The $v_7$, $v_8$, and $v_{11}$ bands of propynal, $C_2HCHO$, in the 650 cm$^{-1}$ region

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1. Introduction

Propynal is a simple six-atomic aldehyde that may be thought of as an acetylene molecule with a carbonyl group substituting for one hydrogen atom, or alternately as a formaldehyde molecule with a $C_2H$ group substituting for one hydrogen atom. Although it is not commercially available, propynal can be prepared relatively easily and stored indefinitely with refrigeration. It also remains reasonably stable at room temperature as a low pressure gas. Propynal has been detected by radio astronomy in interstellar clouds [1] where its abundance and formation mechanism have been of special interest [2].

Microwave spectra of propynal were first reported in 1955 by Howe and Goldstein [3]. Subsequently, Costain and Morton [4] obtained a molecular spectrum based on microwave observations of fifteen isotopic species. A more detailed study of the ground vibrational state, based on microwave and millimeter wave data, was reported by Winnewisser [5]. Propynal exhibits a rich electronic spectrum in the violet to near ultraviolet region, which was studied in detail by Brand et al. [6,7]. Based on this work, and on low resolution infrared and Raman spectra [8,9], a complete assignment of all twelve vibrational modes was obtained [7]. More recently, the electronic spectrum of propynal has been utilized for a variety of studies involving quantum beat spectroscopy, inter-system crossing effects, radiationless transitions and stimulated emission pumping [10].

However, infrared studies of propynal since the original work of [8,9] have been relatively limited, and, to our knowledge, the present paper represents the first broad band high resolution infrared study of propynal. Takami and co-workers [11–13] reported a series of infrared-microwave double resonance measurements of propynal isotopes which revealed numerous perturbations in the rotational levels of excited states around 3000 cm$^{-1}$. Jones [14] reported somewhat similar double-resonance and two-photon data based on CO$_2$ laser probes in the 940 cm$^{-1}$ region, and also gave some preliminary excited state microwave results. Ultraviolet–infrared double resonance has also been demonstrated [15]. Finally, in 1996 Tavladorakis and Parkin reported medium-resolution infrared spectra of the propynal isotope $C_2HCD_2O$ in the 670 cm$^{-1}$ [16] and 3325 cm$^{-1}$ [17] regions.

In this paper, we analyze the spectrum of normal propynal, $C_2HCHO$, in the 570–740 cm$^{-1}$ region as recorded at a resolution of about 0.003 cm$^{-1}$ with a sample temperature and pressure of about 215 K and 0.15 Torr, respectively. This region includes the strong $v_7$ (~651 cm$^{-1}$) and $v_{11}$ (~693 cm$^{-1}$) fundamental bands, as well as the somewhat weaker $v_8$ (~614 cm$^{-1}$) fundamental band, and the $3v_9$ level (~618 cm$^{-1}$) which is mixed with $v_8$. The extensive Coriolis- and Fermi-type interactions among these excited vibrational states ($7^1, 11^1, 8^1$, and $9^3$), and with additional states not explicitly considered here, result in a rather challenging analysis. This challenge involved not so much the rotational assignments of transitions (though these were sometimes tricky) but rather the effort to fit all the assigned lines to something approaching the experimental precision. In the end, we believe that we have achieved a good understanding of these vibrational states and their interactions.

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2. Experimental details

Previous spectroscopic investigators have usually prepared propynal by means of the oxidation of propargyl alcohol with chromic oxide. We used instead a method described by McNab et al. [18] involving vacuum pyrolysis of commercially available ethyl propiolate (diprop-2-ynyl ether) at about 750 °C, following their recipe closely except that we used two liquid nitrogen traps following the quartz pyrolysis tube. At first, we were disappointed by the results since the infrared spectrum of the pyrolysis product seemed to indicate the presence of mostly propyne and acetylene (and likely also allene), with little propynal. But then we obtained good results after realizing that the real propynal was the least volatile portion of our product, a pale yellow liquid which remained when the sample was warmed to room temperature.

