Laser Stark Spectroscopy of Methyl Cyanide in the 10-μm Region: Analysis of the $\nu_4$ and $\nu_7$ Bands, and the $\nu_7$, $3\nu_6$ Interaction

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About 550 Stark tuned resonances of the $\nu_4$ and $\nu_7$ vibration-rotation bands of CH$_3$CN were measured using $^{13}$CO$_2$, $^{15}$CO$_2$, and N$_2$O lasers. These data are combined with 26 microwave measurements and fitted to a model which includes $J$-type doubling in $\nu_4$, $\nu_4$--$\nu_7$, Coriolis coupling, and $\nu_7$--$3\nu_6$ Coriolis and Fermi couplings. The infrared and microwave data can be reproduced with standard deviations of 7 MHz and 40 kHz, respectively. The many vibration-rotation parameters and the dipole moments are determined with great accuracy. A complete list of derived parameters is given in Table I.

INTRODUCTION

Laser-Stark spectroscopy is now a firmly established technique in high-resolution infrared studies (1-3). An effective frequency precision of better than 10 MHz is easily realized and weak transitions may be observed because of the combination of laser power and high detector sensitivity. Resolution and measurement precision beyond the Doppler limit may be obtained by using the Lamb dip saturation technique. In this work we have studied Doppler-broadened spectra of strong $\nu_4$ ($A_1$) and weaker $\nu_7$ ($E$) bands of methyl cyanide (CH$_3$CN). In a few instances we have used the saturation technique to improve the resolution. A satisfactory analysis can be made only by taking into account a number of interactions, and when this is done the standard deviation in the fit to the infrared measurements is less than 10 MHz.

Methyl cyanide has been extensively studied using a variety of other spectroscopic techniques. The ground-state rotational spectrum has been investigated by a number

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of workers using conventional microwave techniques (4, 5), and more recently by Boucher et al. (6), using molecular beam and microwave Lamb dip spectrometers. Microwave spectra have also been analyzed for the \( \nu_8 \) (E:C–C=N bend) (4, 5), \( 2\nu_8 \) (A \(_1\) + A \(_2\) + E) (7), and \( \nu_4 \) (A \(_1\):C–C stretch) (8) excited vibrational states. The infrared spectrum has been examined by a number of workers at both low (9) and high (10) resolution. There is also some astrophysical interest in this molecule (11, 12) and a number of far-infrared lasers may be generated using CH\(_3\)CN by optical pumping (13). Some early laser-Stark measurements of the \( \nu_4 \) band were reported in (14).

Figure 1 shows the vibrational states relevant to the present work. Several authors have pointed out the importance of Fermi and Coriolis interactions between the low lying vibrational states. Moskienko and Dyubko (15), and Bauer and Godon (8) attributed perturbations in the \( \nu_4 \) microwave spectrum to the x-y Coriolis interaction between \( \nu_4 \) and \( \nu_7 \), and the intensity perturbation in \( \nu_9 \) caused by this interaction has been analyzed by Kondo and Person (16). Duncan et al. (17), have discussed the Fermi interaction between \( \nu_4 \) and \( 2\nu_8 \), and also noted the minor interaction between \( \nu_7 \) and \( 3\nu_8 \). The effect of the latter interaction on the \( \nu_7 \) spectrum can be clearly seen in the residues of the fit described by Kondo and Person, and in the infrared spectrum at moderate resolution.

![Diagram](image)

**Fig. 1.** Partial vibrational energy level diagram for CH\(_3\)CN. --- = Coriolis interaction, = Fermi interaction.

It is therefore necessary to make a joint the contributions from the Coriolis interac
tions and the Fermi interaction model and this allows several constants to be
no transitions in that band could be ass
(17), because of the parallel nature of theo
between them is absorbed in the anhar
s, and cannot be separated.

**EXPERIMENT**

Laser Stark spectra of the \( \nu_4 \) band were
described in (2), operated on \(^1\)P(29) around 10.6 \( \mu \)m. The \( \nu_7 \) band w:
laser operating on \(^13\)CO\(_2\) \( \nu(34) \) to \( \nu(8) \),
\( \nu(14) \) to \( \nu(26) \), and \( \nu(10) \) to \( \nu(24) \) at 9
eters were calibrated using CH\(_3\)F spectr
dip measurements. CO\(_2\) frequencies wer
Freed et al. (18) and are believed to hav
N\(_2\)O frequencies were taken from Whitfi
er lines relative to close-lying CO\(_2\) tra
work, however, must be obtained by e:
uncertainties up to a few megahertz. In
usually locked to the gain profile, and fl
ence (18, 19). Thus the reproduc
megahertz because of the laser gain lin
quency uncertainties. Further experimen
(20, 21).

