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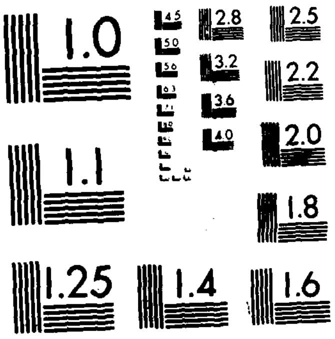

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The $S_2 \leftarrow S_0$ photoexcitation spectrum of jet-cooled acetophenone is presented. The observed homogeneously broadened linewidths indicate S_2 lifetimes $\leq$ 0.26 fs while the measured emission lifetimes range from 540 ± 30 ns for $S_0\ 0^0_0$ excitation to 130 ± 50 ns for $S_2\ 12^1_2$ excitation. The dynamics revealed by the spectrum are discussed in terms of the known photochemical and photophysical rates of the excited states of acetophenone. Arguments are presented which identify the emitting state as a known dissociative triplet state of acetophenone.

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TECHNICAL REPORT #23

"THE S_2 <- S_0 LASER PHOTOEXCITATION SPECTRUM AND EXCITED STATE DYNAMICS OF JET-COOLED ACETOPHENONE"

by

J.A. Warren and E.R. Bernstein

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Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

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I. Introduction.

The application of laser induced fluorescence spectroscopy to the study of the dynamics of the excited states of molecules isolated in supersonic molecular jets has been extensive. The technique has facilitated, for example, determination of the rates of internal conversion and of intramolecular vibrational redistribution in the excited singlet states of a number of species.[1] For aromatic ketones, however, the technique has generally failed because of the low fluorescence quantum yields associated with these molecules.[2-5] The presence of low lying triplet $n\pi^*$ and $\pi\pi^*$ states results in very fast intersystem crossing rates arising from the enhanced spin orbit coupling between states of different orbital character.[6]

The recent development of sensitized phosphorescence spectroscopy in supersonic jet studies by Ito, et al.[2-4] has provided spectroscopic data concerning the first excited singlet states of acetophenone and other aromatic ketones, but has provided little information as to their dynamics. Determination of excited state dynamics is further complicated by the propensity for these species to photodissociate.[7,8] As a result, the application of sensitized phosphorescence spectroscopy will, in general, be limited to photoexcitation in the vicinity of the S_1 origin for a given molecule for which photodissociation yields should be tolerably low.

We report in this discussion the $S_2 \leftarrow S_0$ photoexcitation spectrum of jet cooled acetophenone and discuss the dynamics revealed by the spectrum. The appearance of the spectrum is surprising since, as is the case for many aromatic ketones, acetophenone S_2 excitation is known to result in fast intersystem crossing to the triplet manifold followed by photochemical dissociation with near unit quantum efficiency.[8] Thus, one expects to observe no intensity by standard fluorescence excitation techniques. The observed spectrum, however, appears not in spite of these processes, but as a result of them; at least as a result of the large intersystem crossing yield from S_2 and a small but not vanishing phosphorescence yield. The results imply that the observed emission arises from the dissociative triplet state of acetophenone which is populated by the decay of the prepared S_2 state. The dynamics of both the prepared S_2 levels and the emitting (and dissociating) triplet levels are discussed.

II. Experimental Procedure.

The molecular jet apparatus and the scheme for obtaining photoexcitation spectra have been described in detail elsewhere.[9,10] The nozzle used in this study is a Quanta-Ray PSV-2 pulsed supersonic valve with a 0.5 mm diameter orifice. Thermally equilibrated vapor pressures from liquid acetophenone at temperatures up to 80°C are obtained by placing the sample in a glass vessel inside the heated valve head assembly. Most of the data recorded are taken at sample temperatures of 50-60°C, at which temperature the vapor pressure of acetophenone is ~2 torr. Backing pressures of 20 to 50 psig He are employed. Acetophenone, which is purchased from Fisher (Certified Grade), is used without purification.

Photoexcitation spectra normalized to the laser intensity are obtained by gating a boxcar averager with a 50 ns aperture delayed 30-50 ns after the laser pulse. In this manner, contributions from scattered laser light and from fluorescent impurities in the sample are reduced. Reported lifetimes are obtained from decay curves recorded with a transient digitizer (Tektronix 7912 AD). 3200 laser shots are averaged for each measurement.

