption spectrum, $A_{02}(\nu)$, is also plotted at 1 cm^{-1} resolution (FTIR).

Figure 3. (a) Relative dissociation yield $W_d(\nu/3)$ and second overtone spectrum $A_{03}(\nu)$ (2.5 cm^{-1} resolution, Carey 17). $A_{01}(\nu/3)$ and $A_{02}(2\nu/3)$ --- are also shown. (b) $W_d/A_{01}(\nu/3)$ and the second overtone spectrum. The monotonic decrease of W_d in (a) becomes a broad resonance matching the second overtone spectrum when normalized.

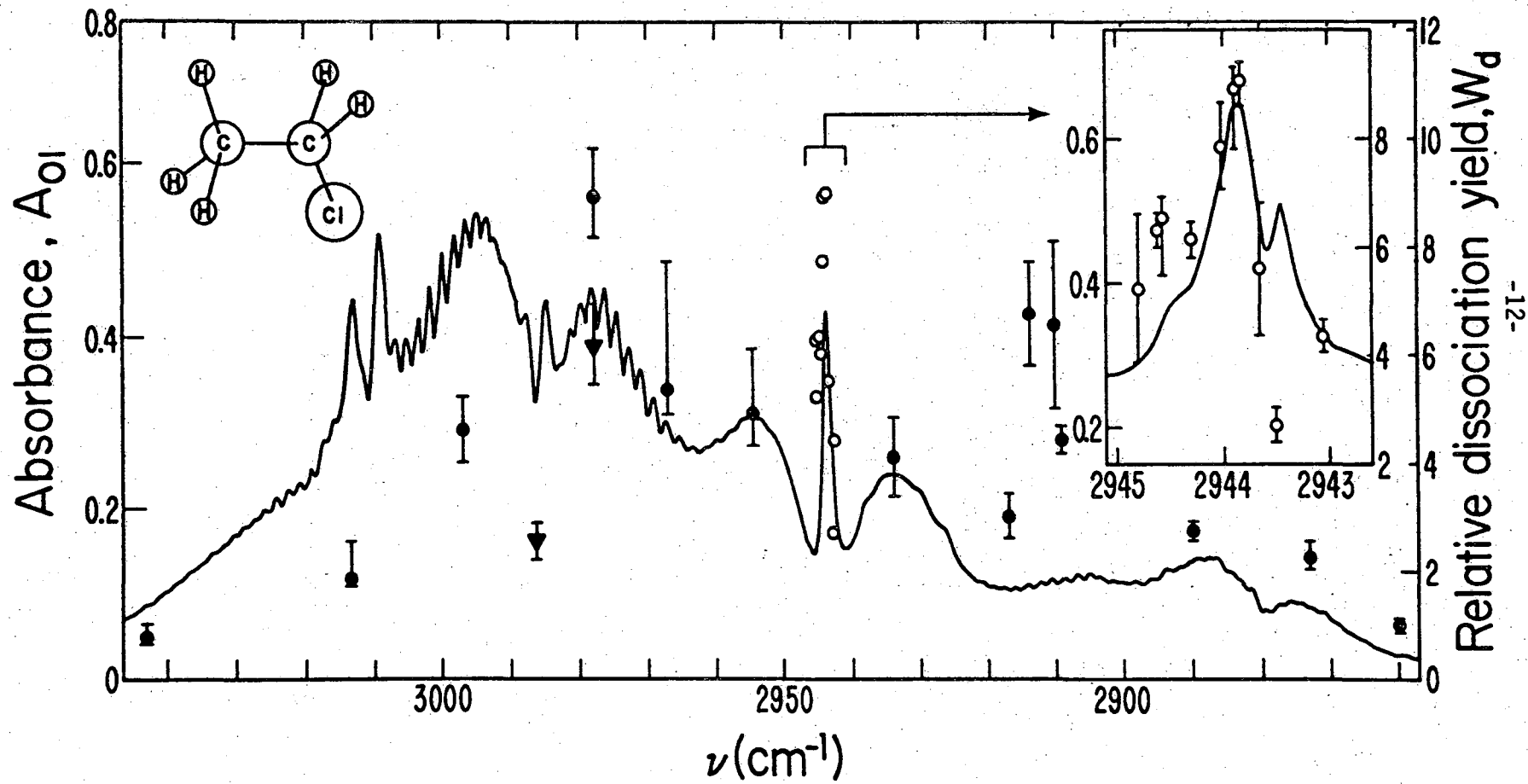
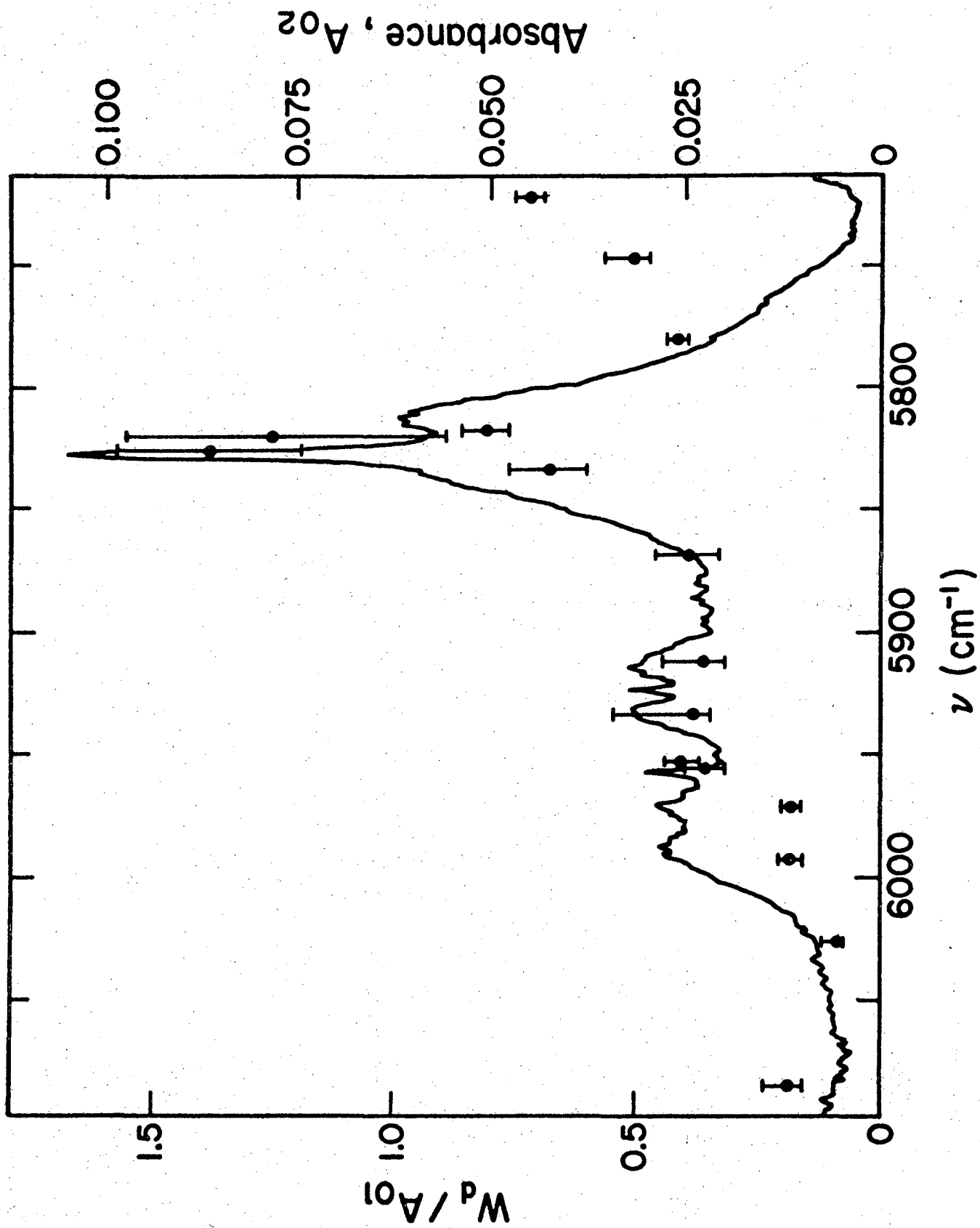


