Vibrational overtone spectroscopy of jet-cooled methanol from 5000 to 14 000 cm\(^{-1}\)

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Spectra of jet-cooled methanol in the overtone and combination region from 5000 to 14 000 cm\(^{-1}\) have been obtained by means of infrared laser-assisted photofragment spectroscopy. Many of the observed features are assigned to combination bands of the type \(n \nu_1 + \nu_6\), \(n \nu_1 + \nu_8\), and \(n \nu_1 + \nu_6 + \nu_8\) \((n = 1,2,3,\) where \(\nu_1\) is the OH stretch, \(\nu_6\) is the OH bend, and \(\nu_8\) is the CO stretch. These bands show sharp torsion-rotation structure with features as narrow as 0.1 cm\(^{-1}\). We also observe CH stretch overtones that are weaker than the OH containing combination bands and lack distinct torsion-rotation structure above \(\nu_{CH}\approx2\). The extent of observed structure on these bands allows us to place limits on the intramolecular vibrational energy redistribution decay rates in the upper vibrational states. We report a global fit of the observed band centers to a simple expression involving low-order anharmonicity constants. © 2005 American Institute of Physics. [DOI: 10.1063/1.1833353]

I. INTRODUCTION

Since the early work of Dennison,\(^1\) the methanol molecule has served as a model for the study of large-amplitude torsional motion. Infrared laser-assisted photofragment spectroscopy (IRLAPS) of jet-cooled methanol has revealed a substantial increase in the torsional barrier with OH stretch \((\nu_1)\) excitation, which reaches almost a factor of two by \(\nu_1 = 6,2,3\) Slit-jet absorption spectroscopy has shown that the torsional tunneling splittings at the \(v=1\) levels of the \(\nu_2\) and \(\nu_9\) CH stretch vibrations are inverted relative to the ground state.\(^4,5\) Spectra of the methyl rock vibration,\(^6\) as well as theoretical treatments of methanol spectra,\(^4,7-10\) confirm that the occurrence of inverted torsional splittings is a general phenomenon that results from the symmetry of the molecule.

Methanol is also an important benchmark system for studies of intramolecular vibrational energy redistribution (IVR). The presence of both low- and higher-order vibrational couplings\(^11\) leads to energy redistribution on multiple time scales.\(^3,12\) Fast IVR implied by strong low-order resonances has been found to occur between the OH and CH stretches in the \(5 \nu_1\) overtone region\(^3,13,14\) and between the OH stretch and the COH bend in the \(7 \nu_1\) region.\(^3,11\) Moreover, there is evidence for strong coupling between the three CH fundamentals and the six HCH bend combinations.\(^4,15,16\) Pearman and Gruebele have shown that the presence of the threefold internal rotor in methanol substantially increases the number of locally coupled states for skeletal vibrations, thereby accelerating IVR.\(^17\)

The spectral region above 5000 cm\(^{-1}\) contains a large number of vibrational bands that may provide insights into the couplings between the various vibrational modes in methanol. Although room temperature photoacoustic spectra have been recorded in the 10 000 to 20 000 cm\(^{-1}\) region\(^18\) and the high-frequency fundamentals\(^4,5,19-22\) and OH overtones\(^3,12-14,23,24\) have been rotationally resolved in a supersonic free-jet, significant parts of the methanol spectrum between 4000 and 10 000 cm\(^{-1}\) remain largely unexplored. We report here IRLAPS spectra of jet-cooled \(CH_3OH\) from 5000 to 14 000 cm\(^{-1}\) as well as selected spectra of \(CH_3OD\) in this region.

After a brief review of the IRLAPS method, we present assignments for the combination bands involving the OH stretch \((\nu_1)\), the OH bend \((\nu_6)\), and the CO stretch \((\nu_8)\) as well as for the CH stretch overtones. We derive anharmonicity constants and discuss the role of IVR in determining the extent of fine structure in the various bands.