III. Results and Discussion.

A portion of the photoexcitation spectrum of acetophenone in the vicinity of the S_2 origin is shown in figure 1(a). The intensity of the weak spectrum increases monotonically with sample temperature from 15-80°C and remains unchanged with helium pressures of from 1-8 atm, indicating that the spectrum involves no contributions from hot bands or van der Waals clusters.

Aside from the 0_0^0 feature at 35402 cm^{-1} several other features in the spectrum are readily associated with vibronic transitions of acetophenone. The band appearing 193 cm^{-1} above the origin band is assigned to the fundamental of the in-plane acetyl-ring bending mode. The vibrational frequency of this mode in the ground state[11] is 225 cm^{-1} and has been reported as 198 cm^{-1} in S_3.[5] Similarly, the 344 cm^{-1} feature in fig. 1(a) is the $6a_0^1$ transition (benzene numbering) with S_0 [11] and S_3 [5] frequencies of 369 and 341 cm^{-1}, respectively. This transition, involving primarily in-plane ring deformation motion, appears often in the lowest $\pi\pi^*$ spectra of substituted benzenes.

Scanning to higher energies from ~600 cm^{-1} above the 0_0^0 band, little discernable structure is observed in the spectrum until the region of 1000 cm^{-1} above the 0_0^0 transition. In this region (figure 1(b)), three bands appear in the spectrum. The intensity of the strongest 966 cm^{-1} feature is about 20% of that of the 0_0^0. This band is most likely assigned to the 12_0^1 transition (999 cm^{-1} in S_0 [11]) in analogy with spectra of other simply substituted benzenes.

Beyond ~1100 cm^{-1}, the intensity and structure of the S_2 photoexcitation spectrum rapidly decrease with no observable intensity $\geq$1300 cm^{-1} above the S_2 origin.

The similarities of the S_2 photoexcitation spectrum of acetophenone with the gas phase absorption spectrum in this region are strong. The latter spectrum[8] indicates an origin transition near ~35450 cm^{-1} with a strong progression-forming vibronic feature ~1000 cm^{-1} to the blue. Little intensity is observed in either spectrum in lower energy vibronic bands. Clearly, the photoexcitation spectrum revealed by fig. 1 is readily generated from the reported vapor phase absorption spectrum of acetophenone with the use of an emission quantum yield function which rapidly decreases with increasing excitation energy. This is confirmed by the emission lifetimes which are measured for excitation of several vibronic features in the spectrum (fig. 1). Emission lifetimes fall roughly linearly with increasing excitation energy commencing with the 0^0_0 feature which has a lifetime of 540 ± 30 ns. The lifetime measured at 12^1_0 excitation is 130 ± 50 ns. Since the emission quantum yields will vary proportionally with the emission lifetimes, we note that the 12^1 emission quantum yield is approximately one fourth that of the origin level.

The most striking aspect of the S_2 photoexcitation spectrum of acetophenone, aside from the fact that we observe it at all, is the magnitude of the observed linewidths. In fig. 2, we show an expanded view of the 0^0_0 photoexcitation band normalized to the laser intensity. The measured linewidth (FWHM) of the band is $\Gamma = 20.5\ \mathrm{cm}^{-1}$ and is independent of helium pressure (i.e., the degree of rotational cooling and the presence of clusters). Furthermore, the lineshape is clearly Lorentzian (see fig. 2), indicating that the source of the linewidth is natural lifetime broadening of the S_2 origin. This lifetime, $\tau = \frac{1}{2\pi\Gamma c}$ is 260 fs. The bands shown in fig. 1(b) are broader than the 0^0_0 band, indicating S_2 vibronic level lifetimes which are still shorter.

Since the natural lifetimes of the S_2 levels which are initially prepared in the photoexcitation process are six orders of magnitude shorter than the measured lifetimes of the resulting emission, the emitting state is evidently not S_2. Apparently, excitation of S_2 levels is followed by rapid (k 3.85 x $10^{12}\ \mathrm{sec}^{-1}$) decay to isoenergetic levels in the emitting state which have much longer lifetimes than the originally excited S_2 levels. The magnitude of the decay rate from S_2 would imply that preparation of the emitting state occurs with near unit quantum efficiency from all levels of S_2. The relative emission lifetimes (and quantum yields) observed are then determined by the lifetimes of the levels thus populated in the emitting state.

