

Electric resonance optothermal spectrum of the 920 cm^{-1} $\nu_{14} + \nu_{15}$ torsional combination band of acetaldehyde

By S. BELOV, G. T. FRASER, J. ORTIGOSO, B. H. PATE and
M. YU. TRETYAKOV

Molecular Physics Division, National Institute of Standards and Technology,
Gaithersburg, MD 20899, USA

(Received 10 May 1993; accepted 22 June 1993)

The 920 cm^{-1} vibrational band of acetaldehyde (CH_3CHO) has been studied at about 2 MHz (FWHM) resolution using an electric resonance optothermal spectrometer and a tunable microwave-sideband CO_2 laser. Microwave and radiofrequency infrared double resonance and precise combination differences are used to assign the spectrum and verify that it originates from the vibrational ground state of the molecule. The band is observed to have a large A–E torsional tunnelling splitting of 1.45 cm^{-1} , with the A state *higher* in energy than the E state. The $K' = 1$ and 2 levels for the E state have large K splittings of 28.8 GHz and 54.5 GHz, respectively, which are similar to the 37.3 GHz and 58.4 GHz splittings found for the first excited torsional vibration of the ground vibrational state. The above observations demonstrate that the 920 cm^{-1} vibrational state has one quantum of torsional excitation, confirming previous low-resolution assignments of the band to the A' $\nu_{14} + \nu_{15}$ combination vibration, consisting of the CH out-of-plane bend ($\nu_{14} \approx 764\text{ cm}^{-1}$) and the CH_3 torsion ($\nu_{15} \approx 143\text{ cm}^{-1}$). An effect of the previously proposed Fermi-resonance interaction between $\nu_{14} + \nu_{15}$ and ν_9 is seen in the much smaller torsional splitting in the $\nu_{14} + \nu_{15}$ state compared with the ν_{15} fundamental. The observation of a large number of forbidden transitions for the E state suggests that caution should be used when invoking intramolecular vibrational redistribution as the source of spectral congestion in molecules with internal rotors.

1. Introduction

Acetaldehyde has long served as a model system for the development of internal rotation Hamiltonians and the investigation of the role of methyl-top internal rotation in vibrational mode coupling and intramolecular vibrational energy redistribution (IVR). The microwave and far-infrared spectra of acetaldehyde have been extensively studied at high resolution [1–10] leading to $V_3 = 407.9\text{ cm}^{-1}$ and $V_6 = -12.9\text{ cm}^{-1}$ [10] for the two leading terms in the barrier to methyl internal rotation. Although no high resolution mid-infrared spectra have been reported for acetaldehyde, a number of low resolution measurements have been made [11–14] in an attempt to assign the normal-mode vibrations.

Initial normal-mode assignments were made by Evans and Bernstein [11], and confirmed by isotopic measurements by Cossee and Schachtschneider [12]. Hollenstein and Günthard [13] performed even more extensive isotopic studies, which they combined with band contour analysis and solid state measurements to reassign many of the previously accepted normal-mode frequencies for acetaldehyde, which are collected in an NBS (NIST) monograph [15]. Normal-mode frequencies obtained

by Wiberg *et al.* [14], by empirically scaling values calculated from a normal-mode analysis of an *ab initio* force field, are consistent with the Hollenstein and Günthard [13] analysis.

More recent investigations have concentrated on the role of methyl-top internal rotation in vibrational-state mixing in acetaldehyde. Since low frequency modes contribute to most of the density-of-states in high energy regimes an investigation of these modes is essential to a quantitative understanding of IVR. With this as a motivation, Kleiner *et al.* [9, 10] have undertaken an initiative to study the onset of torsional mode coupling with increasing torsional excitation. They have investigated the rotational and far-infrared spectrum of the $v_{15} = 0, 1$, and 2 torsional states of acetaldehyde. Their results predict the yet unstudied $v_{15} = 3$ state to lie at the top of the barrier to internal rotation, and the E component of the $v_{15} = 4$ state to be nearly resonant with ν_{10} at 506 cm^{-1} . The ν_{10} mode is the lowest nontorsional fundamental of acetaldehyde.