II. EXPERIMENTAL APPROACH

Figure 1 shows a schematic energy level diagram for IRLAPS as applied to jet-cooled methanol excited to overtone and combination vibrations in the range 5000 to 14 000 cm\(^{-1}\). In the first step of our experiment, a near infrared laser pulse excites ground state methanol to one of these levels. In the second step, a \(CO_2\) TEA laser promotes the excited molecules to the dissociation threshold by multiphoton excitation of the CO stretching vibration \((\nu_8)\), producing OH and \(CH_3\) radicals. Finally, the OH dissociation products are detected by laser-induced fluorescence (LIF). An IR spectrum is obtained by monitoring the LIF intensity as the near infrared laser wave number is scanned.

The experimental setup has been described in detail elsewhere.\(^12\) In the present experiments, the near infrared laser pulse was generated either by stimulated Raman scat-
tering a Nd:YAG pumped dye laser beam in H₂ at the first or second Stokes frequencies, or, in the case of the 3000 cm⁻¹ region, by difference frequency mixing the output of the dye laser and Nd:YAG fundamental in lithium niobate. The infrared wave number is calibrated with a wavemeter (Burleigh WA-4500) which is in turn calibrated to an accuracy of ±0.2 cm⁻¹ against water vapor and O₂ lines. Although the nominal dye laser bandwidth is 0.05 cm⁻¹, the narrowest methanol lines observed were 0.1 cm⁻¹ FWHM. Because of the wide wave number range of the spectra and the use of several laser dyes and infrared generation schemes, it was not possible to obtain reliable relative intensities throughout the entire region. However, within a single trace in each of the figures below, an attempt was made to normalize the relative intensities.

III. ASSIGNMENTS AND DISCUSSION

A. Overview

In the spectrum of jet-cooled methanol between 5000 and 14 000 cm⁻¹, we find 34 features that might be assignable as individual vibrational bands. Of these, seven are the OH stretch overtones and associated torsional combination bands that have been analyzed and reported previously. Many of the other bands in this region are typically 10 to 100 times weaker than the nearby OH stretch overtones. Many of the bands appear as families of combination bands built on the ν₁ overtones (where n is equivalent to the vibrational quantum number ν₁ for the mode ν₁), and these show considerable fine structure attributable to torsion and rotation.

To help assign the various families of combination bands, we employ Birge–Sponer plots as described below. The transition wave number from the ground state to an excited combination vibration is approximated by the standard expression

$$\nu = \sum_i \omega_i \nu_i + \sum_{i=1}^{n} \sum_{j=i}^{n} \chi_{ij} \nu_j, $$

(1)

where the sums extend over the normal modes with vibrational frequencies \(\omega_i\), anharmonicities \(\chi_{ij}\), and vibrational quantum numbers \(\nu_i\) and \(\nu_j\). For each family of combination bands, the contribution of the modes other than \(\nu_1\) is

$$\nu' = \sum_{i=1}^{n-1} \omega_i \nu_i + \sum_{i=1}^{n} \sum_{j=i}^{n} \chi_{ij} \nu_j. $$

(2)

We recover a Birge–Sponer dependence on \(\nu_1\) by subtracting \(\nu'\) from the observed transition wave number \(\nu\):

$$\frac{\nu - \nu'}{\nu_1} = A + Bn. $$

(3)

In analyzing each family of bands, we expect the Birge–Sponer constants \(A\) and \(B\) to be close to values reported for the ν₁ overtones, 3773.2 and -86.3 cm⁻¹, respectively.

B. Combinations of ν₁ with ν₆ and ν₈

Figure 2 shows the portions of the IRLAPS spectrum of CH₃OH containing the families of combination bands, \(n \nu_1 + \nu_6\) and \(n \nu_1 + \nu_8\). In this figure, these families are plotted relative to the wave number of the respective \(n \nu_1\) overtone band in such a way that the bands in a given family appear stacked above one another. The overtone family \(n \nu_1 + \nu_6 + \nu_8\) is similarly shown in Fig. 3. In the absence of detailed rotational assignments, the most intense line of each band is chosen as the band center, \(\bar{\nu}\). Depending on the form of the band, this may introduce an error of about 10 to 15 cm⁻¹ relative to the true band center. The observed wave numbers and assignments are listed in Table I.