Spectra were observed in both parallel
dizations. Voltage measurements of b,
only parallel polarization for cons from the microwave work (6
olution infrared analysis (10), gave t
hundred megahertz for low \( J \) and \( K \), an
ponents to be assigned. For transiti
ecessary to follow the procedure to
determine the direction of tuning and
The large dipole moment of CH\(_3\)CN
tuned into coincidence with more than on
transition was observed on both the \( \nu(3)
position was predicted to move through fo
dicular polarization for fields of less th
more than 50 GHz, crossing CO\(_2\) \( \nu(4)
consequence of the large dipole moment i
to cross the same laser line twice becau
Also, Stark-induced transitions \( \nu(1)\)
LASER STARK SPECTROSCOPY OF CH$_3$CN

It is therefore necessary to make a joint analysis of the $\nu_4$ and $\nu_7$ bands so that the contributions from the Coriolis interaction can be eliminated from the molecular constants. The $\nu_7-3\nu_4^\dagger$ Fermi interaction must also be included in the molecular model and this allows several constants in the $3\nu_4$ state to be determined, although no transitions in that band could be assigned. As pointed out by Duncan et al. (17), because of the parallel nature of the $\nu_4$ and $2\nu_4^\dagger$ bands, the Fermi interaction between them is absorbed in the anharmonic contribution to the rotational constants, and cannot be separated.

EXPERIMENTAL DETAILS

Laser Stark spectra of the $\nu_4$ band were measured in Ottawa using a flowing gas laser, as described in (2), operated on $^{12}$CO$_2$ $P(40)$ to $P(50)$ and N$_2$O $P(18)$ to $P(29)$ around 10.6 $\mu$m. The $\nu_7$ band was observed in Cambridge using a sealed laser operating on $^{12}$CO$_2$ $P(34)$ to $P(8)$, and $R(8)$ to $R(26)$ at 9.4 $\mu$m, and $^{13}$CO$_2$ $P(14)$ to $P(26)$, and $R(10)$ to $R(24)$ at 9.8 $\mu$m. The Stark fields of both spectrometers were calibrated using CH$_3$F spectra at 9.4 $\mu$m (2), including several Lamb dip measurements. CO$_2$ frequencies were taken from the recent measurements of Freed et al. (18) and are believed to have absolute accuracy better than 100 kHz. N$_2$O frequencies were taken from Whitford et al. (19), who measured several N$_2$O laser lines relative to close-lying CO$_2$ transitions. The N$_2$O frequencies used in this work, however, must be obtained by extrapolation of their data, which implies uncertainties up to a few megahertz. In the Stark measurements the lasers were usually locked to the gain profile, and not to the Lamb dip in the 4.3-$\mu$m CO$_2$ fluorescence (18, 19). Thus the reproducibility of our data is expected to be a few megahertz because of the laser gain linewidth, and this probably dominates frequency uncertainties. Further experimental details are given in the relevant theses (20, 21).

Spectra were observed in both parallel ($\Delta m = 0$) and perpendicular ($\Delta m = \pm 1$) polarizations. Voltage measurements of both polarizations were used for the $\nu_4$ band, but only of parallel polarization for the $\nu_7$ band. The ground-state molecular constants from the microwave work (6), together with the results of the high-resolution infrared analysis (10), gave predictions which were accurate to a few hundred megahertz for low $J$ and $K$, and in most cases allowed the sign of the $m$ components to be assigned. For transitions which were very close to the laser line it was necessary to follow the procedure of slightly offsetting the laser frequency to determine the direction of tuning and hence the sign of the $m$ components.

The large dipole moment of CH$_3$CN results in many low-$J$ transitions being tuned into coincidence with more than one laser line. In $\nu_7$, for example, the $^5P_1(2)$ transition was observed on both the $P(32)$ and $P(30)$ spectra, and the $^3Q_2(3)$ transition was predicted to move through four laser lines ($P(10)$ to $P(16)$) in perpendicular polarization for fields of less than 10 kV/mm. In $\nu_4$, $^5P_0(1)$ tunes through more than 50 GHz, crossing CO$_2$ $P(46)$ and $P(23)$, $P(24)$ of N$_2$O. A further consequence of the large dipole moment is that a number of transitions are observed to cross the same laser line twice because the sign of the Stark coefficient changes. Also, Stark-induced transitions $^3Q_0(1)$ and $^3Q_0(2)$ were identified in $\nu_4$. Low-$J$
transitions may be tuned through large shifts, the maximum being 60.4 GHz in \( \nu_4 \), \( ^4R_0(0) \) \( m = 0 \rightarrow 0 \), while even high-\( J \) transitions display useful shifts. The spectrum often becomes quite dense, lines show a great variety of widths and frequently overlap. A range of modulation amplitudes was required to obtain satisfactory measurements on all lines. The rapid tuning and line density near the center of the \( \nu_4 \) band are illustrated in Fig. 2, while Figs. 3 and 4 give examples of observed spectra.