At higher energies, near 1746 cm^{-1} , Walters *et al.* [16] have interpreted the spectral congestion observed in the infrared spectrum of the carbonyl stretch of acetaldehyde as resulting from intermode coupling of the CO stretch to background states involving predominantly torsional combination vibrations. Surprisingly, perdeuteroacetaldehyde shows substantially less spectral congestion, despite the larger density of vibrational states and smaller rotational constants for this system. Laser-induced infrared fluorescence studies by Kim *et al.* [17] reveal significant amounts of mode coupling in the C–H stretching region of acetaldehyde, with the amount of state mixing increasing with rotational angular momentum.

In the present investigation we have used a 2 MHz (FWHM) resolution microwave-sideband CO_2 laser electric resonance optothermal spectrometer to study the 920 cm^{-1} band of acetaldehyde, which overlaps the spectra of both the CO_2 and N_2O lasers. The present results add to the small number of high resolution infrared studies of molecules with internal rotation. Such studies require the resolution and rotational and vibrational cooling available from modern molecular beam spectroscopic techniques. Vibrational and rotational cooling is important to remove spectral overlap from the numerous torsional hotbands and K subbands, and high resolution is necessary to resolve the sometimes small torsional splittings.

Figure 1 shows a low resolution Fourier-transform infrared spectrum of acetaldehyde between 700 and 1000 cm^{-1} . Hollenstein and Günthard [13] assign the weak feature at 920 cm^{-1} to the A' symmetry combination band, $\nu_{14} + \nu_{15}$, consisting of the A'' ν_{14} mode, which is predominantly the out-of-plane aldehyde CH bend, and the A'' ν_{15} torsional mode. In their model, the intensity of the 920 cm^{-1} band comes from an unusually strong 21 cm^{-1} anharmonic interaction with the A' , ν_9 , CC stretch, observed at 867 cm^{-1} in figure 1. The large magnitude of this matrix element suggests the importance of vibrational mode couplings involving torsional vibrations in acetaldehyde and indicates the severity of the breakdown of the adiabatic separation of the low frequency torsional mode from the higher frequency normal modes.

Our molecular beam study of the 920 cm^{-1} band reveals large torsional splitting of $\sim 1.45\text{ cm}^{-1}$, with the E tunnelling state below the A tunneling state. These observations are consistent with a vibrational state having one quantum of torsional excitation, verifying the assignment proposed by Hollenstein and Günthard [13]. The 0.3 cm^{-1} reduction of the tunnelling splitting from that of the torsional fundamental is a result of the 21 cm^{-1} Fermi resonance [13] between $\nu_{14} + \nu_{15}$ and ν_9 . This interaction dilutes the torsional splitting of the $\nu_{14} + \nu_{15}$ state with the much smaller

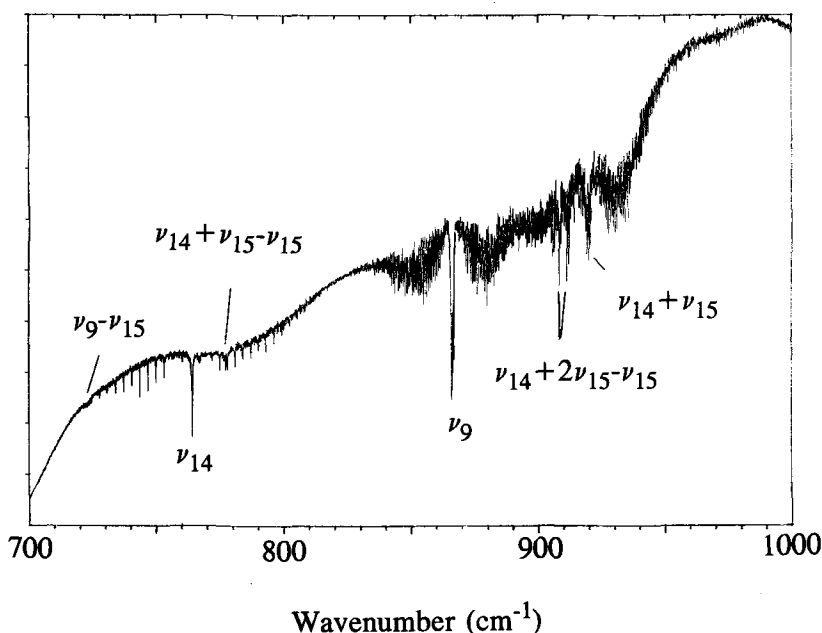


Figure 1. Fourier-transform infrared spectrum of acetaldehyde. The assignments shown, except for those of the $\nu_{14} + 2\nu_{15} - \nu_{15}$ band, are taken from Hollenstein and Günthard [13]. The assignments of the $\nu_{14} + 2\nu_{15} - \nu_{15}$ band are suggested in the present study.