The spectra were recorded using the full resolution of a modified [19] Bomem DA8 Fourier transform spectrometer (maximum optical path difference = 4.5 m, nominal unapodized resolution ~0.0022 cm$^{-1}$, measured line widths ~0.0027 cm$^{-1}$). The 2 m absorption cell [20,21] was set for a path length of 8 m, and cooled to a temperature of about 215 K in order to reduce the strength of hot bands in the spectrum. Two spectra were obtained, with sample pressures of about 0.14 and 0.22 Torr, covering the range 570–740 cm$^{-1}$. This resulted in very strong absorption in the central region around 660–680 cm$^{-1}$, and in retrospect we should also have recorded a spectrum with significantly lower pressure in order to clarify the central region (though it is so congested that higher resolution would also be required). As well, it later became evident that we should have recorded a wider spectral range, since weak, but easily assigned, propynal transitions continue below 570 and above 740 cm$^{-1}$, even at 215 K.

3. Results and analysis

3.1. The propynal molecule

Propynal is a planar near-prolate (A $>$ B $\approx$ C) asymmetric rotor belonging to the C$_{2v}$ point group, with a notably large A rotational constant of 2.27 cm$^{-1}$. Its vibrational states [7] in the energy range below 800 cm$^{-1}$ are shown in Fig. 1. The ground state and in-plane vibrations have A$^\prime$ symmetry, while out-of-plane fundamental vibrations and their odd multiples have A$^\prime$$'$ symmetry. In Fig. 1, the A$^\prime$ vibrational states are labeled in normal type and the A$^\prime$$'$ states are labeled in italics. The vibration-rotation bands linking two states of the same symmetry, or two states of different symmetry, or states X and Z of different symmetry, were as follows:

\[
\langle X, k | H | Y, k \rangle = W(X, Y) + Z_k(X, Y)k^2
\]
\[
(X, k | H | Y, k, \pm 1) = (1/2)(\pm G(X, Y)
\]
\[
\pm Z_k(X, Y)(2k \pm 1)) \times [J(J + 1) - k(k \pm 1)]^{1/2}
\]
\[
(X, k | H | Y, k, \pm 2) = (1/2)Z_1(X, Y)(J(J + 1) - k(k \pm 1))
\]
\[
\times [J(J + 1) - k(k \pm 1)]^{1/2}
\]
\[
(X, k | H | Z, k) = |G_0(X, Z) + Z_6(X, Z)k^2|k
\]
\[
(X, k | H | Z, k, \pm 1) = (1/2)G_0(X, Z) \times [J(J + 1) - k(k \pm 1)]^{1/2}
\]
\[
(X, k | H | Z, k, \pm 2) = \pm (1/2)Z_6(X, Z)(J(J + 1) - k(k \pm 1))
\]
\[
\times [J(J + 1) - k(k \pm 1)]^{1/2}
\]

Here, W is the homogeneous (Fermi-type) parameter, G_0, G_6, and G are Coriolis parameters, and the Z are higher order parameters. When Fermi interactions were present, we fitted in terms of the perturbed band origins (the actual positions of the J_0 = 0_{00} levels) since these are physically well-determined and the resulting fit is less highly correlated [27] than if the deperturbed band origins are used.

The analysis began by using the propynal ground state rotational parameters determined by Winnewisser [5]. However, small discrepancies were noted in ground state combination differences for higher values of K_a, for example a discrepancy of about 0.01 cm$^{-1}$ for the interval K_a = 6 to 8. This problem arises because it was not possible for Winnewisser to determine a value for the parameter K_c. We therefore re-fitted the data of [5] together with a limited set of our own combination differences to determine a new set of ground state parameters, as listed in the last column of Table 1. These are essentially equivalent to those in [5] except for our inclusion of K_c and use of the A-reduced Hamiltonian.

3.2. The $v_7$ and $v_{11}$ fundamental bands

An overview of the propynal spectrum studied here is shown in Fig. 2. As noted by Tavladorakis and Parkin [16] in their medium-resolution study of the $v_7$ and $v_{11}$ fundamentals of the isotopomer
absorbing regions above the m 7 origin, and below the m 7 origin, the strongest absorption features are piled up in the crowded region between the m 7 and m 11 band origins. C3HCO, the large a-type Coriolis interaction between these vibrations has two dramatic effects. First, it greatly increases the effective A rotational constant of the 11 1 state and decreases that of the 7 1 state. Second, it causes a transfer of intensity from the r-type (ΔK′ = +1) to p-type (ΔK′ = −1) subbands of the v11 band and conversely from the p-type to r-type subbands of the v7. A combination of these effects results in the pile-up of intense absorption in the region between the v7 and v11 band origins which is evident in Fig. 2.