Figure 4 shows Birge–Sponer plots for the families \(n \nu_1 + \nu_6\), \(n \nu_1 + \nu_8\), and \(n \nu_1 + \nu_6 + \nu_8\), including the band centers from this work along with those from Fang et al. The Birge–Sponer plot for the family \(n \nu_1\) is included for comparison. The band at 12 939 cm⁻¹ (Fig. 3 and Table I) is likely to be \(3 \nu_1 + \nu_6 + \nu_8\) but is shifted 90 cm⁻¹ to higher wave number from its expected position and therefore is not included in the Birge–Sponer regression. If this assignment is in correct, it implies that this band is affected by a strong perturbation.

The slopes and intercepts of the Birge–Sponer plots in Fig. 4 are similar. Small differences can arise from the determination of the band-center and from cross-anharmonicity between the different vibrational modes. Our confidence in the vibrational assignments is based on these Birge–Sponer plots together with the band contour considerations outlined below.

The combination bands involving the \(\nu_6\) vibration are spread over a wide spectral range and have contours that are markedly different from other bands. This is most clearly visible for the \(\nu_1 + \nu_6\), \(2 \nu_1 + \nu_6\), and \(\nu_1 + \nu_6 + \nu_8\) bands.

FIG. 1. Energy level diagram for infrared spectroscopy of methanol by IRLAPS. Vibrational overtones and combinations are accessed by single photon excitation. The energy levels in the left-hand stack represent observed bands in this or referenced work up to 14 000 cm⁻¹, dashed levels were not included in the fit to Eq. (1). The prepared excited vibrational states are detected by IR multiphoton dissociation (IRMPD). The resulting hydroxyl radicals are probed by laser induced fluorescence (LIF).
Figures 2(c), 2(b), and 3(c)], which have the highest signal-to-noise ratio. In each of these bands, several of the subbands are shifted 50 to 160 cm\(^{-1}\) to higher wave number from the apparent band center. One such subband, expanded in the inset of Fig. 2(b), has the clear P and R branches expected for a \(K = 0\) subband. The simplicity of its structure suggests that this feature is not an entire band in itself, since at the jet temperature of 5 to 10 K, an entire vibrational band would have a dozen or more subbands arising from \(K = -1, 0, 1\) and A and E symmetries. It is more likely to be a subband of \(2n_1 + n_6\).

The spread out structure of the \(n_6\) combination bands can be explained by analogy with the \(n_6\) fundamental. Rotationally resolved spectra of the \(n_6\) fundamental of both \(^{12}\)CH\(_3\)OH (Ref. 28) and \(^{13}\)CH\(_3\)OH (Ref. 29) reveal an exceptionally large torsional tunneling splitting \(\approx 24\) cm\(^{-1}\) for the COH bend upper state as compared to 9.1 cm\(^{-1}\) for the ground state, and this causes the subbands origins to be more widely spread.\(^{29}\) Lees et al.\(^{28}\) found that torsionally excited states of the methyl rocks \((n_7\) and \(n_11))\) and of the CO stretch \((n_8)\) fall in the same region as the \(n_6\) fundamental. The strong mixing among these bands results in intensity transfer to the torsional combination bands, which are more spread out than the fundamentals.

**C. CH stretch overtones**

For the CH stretching overtone bands, we use the local mode labels, \(n_a\) and \(n_b\), employed by Fang et al. for assignment of their photoacoustic spectra.\(^{18}\) The “unique” CH stretch, \(n_a\), refers to a local vibration of the CH bond anti to the OH bond. The stretches of the other two “nonunique” CH bonds (gauche to the OH bond) are equivalent and designated \(n_b\). We label the three corresponding CH bonds as \(a\), \(b\), and \(b'\).