torsional splitting of the ν_9 state. These results show, together with our previous studies on CF_3CH_3 [18], trifluoropropene [19], ethanol [20], propene [21], and 1-butyne [22], that the magnitudes of torsional splittings are a sensitive probe of vibrational state mixing between states of different degrees of torsional excitation. Because of the sensitivity of tunnelling splittings to contamination by vibrational mode coupling, care has to be taken before relating the observed splittings to a barrier height.

In our acetaldehyde study we observed a number of strong forbidden transitions (non *a*- or *b*-type) for the E internal rotor state. These transitions, which are not observed for the A state, arise in the E state from the large diagonal *a*-type Coriolis interaction between *a* axis rotation and the internal rotation angular momentum. Such forbidden transitions may be the source of some of the spectral congestion, attributed to vibrational mode coupling [16, 23], observed in low resolution spectra of acetaldehyde and other molecules with partially hindered internal rotors. An additional source of spectral congestion comes from the tunnelling splittings themselves, which give the spectrum the appearance of two overlapping bands.

2. Experimental

The microwave-sideband CO_2 laser electric resonance optothermal spectrometer used in the present investigation has been described previously [24–26]. A molecular beam of acetaldehyde is formed by an adiabatic expansion of about 5% acetaldehyde in He through a 60 μm nozzle at a stagnation pressure of about 100 kPa. The molecular beam is defined by a 1 mm diameter skimmer located 2.5 cm from the nozzle. Between the nozzle and skimmer, the molecular beam is multiply crossed by

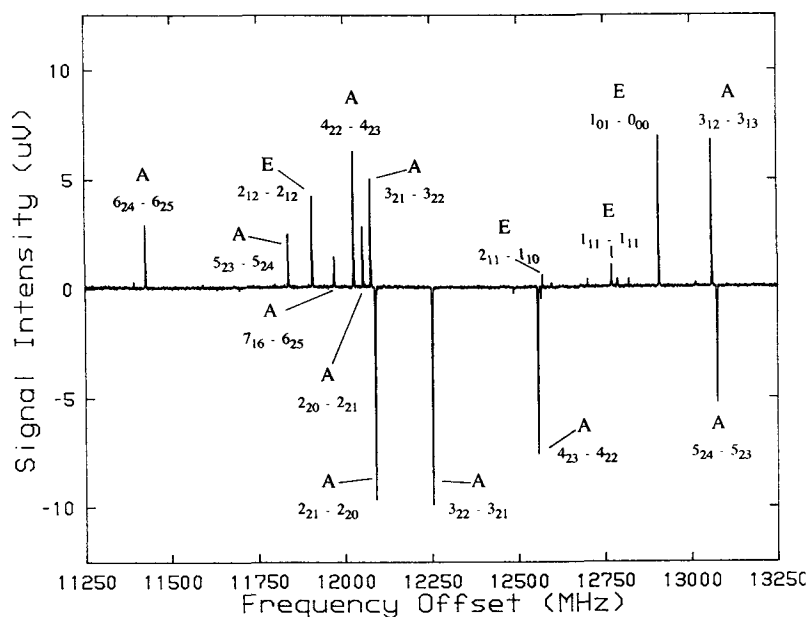


Figure 2. Electric resonance optothermal spectrum of acetaldehyde showing the A, $K=2 \leftarrow 2$ subband. All the transitions are on the lower frequency sideband ('-' sideband) except for the 3₁₂ \leftarrow 3₁₃ and 7₁₆ \leftarrow 6₂₅ A state lines. The CO₂ laser was set to the P(44) line of the 10 μm band at 920.829 122 cm^{-1} . The spectrum was recorded using a 125 ms time constant.