Our analysis began in the less crowded and more weakly absorbing regions above the v11 origin and below the v7 origin, with perpendicular subbands for higher Kc-values where asymmetry doubling was not resolved. As the assignments proceeded, we moved in towards the central region for the subbands involving K′c = 3, 2, 1, and 0 for which asymmetry effects are significant. The process was reasonably straightforward, and from the beginning we included the v7/v11 Coriolis interaction in a two-state fit. To illustrate the spectrum, Figs. 3 and 4 show a series of observed and simulated Q(Jm) branches for v7 and Q(Jm) branches for v11. Although some transitions in these Q-branches were included, the main foundation of the fit was provided by PP(J) lines for v7 and by RR(J) lines for v11, which are widely-spaced and tend to be unblended and easy to assign. In contrast, the r-type subbands of v7 and p-type subbands of v11 tended to be impossibly congested, and the parallel a-type component (ΔK′ = 0) of v7 was relatively weak (and also congested).

After assigning hundreds of transitions for each of the v7 and v11 bands, we found that it was not possible to obtain a satisfactory fit, even with the two-state Hamiltonian including Coriolis and higher-order parameters. It was evident that there must be further relevant interactions involving additional vibrational states, and we thus turned our attention to the v8 band, expected [7] to be centered at 614 cm−1.

3.3. The v8 fundamental band and the 8 1-9 1 interaction

In the region around 575–595 cm−1, where we had already assigned some p-type subbands of v7 (Fig. 3), there were additional Q(Jm) branches which could be assigned without too much difficulty to the v8 band. These are illustrated in Fig. 5. For K′c = 5 to 8. The inclusion of these new data in a three-state analysis resulted in a notable improvement to the fit of the existing v7 and v11 band transitions. But the quality of the fit was still much worse than the experimental accuracy. Moreover, it proved difficult to extend the assignment of the v8 band to lower values of K′c. We managed to locate K′c = 4, for which the Q(Jm)–branch is located near 596.55 cm−1 (not shown here), but these levels were seriously displaced (≈0.1 cm−1) to higher wavenumber from the positions expected on the basis of the fit to K′c = 5 to 8. Many checks, alternate assignments, and higher-order parameters were tried, but there was no way that a three-state analysis could account for our data. The fits of the v7 and v11 bands were (by now) not so bad, but a meaningful fit to the v8 band seemed hopeless.

A long struggle to achieve a satisfactory analysis then took place, but we will not attempt to describe this struggle in detail. Clearly there were significant interactions involving one or more additional vibrational states, and it was not difficult to identify the most likely culprit, namely the 9 3 state (see Fig. 1). On the basis of previous data [7], we expected the origin of 9 3 to be 615.9 cm−1 (harmonic approximation), just 2.2 cm−1 above that of 8 1. Our eventual successful solution of the analysis struggle involves a four-state Hamiltonian (9 1, 8 1, 7 1, 11 1). It is difficult to be sure that this solution is unique in all details, but we believe that it is substantially correct. As outlined below (Section 4.3), the remaining discrepancies can probably be accounted for in terms of a fifth interacting state, 9 12 (see Fig. 1), which, however, we did not include. A satisfying aspect of the four-state fit is that it enabled us to locate and assign the “missing” transitions of the v8 band involving the K′c = 0, 1, 2, and 3 levels. Indeed, for K′c = 3, we observed both the 8 1 (“bright”) and 9 1 (“dark”) upper states, which turn out to be almost completely mixed.

Fig. 2. An overview of the observed spectrum of propynal at 215 K. The origins of the three fundamental bands studied here, which are indicated, are not particularly obvious in the spectrum. The strongest absorption features are piled up in the crowded region between the v7 and v11 band origins.