Figure 5 shows a stack of CH stretch overtone spectra up to \(v_{CH} = 5\). IRLAPS spectra of the higher CH overtones were too weak to be measured. Because the \(n_a\) fundamental occurs at higher wave number than \(n_b\) and the anharmonicities are similar, the splitting between the overtones of these two local modes increases linearly with \(v_{CH}\), reaching 570 cm\(^{-1}\) at \(7v_{CH}\).\(^{18}\) The \(n_a\) overtones are consistently weaker than those of \(n_b\), in part because there is only one anti-CH bond as opposed to two in the gauche position.

In the region of \(v_{CH} \geq 3\), the onset of local mode behavior causes the overtone spectra to be relatively simple. The single-bond anharmonicity \((\lambda_{aa} \approx \lambda_{bb} \approx -60\) cm\(^{-1}\)) causes the local mode overtones (e.g., \(5n_b\)) to become isolated from the nearest local-local combinations (e.g., \(4n_b + n_b\)). The spacing becomes much larger than the local-local coupling

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**FIG. 2.** Stacked combination band spectra of the families \(n_1 + n_6\) and \(n_1 + 2n_6\) for \(n = 1, 2,\) and 3. Each spectrum is plotted on a wave number scale relative to \(v_0\), the transition wave number of the corresponding \(n_1\) overtone band. In this way the abscissa represents the contribution of modes other than \(v_1\) to the transition wave number, and members of a family are aligned vertically. One subband of the \(2n_1 + n_6\) band is enlarged in the inset.

**FIG. 3.** Stacked combination band spectra of the family \(n_1 + n_6 + n_8\) for \(n = 1, 2,\) and 3. Each spectrum is plotted on a wave number scale relative to \(v_0\), the transition wave number of the corresponding \(n_1\) overtone band.
TABLE I. Overtones, combination, and relevant fundamental bands of CH\textsubscript{3}OH.

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<th>Assignment</th>
<th>Observed (cm\textsuperscript{-1})</th>
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<th>Reference</th>
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\textsuperscript{a}Obs-Calc is the difference between the observed and calculated wave numbers. The root mean square deviation of the fit is 12 cm\textsuperscript{-1}.

\textsuperscript{b}These bands have been rotationally assigned in high resolution spectra. The "observed" entries are the band centers (ν\textsubscript{center}), defined as J = 0 to J = 0 energy differences, averaged over the A and E symmetry torsional tunneling states. All other bands listed have not been rotationally assigned and the wave numbers of the absorption maxima are listed.

\textsuperscript{c}Intensity maximum of a broad absorption in a room temperature FTIR spectrum; not included in the fit.

\textsuperscript{d}Calculated transition frequencies for bands that were not included in the fit.

\textsuperscript{e}This band, tentatively assigned to 3ν\textsubscript{1} + ν\textsubscript{6} + ν\textsubscript{8}, is shifted 90 cm\textsuperscript{-1} to higher wave number than calculated, and is therefore not included in the fit.

\textsuperscript{f}This band shows a 50 cm\textsuperscript{-1} splitting because of a strong perturbation in the spectrum; therefore the tabulated value is the zeroth-order level calculated from a deperturbation analysis (Ref. 13).

(\(\lambda = -42.1\text{ cm}^{-1}\))\textsuperscript{4} so that the local mode overtones are not significantly mixed with the local-local combinations. Moreover, in the bond dipole model only the local mode overtones carry oscillator strength, which simplifies the spectrum to a single feature for each bond at each overtone level. Finally, the increasing separation of the ν\textsubscript{a} and ν\textsubscript{b} overtone bands becomes too great for them to be significantly mixed by the local-local coupling (λ), allowing the higher ν\textsubscript{a} and ν\textsubscript{b} overtones to be treated separately. Although each of these simplifications is an approximation, together they provide a reasonable description of the assigned CH stretch features in the ν\textsubscript{CH} = 3 – 7 region.