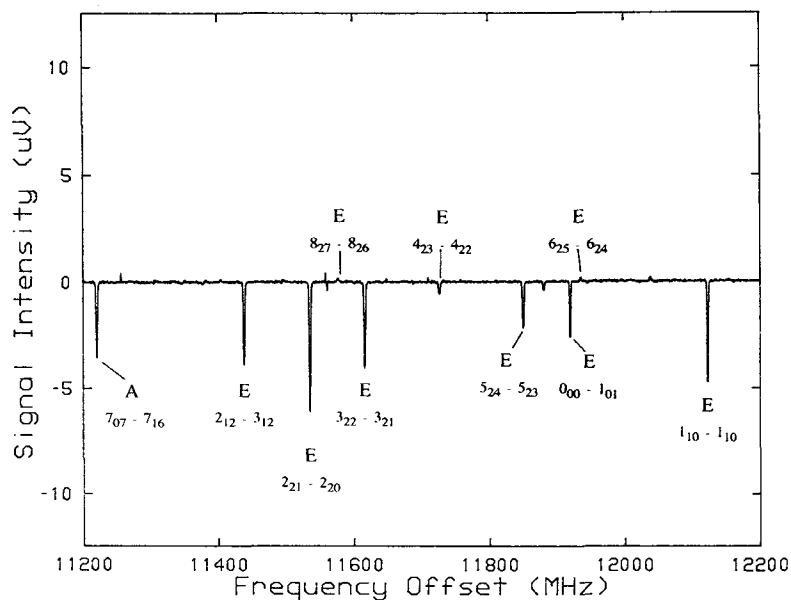


Figure 3. Electric resonance optothermal spectrum of acetaldehyde showing one component of the E symmetry, $K=2 \leftarrow 2$ band. All the transitions are on the higher frequency sideband ('+' sideband) except for the 2₁₂ \leftarrow 3₁₂ E state line. The CO₂ laser was set to the P(46) line of the 10 μm band at 918.718 330 cm^{-1} . The spectrum was recorded using a 125 ms time constant.

the output from a Lamp-dip stabilized CO₂ laser onto which is superimposed tunable microwave sidebands. The sideband power of 1–2 mW is produced by mixing 4–7 W of CO₂ or N₂O laser power with about 20 W of microwave power from a synthesizer-driven travelling-wave-tube amplifier in a stripline GaAs waveguide modulator developed by Cheo [27]. The microwave power is amplitude modulated at about 400 Hz for phase sensitive detection. Microwave and radio-frequency fields are applied between the nozzle and skimmer for double resonance studies.

After the skimmer the molecular beam is collected or focused by a 56 cm long electrostatic quadrupole field onto a liquid-He-cooled bolometer detector. The fact

Table 1. Term values (cm⁻¹) for the 920 cm⁻¹, $\nu_{14} + \nu_{15}$ torsional combination vibration of acetaldehyde referenced to the ground state $J = 0$ level of A symmetry. Also listed are ground state (g.s.) term values from Kleiner *et al.* [29].