<table>
<thead>
<tr>
<th>11 1</th>
<th>7 1</th>
<th>9 1</th>
<th>8 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>692.770(1)</td>
<td>651.314(1)</td>
<td>618.192(1)</td>
</tr>
<tr>
<td>A</td>
<td>2.28071(421)</td>
<td>2.24841(430)</td>
<td>1.889140(240)</td>
</tr>
<tr>
<td>B</td>
<td>0.160913(22)</td>
<td>0.1611490(13)</td>
<td>0.1632442(145)</td>
</tr>
<tr>
<td>c</td>
<td>0.15017801(73)</td>
<td>0.15012496(71)</td>
<td>0.1512492(166)</td>
</tr>
<tr>
<td>(10^7 \times A_c)</td>
<td>0.3145(292)</td>
<td>0.2792(299)</td>
<td>0.6127(139)</td>
</tr>
<tr>
<td>(10^5 \times K_c)</td>
<td>-0.6383(17)</td>
<td>-0.3417(22)</td>
<td>-0.266(30)</td>
</tr>
<tr>
<td>(10^5 \times K_c)</td>
<td>0.63972(95)</td>
<td>0.63735(98)</td>
<td>0.6380</td>
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<tr>
<td>(10^3 \times \Delta \omega_{a})</td>
<td>0.1159</td>
<td>0.1159</td>
<td>-0.165(67)</td>
</tr>
<tr>
<td>(10^2 \times J_{a})</td>
<td>0.11528</td>
<td>0.11528</td>
<td>0.11528</td>
</tr>
<tr>
<td>(10^2 \times \Delta \omega_{b})</td>
<td>0.15(32)</td>
<td>-0.152(294)</td>
<td>-15.5(84)</td>
</tr>
<tr>
<td>(10^2 \times \Delta \omega_{c})</td>
<td>0.2756</td>
<td>-0.2756</td>
<td>-0.2756</td>
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<tr>
<td>(10^3 \times \Delta \omega_{d})</td>
<td>-0.237</td>
<td>-0.237</td>
<td>-0.237</td>
</tr>
</tbody>
</table>

Table 1

Vibrationally diagonal parameters for the coupled 11 1, 7 1, 9 1, and 8 1 states from a 4-state fit and for the ground state of propynal in cm−1:

- Quantities in parentheses correspond to 1σ from the least-squares fit. Parameters without an uncertainty were fixed at the indicated values. These parameters go together with those in Table 2.
- These are the perturbed vibrational origins (see text), that is, the actual energies of the \(J_{acs}=\theta_0\) levels. The deperturbed origins are: 617.5954 and 614.6113 cm−1.
unexpected for the following reason: even though the origin of $9^1$ is slightly above that of $8^1$, its effective $A$ rotational constant is considerably smaller. Thus the $K'_0 = 0, 1, 2$ levels of $9^1$ lie above those of $8^1$ (so the Fermi interaction “pushes” these $8^1$ levels down), but the $K'_0 = 4, 5, 6, \text{ etc.}$ levels of $9^1$ lie below those of $8^1$ (so the Fermi interaction pushes these $8^1$ levels up). The $K'_0 = 3$ levels of the two states are almost coincident in zeroth order, and so become highly mixed by the Fermi interaction. The situation is illustrated in Fig. 6, which is a calculated energy level diagram showing $J = 12$ levels of the $8^1$ and $9^1$ vibrational states. The deperturbed (zeroth order) levels are on the outside, and the actual (perturbed) levels on the inside, as indicated at the top of the figure. Perturbations of higher ($K'_0 > 5$)
levels become progressively smaller since $8^1$ and $9^1$ become increasingly out of step with each other, which explains why the $K_a = 4$ levels of $8^1$ were observed to be pushed up relative to our original expectations. The $K_a = 0$–3 levels are massively affected, which explains why we originally could not find them at all.