Figure 1

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Figure 2



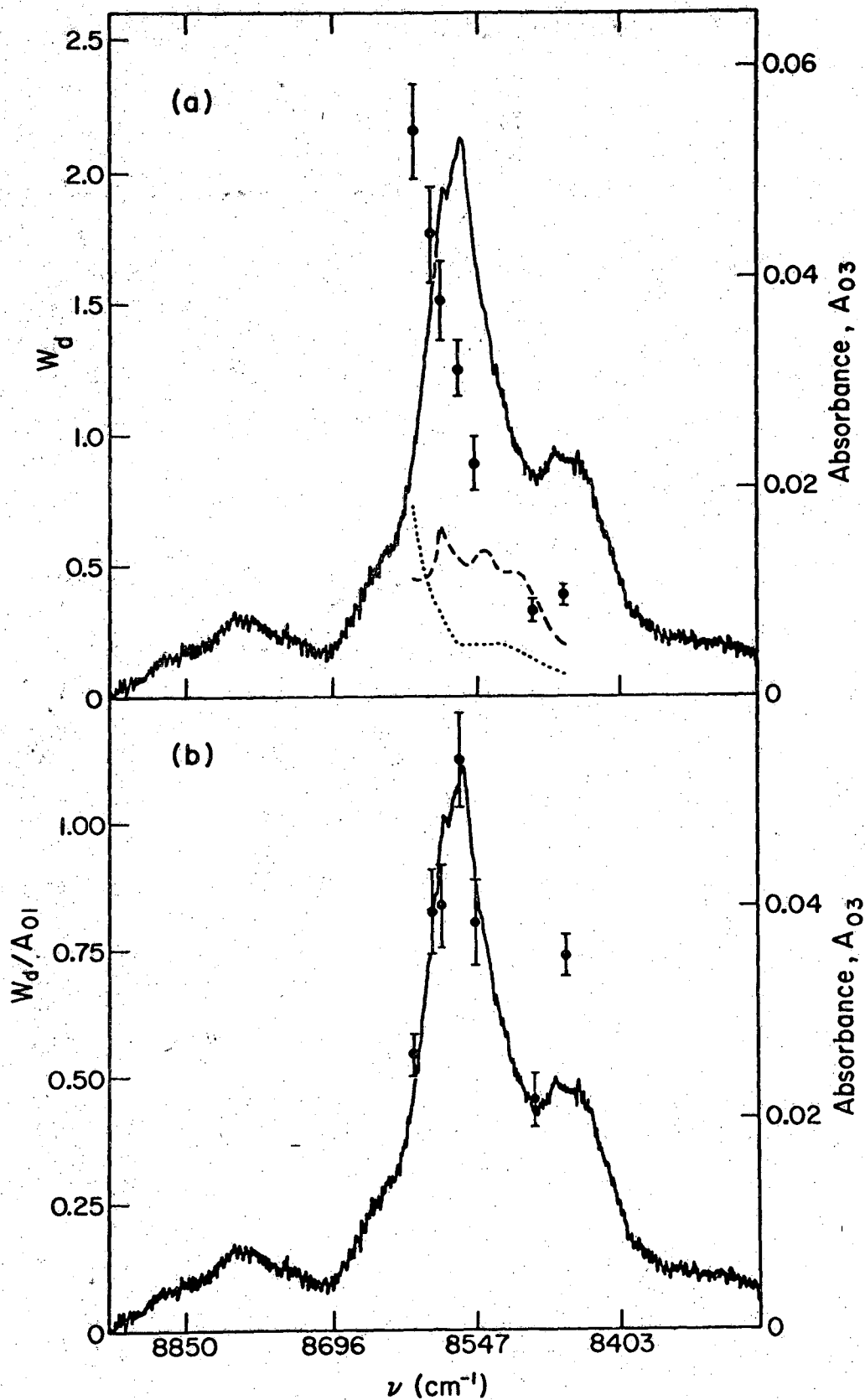


Figure 3

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