In the CH stretch fundamental region [Fig. 5(e)], the local-local coupling is dominant and results in three normal vibrations. The situation is further complicated by rapid torsional tunneling, which interchanges the identity of the a, b, and b’ CH bonds. The torsion-rotation structure of the CH fundamentals has been assigned at high resolution\textsuperscript{43,50} to yield the three normal mode frequencies, ν\textsubscript{a} = 2844.69, ν\textsubscript{b} = 2956.91, and ν\textsubscript{b’} = 2998.77 cm\textsuperscript{-1}.\textsuperscript{4} The internal coordinate Hamiltonian of Wang and Perry\textsuperscript{4} which includes the CH local-local coupling and the lowest order torsion-vibration coupling, successfully reproduces the three fundamental frequencies and corresponding torsional tunneling splittings. Although the CH fundamentals appear in the spectrum as three normal modes, it is possible to use the Wang–Perry Hamiltonian to derive theoretical fundamental transition frequencies for the local modes, ν\textsubscript{a} and ν\textsubscript{b}. With the torsional angle frozen at the equilibrium geometry and neglecting the local-local coupling between the CH bonds, their Hamiltonian matrix reduces to

\[\hat{H} = \begin{pmatrix}
\omega + 3\mu & 0 & 0 \\
0 & \omega - \frac{1}{2}\mu & 0 \\
0 & 0 & \omega - \frac{1}{2}\mu
\end{pmatrix},\tag{4}\]

where \(\omega = 2933.48\text{ cm}^{-1}\) is the frequency of the three equivalent CH local modes in the G\textsubscript{b} molecular symmetry group. In
Eq. (4), we have kept the torsion-vibration coupling parameter, $\mu = 12.4 \text{ cm}^{-1}$, which gives rise to the frequency difference between $v_a$ and $v_b$. From Eq. (4) we determine the fundamental frequencies of $v_a$ and $v_b$ to be 2970.68 and 2914.88 cm$^{-1}$, respectively. Note that these derived values are approximate, because the treatment of Wang and Perry neglects the interactions of the CH stretches with the six HCH bend overtones and combinations that fall in this region.

The $2v_{CH}$ bands [Fig. 5(d)] fall in the transition region between the normal mode and local mode limits and are therefore more complicated than either the fundamental or the higher overtones. In Fig. 5(d), features appear at the expected positions of the local mode bands $2v_a$ and $2v_b$ as well as in the general region of the local-local combinations. Local-local combinations with reasonable intensity have been observed in $2v_{CH}$ spectra of other molecules.\textsuperscript{31} Moreover, there are 18 CH bending combinations of the form $v_{CH} + 2v_{bend}$ that will interact with and borrow intensity from the six possible $2v_{CH}$ bands. As expected, Fig. 5(d) shows many bands and a complicated structure throughout the extended $2v_{CH}$ region. Hänninen and Halonen\textsuperscript{32} have employed \textit{ab initio} calculations to determine the Fermi and Darling–Dennison resonance coupling constants for methanol. These constants, together with a fit to a set of experimental band centers, enabled them to calculate the 24 transition frequencies and wave functions in the $2v_{CH}$ region. As shown in Fig. 5(d), their calculated transition frequencies for the eight bands with the highest percentage of CH stretch character show a good qualitative correspondence with the observed spectrum.

In the $3v_{CH}$ to $5v_{CH}$ region, some of the CH overtone bands are overlapped by OH overtone and combination bands. In Fig. 5(a), only the $5v_b$ band at 13,295 cm$^{-1}$ is distinguishable, because $5v_a$ is obscured by the much stronger $4v_1$ band. The unstructured contour of the $3v_a$ band [Figs. 5(c) and 2(b)] at 8544 cm$^{-1}$ is overlapped by the nearby $2v_1 + v_6$ combination band. In Fig. 5(b), the sharp rotational lines of the OH stretch combinations, $3v_1 + v_{12}$ and $3v_1 + 2v_{12}$, which have been assigned and fit to a torsion-rotation Hamiltonian,\textsuperscript{2} are superimposed on the broad, featureless $4v_b$ band at 10,820 cm$^{-1}$. The $4v_a$ band, which is centered at 11,181 cm$^{-1}$, is free from overlapping bands but is much weaker than $4v_b$. To confirm the assignments in the $4v_{CH}$ region, we present the corresponding spectrum of CH$_3$OD and compare it with CH$_3$OH in Fig. 6. As expected, the sharp lines of the OH stretch combinations are absent from the CH$_3$OD spectrum, while the CH stretch bands occur in nearly the same position for the two isotopomers.