### 3.4. The four-state fit

Our final fit included a total of about 1400 transitions, of which about 670 were from the $m_7$ band, 420 from the $m_{11}$ band, and 310 from the $m_8$ band (including a few perturbation-allowed transitions of $3m_9$). These are listed in Tables A1, A2, and A3 of the Appendix. The data include many transitions with values of $J$ up to about 40, and, in a few cases, 49. The range of $K_a$-values is from 0 to 11 for the $m_7$ band, from 0 to 7 for $m_{11}$, and from 0 to 9 for $m_8$. Transitions which were blended, very weak, or very strong (saturated) were given weights of 0.1 or zero in the fit. The choice of which parameters to vary was difficult, and necessarily somewhat arbitrary. In the end we settled on a set of 47 parameters, with results as listed in Tables 1 and 2. The quality of the fit was quite good, with root mean square deviations of only about 0.0003 cm$^{-1}$ for 1179 transitions with unity weight, 0.0008 cm$^{-1}$ for 134 transitions with weight of 0.1, and 0.010 cm$^{-1}$ for 92 transitions with zero weight. Many of the zero weight transitions occur in regions of local perturbations, as discussed below in Section 4.3.

With the help of the PGopher program [23], we attempted to get an approximate idea of the relative values of the various transition dipole moments involved in the spectrum. Starting with an arbitrary $c$-type transition moment of 1.0 for the $m_{11}$ band, satisfactory agreement with the observed spectrum was obtained with the following relative dipole moments: 1.0 for the $m_7 b$-axis component, 0.25 for the $m_7 a$-axis component, 0.25 for the $m_8 b$-axis component, 0.15 for the $m_8 a$-axis component, and zero for the $3m_9$ band moments.

### 4. Discussion and conclusions

#### 4.1. General discussion of parameters

The band origin determined in 1963 by Brand et al. [7] for $v_{11}$, 692.7 cm$^{-1}$, is in almost perfect agreement with our value of

![Fig. 4. Portions of the observed (upper traces) and simulated (lower traces) of propynal, showing 'Q_0(J)' branches of the v_{11} band.](image-url)
692.7707 cm\(^{-1}\), while their value for \(v_7\) was low by 1.3 cm\(^{-1}\) (650.0 vs. 651.3413 cm\(^{-1}\)), and that for \(v_8\) was low by 0.3 cm\(^{-1}\) (613.7 vs. 614.0146 cm\(^{-1}\)). The large \(a\)-type Coriolis interaction between the 71 and 111 vibrational states is characterized by the parameter \(G_{a}(71,111) = 4.26\) cm\(^{-1}\), which implies a value of about \(f_{71,111} = 0.939\) for the dimensionless Coriolis zeta, slightly larger than previous determinations of 0.922 [7] or 0.92 (for C\(_2\)HCD) [16]. If one tries to fit the spectrum (or energy levels) without including this interaction, then one obtains quite disparate values for the \(a\)-axis parameters: for example, effective \(A\) and \(\Delta_{ae}\)-values of about 1.84 and -0.0024 cm\(^{-1}\) for the 71 state and about 2.70 and +0.0028 cm\(^{-1}\) for 111. But with the Coriolis interaction properly accounted for, these parameters retain their normal values, as seen in Table 1 where the \(A\) values for 71, 111, and the ground state are all within 0.033 cm\(^{-1}\) of one another. The \(B\) and \(C\) rotational constants in these two excited states also change very little (<0.1%) from the ground state values.

![Image](59x163 to 277x726)

**Fig. 5.** Portions of the observed (upper traces) and simulated (lower traces) of propynal, showing \(Q_k(j)\) branches of the \(v_6\) band.

![Image](366x419 to 508x726)

**Table 2**

<table>
<thead>
<tr>
<th></th>
<th>(X, Y)</th>
<th>(Z, 8^1)</th>
<th>(8^1, 9^1)</th>
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<tbody>
<tr>
<td>(W(X, Y))</td>
<td>0.0</td>
<td>1.46180(81)</td>
<td></td>
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<tr>
<td>(Z(X, Y))</td>
<td>0.0</td>
<td>-0.009139(100)</td>
<td></td>
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<tr>
<td>(G(X, Y))</td>
<td>0.0</td>
<td>0.008038(32)</td>
<td></td>
</tr>
<tr>
<td>10(^3) (Z(X, Y))</td>
<td>-0.1294(21)</td>
<td>0.0319(58)</td>
<td></td>
</tr>
<tr>
<td>10(^4) (Z(X, Y))</td>
<td>0.0</td>
<td>0.805(58)</td>
<td></td>
</tr>
<tr>
<td>(X, Z)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Z, 11^1)</td>
<td></td>
<td>11^1, 8^1</td>
<td></td>
</tr>
<tr>
<td>(G(X, Z))</td>
<td>4.2599(209)</td>
<td>0.8326(67)</td>
<td></td>
</tr>
<tr>
<td>(G(X, Z))</td>
<td>0.07729(34)</td>
<td>-0.07713(55)</td>
<td></td>
</tr>
<tr>
<td>10(^3) (Z(X, Z))</td>
<td>-1.25(13)</td>
<td>0.00416(21)</td>
<td></td>
</tr>
<tr>
<td>10(^4) (Z(X, Z))</td>
<td>0.249(65)</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