Perhaps the most likely candidate for the emitting state is S_1; in this case, emission would originate with higher vibronic levels of the S_1 manifold. Under this assumption, emission should also be expected by direct excitation of S_1 near the origin region (3650-3700 Å) and the absorption Franck-Condon maximum region (3100-3400 Å): no emission has been observed in either of these regions. Ito et al.[4] have similarly failed to observe S_1 emission by fluorescence excitation. Indeed, under no conditions of phase, medium, and temperature has fluorescence ever been reported for S_1 excitation. Intersystem crossing[12] and internal conversion into the S_0 vibrational manifold[13] appear to be the only channels operative for S_1 decay. The emitting state following S_2 excitation is, therefore, probably not S_1.

The elimination of S_1 as the emitting state is further supported by the intensity of the S_2 photoexcitation spectrum. The absorption spectrum of acetophenone vapor[8] indicates an oscillator strength for the $S_1 \leftarrow S_0$ system of $\sim 1 \times 10^{-3}$. The radiative lifetime of S_1, $\tau^{S_1}_{rad}$, is therefore roughly 2 μs. If S_2 origin excitation results in S_1 emission with the measured ~ 540 ns lifetime, then the quantum yield for the emission is thus ~ 0.3: a number in stark contrast to the observed emission intensity quoted above. The observed S_2 emission quantum yield for S_2 0^0_0 excitation is estimated to be in the range 10^{-3} to 10^{-4}. That is, the intensity of the S_2 spectrum is much too weak to involve solely S_1 emission.

This discrepancy is conceivably a result of complexation of acetophenone in the jet (resulting in lower than expected emission yields) or of a less than unit efficiency in the internal conversion from S_2 to S_1; however, fluorescence with a 540 ns lifetime originating ~ 8100 cm^{-1} into the S_1 manifold seems highly unlikely in view of the fast nonradiative decay rates known to occur at the S_1 origin.

In the absence of any other accessible singlet states, one is forced to conclude, with trepidation, that the emitting state is a triplet state of acetophenone. The dominant decay channel from S_2 is, then, intersystem crossing with $k_{ISC} = 3.85 \times 10^{12}$ sec^{-1} from the S_2 origin. The measured emission lifetimes are those of levels in the triplet manifold. We note that if the emitting state is T_1, which has a known $\tau^{T_1}_{rad} = 1.2$ ms [8], emission following S_2 0^0_0 excitation with a 540 nsec lifetime would reflect an emission quantum yield of $\sim 5 \times 10^{-4}$ which is within our estimated yield. The absence of observed phosphorescence from S_1 excitation is likely the result of a lower intersystem crossing yield arising from the known faster internal conversion rate $S_1 \rightarrow S_0$ relative to $S_2 \rightarrow S_0, S_1$.[13]

Although the emission from S_2 excitation is too weak to obtain a dispersed emission spectrum, the bulk of the emission is centered in the region near 4000 Å: this represents a substantial Stokes shift. The phosphorescence of acetophenone[12] (including vibrationally excited triplet levels[14]) is centered in this region as well. The observed lifetimes of the emitting triplet state can be correlated with the rates of photodissociation previously measured for acetophenone. Excitation into the S_2 state of acetophenone results in photodissociation, presumably from a dissociative triplet state, with a near unit quantum efficiency in the room temperature vapor at low pressure.[8,12,15,16] Values for the lifetime of the dissociative state of from 20 ns to 380 ns are inferred from the measured dissociation rates. Such lifetimes are entirely consistent with our observed emission lifetimes following S_2 excitation in the jet. Furthermore, the results of Rennert and Steel[15] and of Hirata and Lim[16] indicate that the rate of dissociation following S_2 12^1_0 excitation is 4-5 times faster than that following S_2 0^0_0 excitation. Again, this is consistent with our observed emission lifetimes. Therefore, the emission reported herein following S_2 excitation probably originates from the dissociative triplet state of acetophenone; the observed emission lifetimes probably reflect the rate of dissociation from that state.

Since the endothermicity for the lowest energy dissociation process[17] is 80.7 kcal/mole (or ~28200 cm^{-1}), excitation into the S_2 origin of acetophenone (~35400 cm^{-1}) leaves only ~7200 cm^{-1} for excitation of the dissociation products. The observed emission from S_2 excitation is centered at ~4000 Å (~25,000 cm^{-1}), and clearly must not arise from excitation of the photofragments.