Figure 7 shows Birge–Sponer plots for the $v_a$ and $v_b$ CH stretch overtones. The residuals of the fits are well within

![FIG. 5. Spectra of the CH stretch overtone bands. The wave number scale is relative to the values of $v_0$, 13,455, 11,000, 8445, 5745 and 2940 cm$^{-1}$, respectively (a)–(e). The dashed lines serve as a guide to the eye to follow the positions of the $v_a$ and $v_b$ overtone bands at each overtone level. The triangles under trace (d) indicate band positions predicted in Ref. 32.](image)
the band contours of the assigned spectral features, consistent with our simplified treatment of the $\nu_{\text{CH}} = 3-7$ overtone region and our approximate derivation of $n_a$ and $n_b$ local mode frequencies from the CH fundamentals. A more realistic model of the CH overtone bands would include couplings between the local CH stretch modes (i.e., local-local coupling) as well as stretch-bend and stretch-torsion coupling. The application of such a detailed stretch-bend model requires additional constraints, either from experiment or from \textit{ab initio} theory.\textsuperscript{32}

The smooth contours and lack of obvious torsion-rotation structure in the $3n_{\text{CH}}$, $4n_{\text{CH}}$, and $5n_{\text{CH}}$ bands are likely the result of rapid IVR, and our observed band profiles place limits on the initial IVR rates. Even though torsion-rotation structure will contribute to the band profiles, the overall width of the CH overtone bands defines an upper bound to the IVR rate. For example, the best Lorentzian fit to the $3n_b$ band in Fig. 5 gives a FWHM of 50 cm$^{-1}$, which would correspond to a decay time of 100 fs if this band were coherently excited. At the other limit, a lower bound to the IVR rate is determined by the minimum coupling width needed to smooth out the torsion-rotation structure that is seen in other bands. By comparing the $3n_b$ band with the structured $2n_{11}$ band, we estimate that a coupling width of at least 5 cm$^{-1}$ would be required to produce a smooth contour, corresponding to an IVR lifetime of 1 ps. These estimates of IVR lifetimes serve to highlight the qualitative difference in the hypothetical dynamics subsequent to coherently excitation of the OH stretch combinations and the CH overtones. For example, the narrowest features in the $2n_{11}$ band (Fig. 5(c)) are 0.1 cm$^{-1}$ wide, corresponding to a nominal IVR lifetime of ~50 ps. More confident estimates of these methanol IVR lifetimes will have to await double resonance experiments that eliminate inhomogeneous spectral structure.

**D. Combinations of the OH and CH stretches**

Figure 8 shows the spectral region containing the binary combinations of the CH stretches with the OH stretch. We assign the $n_1 + n_3$, $n_1 + n_9$, and $n_1 + n_2$ bands based on the their coincidence with the sum frequencies calculated from the rotationally assigned fundamental spectra.\textsuperscript{5,21,30} Since the time that the spectrum of Fig. 8 was recorded, the $n_1 + n_1$

![FIG. 6. Spectra of the 4$\nu_{\text{CH}}$ regions of CH$_3$OH and CH$_3$OD. The sharp lines of the OH stretch-torsion combinations appear only in the CH$_3$OD spectrum, while the CH stretch overtones occur in nearly the same position in both spectra.](image1)

![FIG. 7. Birge–Sponer plots for the CH stretch overtone bands. Hollow symbols represent the room temperature photoacoustic spectra of Fang et al. (Ref. 18).](image2)