*Quantities in parentheses correspond to 1\(\sigma\) from the least-squares fit. These parameters go together with those in Table 1.*
Interestingly, we also determined a smaller but still substantial α-type Coriolis interaction connecting the 81 and 111 states. G_α(81, 111) = 0.83 cm^{-1}. Since 71 and 111 are already highly mixed, this automatically gives an effective mixing of 81 and 71, which becomes stronger as K_a increases, and which is important since 71 is located closer to 81 than is 111. But the most significant perturbation of the 81 state is due to 91, as already mentioned. Our analysis indicates that the unperturbed origin of 91 lies just 2.98 cm^{-1} above that of 81, a separation which increases to 4.18 cm^{-1} when the Fermi interaction is “turned on”. This interaction was illustrated in Fig. 6 and is further explored below in Section 4.2. Its consequences are particularly prominent because the values of the rotational constants, A and (B + C)/2, are rather different for the two states, which results in many level crossings.

Since only a few transitions actually involving the 93 state were observed, one might question whether the values obtained here for its rotational constants (Table 1) are meaningful. It seems reasonable that the effective A value in 93 should be low, as observed, since we expect a substantial α-type Coriolis interaction between the γ_9 and γ_12 modes. More quantitatively, we can estimate the effects of this interaction on the 93 state by setting up a four-state calculation involving the 91, 9′12, 9′12, and 9″12 states (see Fig. 1). We assume that each state starts with ground state rotational parameters, and that their successive separations are 61.2 cm^{-1}, as given by the harmonic approximation and the fundamental frequencies from [7]. In the calculation, the actual interactions between 91 and 9′12, and between 9′12 and 9″12, are expected to be √3 × G_α(9, 12), and that between 9″12 and 9′12 is expected to be 2 × G_α(9, 12), where G_α(9, 12) denotes the α-type Coriolis interaction between the fundamental states 91 and 121. It then turns out that a value of about G_α(9, 12) = 2.65 cm^{-1} is needed in order to give an effective value of A = 1.89 cm^{-1} as observed for 93. This implies that A_93 = 5.82, which is a bit smaller than the value of 6.39 obtained from the electronic spectrum [7]. In other words, the effective A-value for the 93 state should be at least as small as we obtained, if not slightly smaller. Turning to the B and C values, we know from early microwave work on propynal [3] that the value of (B + C)/2 for the 93 state is about 0.26% higher than in the ground state, and on this basis our value for 93, which is about 1.1% higher than the ground state, seems acceptable. Moreover, in 1980 Jones [14] reported an approximate determination of B and C for the 93 state, based on unpublished microwave data. These values (0.1628 and 0.1511 cm^{-1}) are quite close to ours (0.1632 and 0.1512 cm^{-1}), especially considering the fact that his analysis may have been contaminated by effects of the interaction with the 81 state. In conclusion, we believe that the 93 state parameters in Table 1 are realistic, although direct observation of a wider range of transitions involving this state would of course be desirable.

Returning to the well-characterized states 111, 71, and 81, we can also compare our B and C values with those of Jones [14], bearing in mind that we do not expect perfect agreement since our analysis incorporates various Coriolis and Fermi interactions while his single-state analysis gives effective parameters. The agreement is actually rather good (better than 0.00014 cm^{-1} or 0.05%), as long as we interchange Jones’ labels for γ_7 and γ_9, which were only tentative since they were based on small differences in observed microwave intensities.