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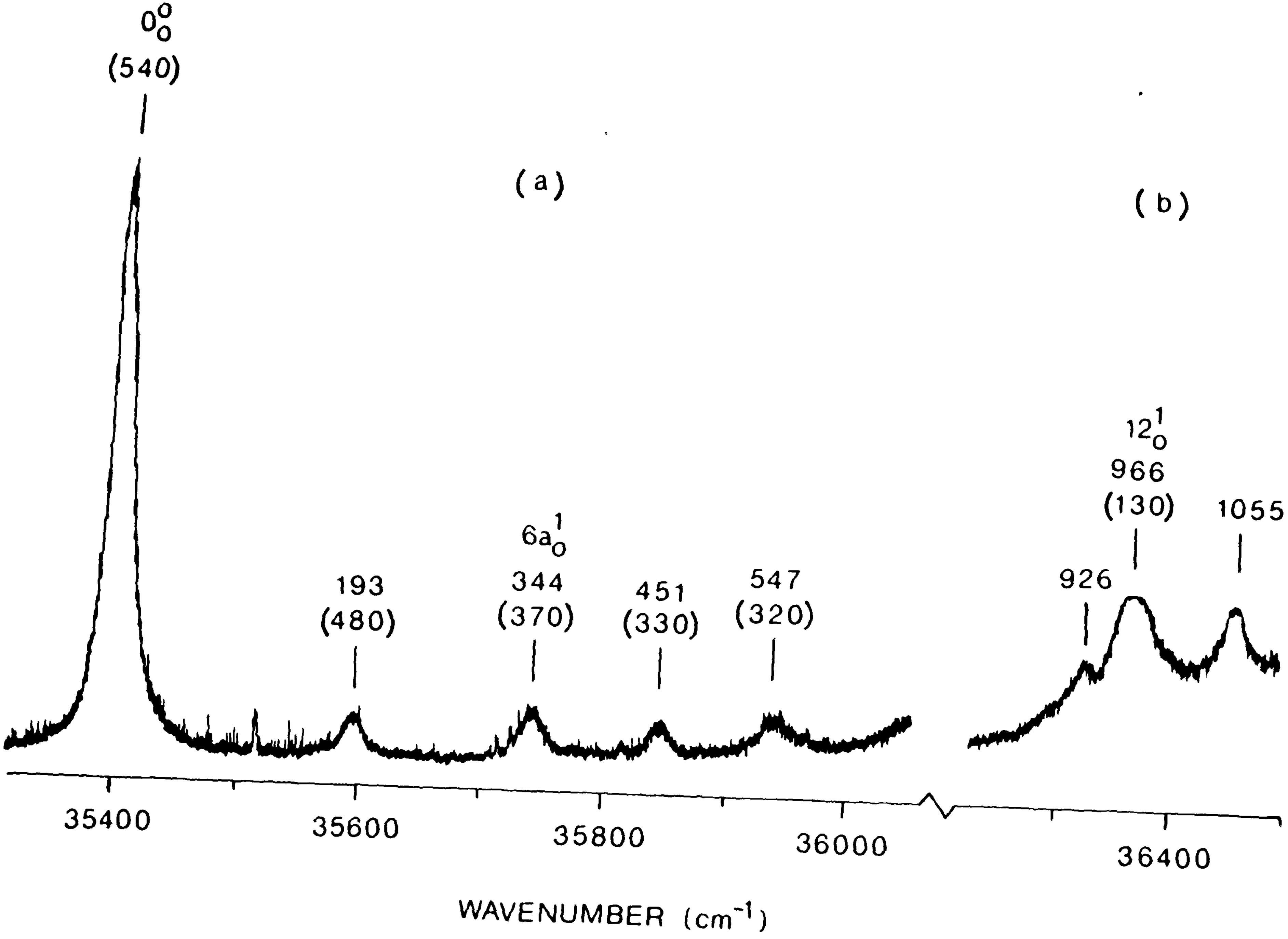
FIGURE CAPTIONS

Figure 1 $S_2 \leftarrow S_o$ Photoexcitation Spectrum of Acetophenone. The spectra are normalized to the laser intensity. Intensity scales in (a) and (b) are different. In (b), the 12^1_o band is shown truncated at ~85% of its true peak intensity which is ~20% of the 0^o_o intensity. Vibronic band positions are indicated relative to the 35402 cm^{-1} 0^o_o transition. Assignments are given in the figure for some of the features and selected lifetimes are shown in parentheses (in ns). The reported lifetimes are measured in emission by single vibronic level excitation of the vibronic bands indicated. Several weak features appear in the spectrum with narrow (2-3 cm^{-1}) linewidths and are assigned to impurities in the sample.