**ANALYSIS**

A computer program was written to analyze the Stark spectra by the method of least squares. For each assigned transition the Stark-shifted transition frequency was calculated by setting up and diagonalizing the upper- and lower-state Hamiltonians, given by expressions:

\[ H = H_0 + H_1 + H_s + H_E. \]  

\[ \langle \nu_\varepsilon, J, k | H_0 | \nu_\varepsilon, J, k \rangle = E, + B_s J (J + 1) \]

\[ E = D, + B_s J (J + 1), \]

\[ \langle \nu_\varepsilon, J, l | H_1 | \nu_\varepsilon, J, k \rangle = E, + B_s J (J + 1), \]

\[ \langle \nu_\varepsilon, J, k, l = -1 | H_s | \nu_\varepsilon, J, k, l = -1 \rangle = -1/2 \Omega, \]

\[ \langle \nu_\varepsilon, J, k \pm 1, l = \pm 1 | H_s | \nu_\varepsilon, J, k \rangle = \]

\[ \langle J, k, m | H_E | J, k, m \rangle = \]

Symbols used above have their usual meaning. \( E \) is the Stark field, \( \mu \) the molecular dipole. The transition frequency was then found from the two matrices. Since the second Stark splitting \( \Delta \mu \) is necessary to introduce a true matrix. Previous authors have used fixed matrices. Previous authors have used fixed matrices.
\[ \langle v_n, J, k | H_0 | v_n, J, k \rangle = E_s + B_s J(J + 1) + (A_s - B_s)K^2 - D_{J^2}J(J + 1) - D_{J^2}J(J + 1)K^2 - D_{K^2}K^4, \quad (2) \]

\[ \langle v_n, J, k, l | H_0 | v_n, J, k, l \rangle = E_r + B_r J(J + 1) + (A_r - B_r)K^2 - 2(A_s')k \]

\[ \times [1 + \eta_s J(J + 1) + \eta_K K^2] - D_{J^2}J(J + 1)^2 - D_{J^2}J(J + 1)K^2 - D_{K^2}K^4, \quad (3) \]

\[ \langle v_n, J, k = l = \pm 1 | H_0 | v_n, J, k = l = -1 \rangle \]

\[ = -1/2(q_s + q_J(J + 1) + q_J^2(J + 1)^2)J(J + 1), \quad (4) \]

\[ \langle v_n, J, k \pm 1, l = \pm 1 | H_0 | v_n, J, k \rangle = \pm \sqrt{2}B'\Omega_{s,s}[(J \mp k)(J \pm k + 1)]^{1/2}, \quad (5) \]

where

\[ \Omega_{s,s} = [(\omega_s/\omega_s)^{1/2} + (\omega_s/\omega_s)^{1/2}]/2, \]

\[ \langle J, k, m | H_0 | J, k, m \rangle = -\mu Ekm / J(J + 1), \quad (6) \]

\[ \langle J, k, m | H_0 | J - 1, k, m \rangle = +\mu E \left[ \frac{(J^2 - k^2)(J - m^2)}{(2J - 1)(2J + 1)} \right]^{1/2} \]

Symbols used above have their usual meanings; \( k, l, m \) are signed quantum numbers, \( E \) is the Stark field, \( \mu \) the molecular dipole. The sign conventions should be noted. The transition frequency was then found by subtracting the relevant eigenvalues of the two matrices. Since the second Stark matrix element in Eq. (6) is off-diagonal in \( J \), it is necessary to introduce a truncation limit to avoid unmanageably large matrices. Previous authors have used fixed truncation limits, for example, truncating at \( J \pm 4 \) for \( J > 4 \) and \( J + 8 \) for \( J < 4 \), but this method is inefficient since
accommodate the large Stark shifts of a few transitions it is necessary to use large matrices throughout the analysis. This is particularly true of CH₂CN, where the large dipole moment results in some extremely large Stark shifts. A second program was therefore written to optimize the truncation limits. For each transition this program repeatedly calculated the Stark shifts of both upper and lower levels, each time increasing the number of \( J \) states included in the matrices. This was repeated until the inclusion of one more \( J \) state altered the result of the calculation by less than 300 kHz. The output from the program, giving independent truncation limits for both upper- and lower-state Hamiltonians, was then input to the fitting program alongside the transition assignment data. Effects of the \(^{14}\text{N}\) nuclear spin were estimated at about 1 MHz for small \( J \) and reduce rapidly with increasing \( J \) so that they can be neglected. Polarizability shifts are too small to be determined here, and were not included in the calculation (20, 21).