![FIG. 8. Spectra of the CH stretch plus OH stretch combination bands. The vertical marks indicate the sums of the wave numbers of the corresponding fundamental bands.](image3)
band has been recorded at high resolution using CW cavity ringdown spectroscopy and analyzed in detail.\textsuperscript{33} In analogy to the spectra in the CH fundamental region, it is likely that the large feature between the $v_1 + v_3$ and $v_1 + v_9$ bands is made up of six overlapping combination bands of the form $v_1 + 2v_{bend}$, where the CH bands are $v_4$, $v_5$, and $v_{10}$.

### E. Global fit

To characterize the band positions in the overtone region, we carried out a least squares fit of the transition wave numbers in Table I to the anharmonic expression in Eq. (1). Where the data are available, the band centers in Table I are derived from rotationally assigned high-resolution spectra. These band centers, $\nu$, which represent the energy difference between the $J=0$ levels of the upper and lower states, are not equal to the band origins that result from fitting high resolution data to a torsion-rotation Hamiltonian. The latter would be the difference between the minima of the one-dimensional effective torsional potentials for the upper and lower states, and they differ from our measured $\nu$ by the change in torsional zero-point energy upon vibrational excitation (a difference of 9 to 24 cm$^{-1}$ for the bands $v_1$ to 3$v_1$).\textsuperscript{2,20} We have chosen to use the band centers $\nu$ in our fits because the data are available for more bands. For the many bands without detailed rotational assignments, each $\nu$ tabulated in Table I is approximated as the wave number of the absorption maximum in the band profile.

Our fit differs from that of Hänninen and Halonen\textsuperscript{32} in several respects. Most importantly, its fit uses dozens of fixed parameters derived from \textit{ab initio} calculations, whereas ours is strictly empirical. A full understanding of the methanol spectra will certainly require an effective synthesis of theory and experiment, but the purpose of our present fit is just to characterize the experimental data. Second, we have included CH overtone data in the range $v_{CH}=3-7$. Finally, the experimental wave numbers for $v_1$, $v_2$, and $v_9$ on which the two fits are based differ by as much as 10 cm$^{-1}$ because of differences in the way torsional tunneling and torsional zero point energy are handled. Neither fit includes the torsional tunneling dynamics explicitly.

A total of 36 bands were included in the fit, yielding a root mean square deviation of 12 cm$^{-1}$. The resulting spectroscopic parameters, shown in Table II, include the harmonic frequencies $\omega_i^0$ of the six relevant vibrational modes and their anharmonicities $x_{ij}$ and $x_{ij}$. The OH and CH stretch parameters are in agreement with those of Fang et al.,\textsuperscript{19} except that the confidence intervals are reduced and the CH anharmonicities are a little larger in magnitude. The difference between $x_{aa}$ and $x_{bb}$ is now significant and it is evident visually as the divergence of the slope lines in Fig. 7. This difference implies that the torsion-vibration coupling parameter $\mu$ increases with CH stretch excitation. The parameters involving the CO stretch and COH bend are poorly determined because of the uncertainty in the band origins and the low level of excitation of these modes in the observed combination bands.

### IV. CONCLUSIONS

We have measured the infrared spectrum of methanol from 5000 to 14 000 cm$^{-1}$ using the IRLAPs technique and have assigned most of the observed bands. The spectrum is dominated by the OH stretch overtones and combination bands involving the OH stretch, CO stretch, and COH bend. The band positions were fit to a simple expression involving the low order anharmonicity constants.

All of OH stretch combination bands show sharp rotational structure, which remains unassigned for many of the bands. In contrast, the CH overtone bands are weaker, often structureless, and fewer combinations with other modes are evident in the spectrum. It appears that the observed CH overtones undergo faster IVR than nearby OH stretch combinations.

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36 I. Mukhopadhyay, V.-M. Hornemann, and D. S. Perry, unpublished results.