Figure 2 Expanded View of the Acetophenone S_2 0^o_o Band observed in Photoexcitation. The spectrum is normalized to the laser intensity and displayed relative to the center-line wavenumber of 35402 cm^{-1}. The open circles in the lower left portion of the band are fit to a Lorentzian lineshape with $\Gamma = 20.5$ cm^{-1}.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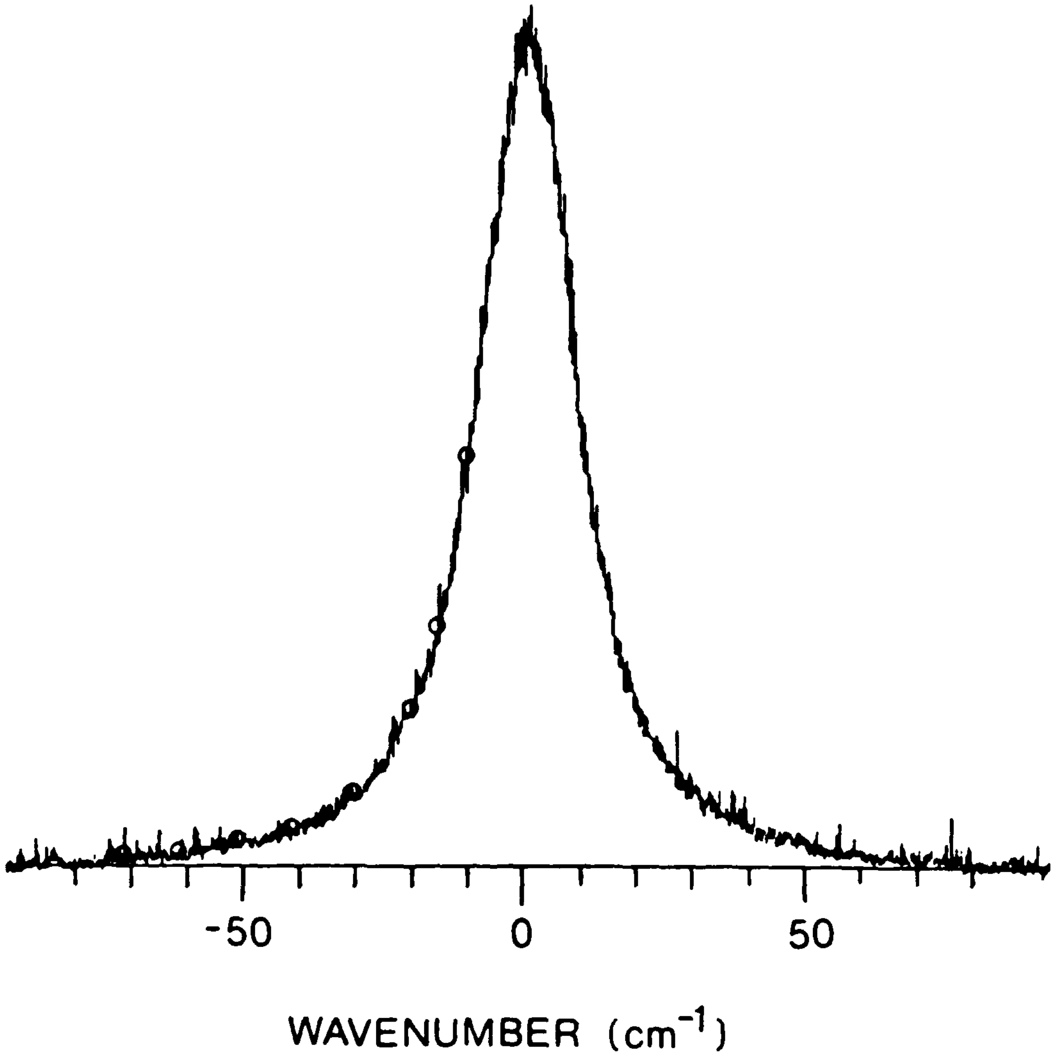
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