Preliminary values of the band origins and molecular constants showed that the Coriolis interacting levels in \( \nu_4 \) and \( \nu_7 \) approach resonance for \( K = 23 \) \(( -J \rangle \) which is well outside the region of the observed spectra. It was therefore possible to reduce further the size of the Hamiltonian matrices by including the off-diagonal Coriolis elements only for the states \( J' - 1, J', \) and \( J' + 1 \) in the case of a transition to the state \( J' \). That is, only the state involved in the transition and the states with which it is directly mixed by off-diagonal Stark elements were corrected for the Coriolis interaction.

The band origin of \( 3\nu_4 \) can be calculated from the \( \omega, x, \) and \( g \) data (17) to be about 1078 cm\(^{-1}\). Taking \( \xi \) from the \( \nu_8 \) condition shows that the states \( K' = 7, \xi \) et al. (17) estimated the interaction ma although this is a minor resonance in the spectrum, on the level of laser-Stark me: Two observations concerning the Ferr of the treatment of this interaction. Fir:
# Laser Stark Spectroscopy of CH$_3$CN

## Table I

Molecular Constants of CH$_3$CN

<table>
<thead>
<tr>
<th>$V_i$ : $V_0$</th>
<th>$V_f$ : $V_0$</th>
<th>Dipole moments (Debye)</th>
<th>Ground state cm$^{-1}$</th>
</tr>
</thead>
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<tr>
<td>$920.28847(1)$</td>
<td>$1041.8382(2)$</td>
<td>$925191(48)$</td>
<td>$5.28$ (b)</td>
</tr>
<tr>
<td>$A$</td>
<td>$5.2729630(11)$</td>
<td>$A$</td>
<td>$5.28$ (b)</td>
</tr>
<tr>
<td>$B$</td>
<td>$0.3054263(13)$</td>
<td>$B$</td>
<td>$0.3052995$ (c)</td>
</tr>
<tr>
<td>$D_J$</td>
<td>$1.3025(54)x10^{-7}$</td>
<td>$D_J$</td>
<td>$1.284(5)x10^{-7}$ (d)</td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>$5.9121(30)x10^{-6}$</td>
<td>$D_{JK}$</td>
<td>$6.154(2)x10^{-6}$ (d)</td>
</tr>
<tr>
<td>$D_K$</td>
<td>$8.6228(24)x10^{-5}$</td>
<td>$D_K$</td>
<td>$8.4x10^{-5}$ (b)</td>
</tr>
<tr>
<td>$A$</td>
<td>$5.309694(72)$</td>
<td>$A$</td>
<td>$5.3095(51)$</td>
</tr>
<tr>
<td>$B$</td>
<td>$0.30658769(76)$</td>
<td>$B$</td>
<td>$0.30658769(76)$</td>
</tr>
<tr>
<td>$D_J$</td>
<td>$1.1321(11)x10^{-7}$</td>
<td>$D_J$</td>
<td>$1.1321(11)x10^{-7}$</td>
</tr>
<tr>
<td>$D_{JK}$</td>
<td>$6.1443(39)x10^{-6}$</td>
<td>$D_{JK}$</td>
<td>$6.1443(39)x10^{-6}$</td>
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<tr>
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<td>$8.8882(20)x10^{-5}$</td>
<td>$D_K$</td>
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<tr>
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<td>$\Delta s^2$</td>
<td>$2.230(15)$</td>
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<tr>
<td>$\eta_J$</td>
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<td>$\eta_J$</td>
<td>$-1.358(31)x10^{-6}$</td>
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<tr>
<td>$\eta_K$</td>
<td>$-4.572(29)x10^{-5}$</td>
<td>$\eta_K$</td>
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<tr>
<td>$\eta_J'$</td>
<td>$-4.58(13)x10^{-5}$</td>
<td>$\eta_J'$</td>
<td>$-4.58(13)x10^{-5}$</td>
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<tr>
<td>$\eta_K'$</td>
<td>$-1.604(77)x10^{-7}$</td>
<td>$\eta_K'$</td>
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<tr>
<td>$\Sigma_T^*$</td>
<td>$+2.93(11)x10^{-10}$</td>
<td>$\Sigma_T^*$</td>
<td>$0.2015(10)$</td>
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</table>