J	K _a	K _c	E _A $\nu_{14} + \nu_{15}$	E _E $\nu_{14} + \nu_{15}$	E _A g.s.	E _E g.s.
0	0	0	921.280663	919.827145	0.000000	0.068929
1	0	1	921.921212	920.467226	0.642616	0.711445
1	1	1	923.274163	921.426563	2.202213	2.242416
1	1	0	923.307075	922.645310	2.237740	2.304113
2	0	2	923.201715	921.746973	1.927241	1.995868
2	1	2	924.521900	922.713681	3.451884	3.499517
2	1	1	924.620608	923.931206	3.558463	3.617106
2	2	1	928.658557	927.388022	8.232305	8.207120
2	2	0	928.659131	929.206084	8.232905	8.285144
3	0	3	925.120964	923.665495	3.852662	3.920982
3	1	3	926.393131	924.639766	5.326006	5.376322
3	1	2	926.590527	925.863460	5.539151	5.594654
3	2	2	930.583145	929.319381	10.159977	10.136080
3	2	1	930.586048	931.127849	10.162978	10.213806
3	3	1	937.739366	937.641970	18.024555	17.957132
3	3	0	937.739382	----	18.024561	18.027263
4	0	4	927.677176	926.221438	6.417068	6.484971
4	1	4	928.887441	927.199576	7.824123	7.875522
4	1	3	929.216336	928.446000	8.179316	8.233123
4	2	3	933.148706	931.895694	12.729708	12.708741
4	2	2	933.157405	933.691949	12.738703	12.786442
4	3	2	940.308132	----	20.595765	20.528748
4	3	1	940.308179	----	20.595810	20.598457
5	0	5	930.867992	929.413043	9.618065	9.685433
5	1	5	932.004260	930.386876	10.945647	10.997523
5	1	4	932.497397	931.683350	11.478297	11.530848
5	2	4	936.354785	935.117893	15.941072	15.925153
5	2	3	936.375078	936.899106	15.962022	16.004519
5	3	3	943.519580	----	23.810249	23.743786
5	3	2	943.519759	----	23.810427	23.812960
6	0	6	934.690526	933.237816	13.452714	13.519424
6	1	6	935.742930	934.195521	14.689861	14.741930
6	1	5	936.432872	935.579679	15.435240	15.486650
6	2	5	940.200786	938.987059	19.793534	19.784325
6	2	4	940.241265	940.750127	19.835306	19.870871
6	3	4	----	----	27.668284	27.602591
6	3	3	947.374511	----	27.668818	27.671113
7	0	7	939.141468	937.692920	17.917607	17.983529
7	1	7	940.102682	938.620542	19.055942	19.108043
7	1	6	941.021717	940.137675	20.049086	20.099341
7	2	6	944.686033	----	24.286458	24.283958
7	2	5	944.758576	945.246046	24.361287	24.389889
7	3	5	----	----	32.170173	32.105576
7	3	4	----	----	32.171507	32.173330
8	0	8	----	----	23.008969	23.073971
8	1	8	----	943.658879	24.042975	24.094997
8	1	7	----	----	25.318552	25.367576
8	2	7	----	948.670388	29.419098	29.421736
8	2	6	----	----	29.542941	29.566122
8	3	6	----	----	37.316223	37.253210
8	3	5	----	----	37.319153	37.320107
9	0	9	----	----	28.722822	28.786772
9	1	9	----	----	29.649969	29.701830
9	1	8	----	----	31.242104	31.289788
9	2	8	----	----	35.190609	35.196534
9	2	7	----	----	35.383338	35.402909
9	3	7	----	----	43.106727	43.046003
9	3	6	----	----	43.112574	43.112050

that the upper and lower states of a transition are focused onto the detector at different efficiencies by the field allows us to observe a transition as a modulation of beam flux at the detector. Both positive and negative signals are seen, depending on whether molecules in the upper or lower state are preferentially focused by the quadrupole field.

Sample spectra for acetaldehyde are shown in figures 2 and 3. Spectra were recorded for the P(36) through P(50) lines of the 10 μm band of the CO_2 laser and the P(14) and P(18) through P(21) lines of the 10 μm band of the N_2O laser. These laser lines provide about 48% coverage of the 913.82–929.62 cm^{-1} region. The frequency precision of the measurements is estimated to be 0.25 MHz from comparison of the infrared combination differences with those determined from microwave and far-infrared data. The absolute frequencies were calibrated to an accuracy of about 2 MHz by using the R(0) transition of NH_3 for which Lamb-dip saturation measurements are available [28].

Initial rotational assignments were made by microwave- or radiofrequency-infrared double resonance, with microwave or radiofrequency transitions observed in both the ground and vibrationally excited states. Assignments were also guided by the large number of precise combination differences possible for an a/b hybrid band with forbidden transitions for the E internal rotor state. Some of these forbidden transitions are seen in the spectra of figures 2 and 3. The 335 assigned transitions were combined with accurate ground state energies to calculate precise excited state term values, referenced to the $J = 0$ ground state of A symmetry. The upper-state term values and the ground state rotational energies used [29] to determine these term values are listed in table 1. The rotational state labels designate the asymmetric top level that a state correlates to in the high barrier limit.