4.2. General discussion of perturbations

There are many perturbations in the propynyl spectrum analyzed here. Some of these are global in nature, affecting many rotational levels, like those caused by the large α-type Coriolis interaction between the 111 and 71 states which become especially significant as K_a increases. Other perturbations are local in nature, affecting a limited number of levels, particularly where a series of levels of one vibrational state crosses a series from another state. The various perturbations can be examined in detail using the listing of calculated energy levels given in Table A4 of the Appendix, which is based on the molecular parameters from Tables 1 and 2. However, the limits of validity of this table should be kept in mind; for example, our observations of the v11 band extend only up to K_a = 7, so the calculations beyond this point represent an extrapolation. In particular, the calculated levels for the 93 state are obviously less certain than the others since only a few transitions directly involving this state were observed.

Perhaps the most dramatic perturbation encountered here is that affecting the K_a = 3 levels of the 81 and 93 states, which are almost coincident in the zeroth order calculation before the Fermi interaction is turned on, as shown in Fig. 6. The mixing of K_a = 3 is sufficiently large that we were able to observe transitions to both the bright 81 levels and the dark 93 levels. Thus there are two observed P_{90}(J) branches (the first around 598.5 cm^{-1} and the second, somewhat weaker, around 601.3 cm^{-1}), together with accompanying P_{92}(J) branches. Since the first of these P_{90}(J) branches is stronger, it seems evident that the “true” K_a = 3 levels of the 81 state lie below those of the 93 state. However, our computer program actually labels these levels the other way around for J < 18, and we retain this automated labeling in Fig. 6 and Table A4. The explanation of this paradox is straightforward, but a bit subtle. The computer labeling is based on calculated eigenvectors: although the program tries to make intelligent choices, the “winner” tends to be whichever basis state makes the largest contribution to each level. But the 81 state is already fragmented by interactions with 111 and 71, so it tends to be “weakened” in the “competition” with 93. The observed transitions involving the K_a = 3 levels of 93 are included along with the main 81 transitions in Table A3 of the Appendix (but recall that the vibrational labeling is a bit arbitrary). The K_a = 4 and (especially) 2 levels of 81 and 93 are also rather mixed, but for these we were only able to assign transitions to the dominant 81 levels. Transitions to the dark 93 levels were too weak to detect reliably, even though we had a pretty good idea of their expected locations.

4.3. Local perturbations of the 71 state

We observed a series of local perturbations affecting K_a = 9, 10, 11, and 12 levels of the 71 state. For K_a = 9, the crossing is visible as a gap in the P_{90} – branch (see Fig. 3) but it occurs at a J-value higher than our assignments extended. For K_a = 10, there are two level-crossings, the first at J = 22 and another at J = 33. For K_a = 11, there is one crossing at J = 24, and for K_a = 12, there is one at J = 27. These perturbations are quite visible in the relevant P_{90}(J) branches, as illustrated in Fig. 7 for K_a = 9. They could also be assigned in the P_{92}(J) branches for K_a = 10 and part of 11, but not for K_a = 12 because of the cutoff of our experimental spectrum at 570 cm^{-1}. As our analysis proceeded, it became evident that some of these perturbations were almost certainly caused by ∆K_a = 1 interactions with the 93 state (e.g. K_a = 11 of 93 perturbing K_a = 10 of 71). But not all of them, since there was no way to explain two crossings of the K_a = 10 stack. Deciding on the most likely assignment was tricky, but we eventually chose a solution in which the 93 state was responsible for the K_a = 10 crossing at J = 34, and for all the K_a = 9, 11, and 12 crossings. We explicitly included in the final least-squares fit the 71 transitions for K_a = 11, both below and above the crossing point. Interestingly, this perturbation could be fit very well without introducing any new parameters. Even with no direct interaction linking 71 with 93, the existing indirect link (proceeding mostly from 93 through 81 through 111 to 71) was just right! The K_a = 12 levels of 93 responsible for perturbing K_a = 11 of 71 were now effectively pinned down in the fit. This then resulted in a
predicted crossing of the $K_0' = 9 \text{ stack of } 7^1$ by $K_0' = 10 \text{ of } 9^3 \text{ between } J = 45 \text{ and } 46$, in qualitative agreement with the spectrum (Fig. 3). It predicted a crossing of the $K_0' = 10 \text{ stack of } 7^1$ by $K_0' = 11 \text{ of } 9^3 \text{ between } J = 32 \text{ and } 33$, close to what was observed in the spectrum. The quality of the fit here was thus improved, but it was still not great. We blame the remaining disagreement on the effect of the other (as yet unexplained) crossing of the $K_0' = 10 \text{ stack at } J = 22$, and decided to give zero weight to all transitions involving $7^1 \text{ state levels with } K_0' = 10 \text{ and } J > 12$. For the $7^1 \text{ state levels with } K_0' = 12$, the analysis predicted a crossing by $9^3 \text{ levels with } K_0' = 13 \text{ between } J = 29 \text{ and } 30$, again close to what is observed in the spectrum. (Note that there was a labeling problem for the $K_0' = 12 \text{ levels} – \text{see Table A4$.$ However, it was not possible to include any } K_0' = 12 \text{ transitions of } 7^1 \text{ in the analysis, mainly because the } ^9P_{13}(J) \text{ branch was outside the range of our spectrum so that the exact numbering of the } ^9Q_{23}(J) \text{ branch could not be confirmed.}