Notes: (a) Figures in brackets represent one standard deviation to be added to last quoted figures. (b) Kondo and Person (11), (c) Bauer and Godon (7). (d) Boucher et al. (6); $H_J$, $H_{JK}$, $H_K$ also included.

About 1078 cm$^{-1}$. Taking $\delta_2$ from the $\nu_8$ microwave data (5), the Fermi resonance condition shows that the states $K' = 7, 8$ (+1) will be close to resonance. Duncan et al. (17) estimated the interaction matrix element to be of order 1 cm$^{-1}$, and although this is a minor resonance in the conventional high-resolution infrared spectrum, on the level of laser-Stark measurements it is a major perturbation.

Two observations concerning the Fermi resonance term allow a simplification of the treatment of this interaction. First, since the Fermi matrix element is in-
dependent of $J$ its effect on a particular state will not depend on the degree of Stark mixing in that state. Second, because the matrix element is diagonal in all rotational quantum numbers, the separation of the interacting states will only depend on the Stark field as a result of the small difference in dipole moments.
TABLE II—Continued

<table>
<thead>
<tr>
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<th>J'</th>
<th>K'</th>
<th>6</th>
<th>J''</th>
<th>K''</th>
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<th>Ee (GHz)</th>
<th>Freq(cm)</th>
<th>Shift</th>
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<td>6</td>
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<td>16618</td>
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**TABLE II—Continued**

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The Fermi perturbed energies of the \( \nu \) the quadratic secular equation for the \( i \) were approximated using ground-state the coefficient of the vibrational angular floating parameters in the fit. These p Hamiltonian described above, which w Stark shifted energy.

The microwave data of Bauer and a weight of \( (\sigma_o / \sigma_{mw})^2 = (5 \text{ MHz/0.0}) \) data. The values of the constants \( B_u, \lambda \) determined by the microwave data. T to the microwave values of Boucher et was included in the fit. A few laser-Stark In these cases both possibilities were ir of \( 1/4 \). A complete list of the data inc field frequencies and residues is given
between the two states. Since the dipole moment in the $3\nu_8$ state is not known and can at best be assumed equal to that in $\nu_7$, these two factors allow the Fermi interaction to be treated separately from the full diagonalization described above.

In expanding the vibrational potential energy, contributions to the Fermi interaction are derived from products of the vibrational momenta and coordinate ladder operators; in general one for $\nu_7$ and three for $\nu_8$ to give coupled states $|J, k, \nu_7 = 1, l = +1\rangle$ and $|J, k, \nu_8 = 3, l = +1\rangle$. Since it is impossible to separate the various contributions from our measurements, all of the terms were included in a single energy, $W_{7888}$. The same states must also be coupled through a $k$-dependent $z$-Coriolis term. Calling the Coriolis energy $W_k$, the combined coupling term, $H_f$, is conveniently written as

$$H_f = W_{7888} - W_k kl.$$  \hfill (7)

The Fermi perturbed energies of the $\nu_7$ states were therefore calculated by solving the quadratic secular equation for the interacting $\nu_7$ and $3\nu_8$ states. The $3\nu_8$ energies were approximated using ground-state constants, except that the band center and the coefficient of the vibrational angular momentum term, $A_{\text{eff}}$, were included as floating parameters in the fit. These perturbed energies were then included in the Hamiltonian described above, which was diagonalized to give the final Coriolis and Stark shifted energy.

The microwave data of Bauer and Godon (8) was also included in the fit with a weight of $(\sigma_u/\sigma_{\text{mw}})^2 = (5 \text{ MHz}/0.05 \text{ MHz})^2 = 10^4$, relative to the laser Stark data. The values of the constants $B_k$, $D_{jk}^b$, and $D_{jk}^x$ are therefore almost completely determined by the microwave data. The ground-state constants were constrained to the microwave values of Boucher et al. (6), but the ground-state dipole moment was included in the fit. A few laser-Stark lines could be assigned to two transitions. In these cases both possibilities were included in the fit, each with a relative weight of $1/4$. A complete list of the data included in the fit together with predicted zero field frequencies and residues is given in Table II.
DISCUSSION

The values of the molecular constants determined in the final fit are presented in Table I, together with some previously reported values for comparison. As already noted, the expected precision of our measurement is a few megahertz. After eliminating a small number of overlapped and skew lines, the worst fit to the infrared data is 30 MHz, which is about a Doppler half-width. All remaining lines are well resolved according to the Rayleigh criterion, and the standard deviation of the laser Stark fit is 7 MHz; close to the experimental measurement precision. It would be arguably more correct to weight individual measurements according to the expected precision, which is a function of signal-to-noise, laser line, Stark shift, etc. It is doubtful, however, if this would have any significant effect on the derived constants. The standard deviation of the microwave data, which was 60 kHz in the original analysis (8), is reduced to 40 kHz by the inclusion of the Coriolis interaction. The poor fit around $K = 7$ observed by Moskienko and Dyubko (15) in the $v_4 = 1$ microwave spectrum at high $J$ is now explained as being due to the Fermi resonance in $v_7 = 1$, the effect of which is transferred to $v_4$ by the Coriolis interaction. The effect is not observed in the low-$J$ microwave data included in the fit because of the $(J(J + 1) - K(K + 1))^{1/2}$ dependence of the Coriolis term.

It is interesting to note that, away from the Fermi resonance, the observed spectra can be superficially fitted very well with a much simpler model than that used here. For example, by taking a carefully selected set of strong, isolated, symmetrical lines, a $v_4$ fit can be obtained with a standard deviation of 3.5 MHz (20). Neglecting the Fermi and Coriolis interactions, a restricted $v_4$ fit yields well-determined values for the rotational constants, but some of these, notably $B_3$ and $D_K$, are quite different from the ground state and from the parameters determined here. This emphasizes the need to use a sufficiently complete Hamiltonian for analysis at such high resolution if any clear meaning is to be given to the resulting constants in, for example, force field calculations. Table I shows that the centrifugal terms have only small variations from state to state, and that the $\eta$ and $q$ terms are well determined, as are the Fermi and Coriolis terms coupling $v_7$ and $3v_8$. These observations all imply that the model used is both necessary and adequate. We do note, however, that there are strong correlations between $v_7$, $W_{7888}$, and between $B_3^{12}$.

The higher-order $l$-doubling terms $q'_7$ and $q''_7$ were included in the analysis at a late stage, in order to improve the fit of the transitions to high-$J'$ $l$-doubled states. From the values given in Table I, the contribution to the energy from $q'_7$ will be larger than the standard deviation of the fit for $J' > 6$, and that from $q''_7$ for $J' > 9$. These coefficients are therefore essentially determined by five transitions involving $J' = 7, 10, 13, 16,$ and 22. In previous laser Stark analyses these coefficients have only been determined once, for CD$_3$Cl, by including high-$J$ direct $l$-doubling microwave transitions in the fit ($J$). The relative sizes of the coefficients determined here are similar to those for CD$_3$Cl, and the relative signs are the same, the effects of $q'_7$ and $q''_7$, respectively adding to and subtracting from the effect of $q_7$.

The sign of the Fermi interaction term $W_{7888}$ is not determined, although the relative signs of this term and the $z$-Coriolis term $W_4$ are found to be the same.

About 200 observed Stark transitions remain unassigned. A number of these may have been due to the $3v_8$ band, but difficult because $(A-B) \sim A_2^{12}$ in the $u_{ij}$ the perpendicular band structure and $\pi$ turn number. It is for this reason that $t$ for $3v_8$, even though the $v_7$, $3v_8$ interact remaining transitions must belong to

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LASER STARK SPECTROSCOPY OF CH$_3$CN

may have been due to the 3$v_8$ band, but assignment of transitions in this band is difficult because $(A-B) \sim A^*_1$ in the upper state. This has the effect of collapsing the perpendicular band structure and making it difficult to determine the $K$ quantum number. It is for this reason that the rotational constants are not determined for 3$v_8$, even though the $v_7$, 3$v_8$ interaction can be well characterized. Many of the remaining transitions must belong to hot bands involving $v_8$ or 2$v_8$ (9).

CONCLUSION

About 550 lines have been measured in the Stark spectrum of the $v_4$ and $v_7$ bands of CH$_3$CN near 10 $\mu$m. These have been combined with microwave data on the ground and $v_4$ vibrational states to yield a precise set of molecular parameters describing the $v_4$ and $v_7$ states and the interactions between $v_4$, $v_7$, and 3$v_8$.

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