What about the unexplained crossing of the $K_0' = 10 \text{ stack of } 7^1 \text{ at } J = 22$? It is very likely that this is due to an interaction with the $9^212^1 \text{ state, which lies approximately } 20 \text{ cm}^{-1} \text{ higher than } 7^1 \text{ (see Fig. 1$.$ We estimate that the } K_0' = 9 \text{ levels of } 9^212^1 \text{ should occur very close to } K_0' = 10 \text{ of } 7^1 \text{, based on the four-state calculation described above in Section 4.1$.$ Moreover, it is clear that further perturbations of } 7^1 \text{ by } 9^212^1 \text{ are probable for other } K_0' \text{–values, and it is thus no wonder that we encountered some difficulties in fitting perfectly all these perturbations in the } K_0' = 9 \text{ to } 12 \text{ range without the inclusion of the } 9^212^1 \text{ state. We considered trying an analysis with five (or more) interacting vibrational states, but decided against it for a number of reasons. Most importantly, it was possible to achieve an excellent fit to most of the observed spectrum for } J < 40 \text{ with the four-state analysis reported here. If more states were added, there would be relatively little unexplained experimental data to help constrain their parameters. And if the } 9^212^1 \text{ state were included, then it would be difficult not to include the } 9^112^2 \text{ and } 12^2 \text{ states as well! Furthermore, there are serious practical problems, not so much in the computing power or time required, but rather in the challenge of sorting and labeling the energy levels, which rapidly becomes more difficult as more states are included in a fit.}

### 4.4. Conclusions

The $v_{7}$, $v_{8}$, and $v_{11}$ fundamental bands of propynal, $\text{C}_2\text{HCHO}$, in the 600–700 cm$^{-1}$ range have been observed with high spectral resolution ($\sim 0.003 \text{ cm}^{-1}$) and rotationally analyzed in detail. Coriolis interactions among the three upper states, $7^1$, $8^1$, and $11^1$ are significant and were included in the analysis. A satisfactory fit to the observations could not be achieved without the inclusion of a fourth vibrational state, $9^3$, because there is a significant Fermi-type interaction between $9^3$ and $8^1$ which has important effects on the spectrum. The resulting four-state analysis, which is reported here, accounts very well for most of the observed spectrum for $J$-values up to 40 or 50. We believe that this work represents the first systematic high-resolution infrared study of propynal. In the future, it would be worthwhile to extend this work into the far infrared region in order to study the lowest-lying fundamentals, $v_9$ and $v_{12}$, in the 200–300 cm$^{-1}$ range, and their binary combinations, the $9^2, 9^112^1$, and $12^2$ states in the 500 cm$^{-1}$ range. As well, it should now be relatively straightforward to extend the analysis of the pure rotational spectra of excited vibrational states of propynal by means of microwave, millimeter wave, and far-infrared FT spectroscopy.

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### Appendix A. Supplementary data

Supplementary data for this article (Tables A1–A4) are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jms.2008.09.002.

### References