3. Results

3.1. Tunnelling and vibrational dynamics

The term values listed in table 1 provide information about the tunnelling and vibrational dynamics of the $\nu_{14} + \nu_{15}$ state. We find that the $\nu_{14} + \nu_{15}$ A and E excited states are 921.28066 cm^{-1} and 919.82717 cm^{-1} , respectively, above the A, $J = 0$ ground state. In frequency space, the $A \leftarrow A$ band origin is at 921.28066 cm^{-1} and the $E \leftarrow E$ band origin is at 919.75822 cm^{-1} . The energy difference between the $J = 0$, A and E excited states gives an excited state torsional tunnelling splitting of -1.4535 cm^{-1} . This splitting can be compared with the $+0.069 \text{ cm}^{-1}$, -1.75 cm^{-1} , and $+13.9 \text{ cm}^{-1}$ tunnelling splittings of the ground ($\nu_{15} = 0$) and first two excited torsional levels ($\nu_{15} = 1$ and 2) of the ground vibrational state. This comparison shows that both the sign and magnitude of the observed $\nu_{14} + \nu_{15}$ tunnelling splittings are closest to that of the $\nu_{15} = 1$ state.

The K splittings for the E component of the $\nu_{14} + \nu_{15}$ excited state also more closely resemble those of the $\nu_{15} = 1$ state than those of the $\nu_{15} = 0$ or $\nu_{15} = 2$ state. For the E species, the K splittings result primarily from the Coriolis interaction between a axis rotation (i.e., K) and the internal rotation angular momentum. We find for the $\nu_{14} + \nu_{15}$ state that the E, $J = 2$, $K = 2$ levels are split by 54.5 GHz and the E, $J = 1$, $K = 1$ levels are split by 28.8 GHz. These values are similar to the 58.4 GHz and 37.3 GHz splittings for the E, $J = 2$, $K = 2$ and E, $J = 1$, $K = 1$ states of the $\nu_{15} = 1$ torsional state. For the $\nu_{15} = 0$ state the E state K splittings are

2.3 GHz and 1.8 GHz for $J = 2, K = 2$ and $J = 1, K = 1$, while for the $\nu_{15} = 2$ state they are 18.01 cm^{-1} and 12.56 cm^{-1} . The increase in the magnitude of the splittings with ν_{15} excitation is due to the greater amount of unquenched internal rotation angular momentum in the higher ν_{15} states.

As seen above, both the tunnelling splittings and the E state K splittings are consistent with the Hollenstein and Günthard [13] assignment of the 920 cm^{-1} band to a vibration with one quantum of excitation in the torsional mode. Hollenstein and Günthard [13] find from isotopic studies at low resolution that the $\nu_{14} + \nu_{15}$ state is in strong Fermi resonance through an anharmonic matrix element of 21 cm^{-1} with the ν_9 state observed at 867 cm^{-1} . Because of this interaction, the tunnelling splitting of the $\nu_{14} + \nu_{15}$ state is reduced, being partially averaged with the much smaller tunnelling splitting of the ν_9 state. Moreover, the $\nu_{14} + \nu_{15}$ state is pushed away from the ν_{14} state, making the $\nu_{14} + \nu_{15} - \nu_{14}$ spacing of 157 cm^{-1} much larger than the ground-state ν_{15} frequency of 143 cm^{-1} .

We can test the proposed anharmonic coupling model of Hollenstein and Günthard [13] by seeing if a 21 cm^{-1} interaction matrix element between $\nu_{14} + \nu_{15}$ and ν_9 could lead to the observed $\nu_{14} + \nu_{15}$ tunnelling splitting. In this analysis we use 910 cm^{-1} and 877 cm^{-1} values of Hollenstein and Günthard [13] for the unperturbed $\nu_{14} + \nu_{15}$ and ν_9 origins and 21 cm^{-1} for the anharmonic matrix element. For the unperturbed tunnelling splittings we take the $\nu_{15} = 1$ value of -1.750 cm^{-1} for the $\nu_{14} + \nu_{15}$ state and the $\nu_{15} = 0$ value of $+0.069 \text{ cm}^{-1}$ for the ν_9 state. We assume that the tunnelling splittings are symmetric about 910 cm^{-1} and 867 cm^{-1} . The calculated tunnelling splittings for the perturbed $\nu_{14} + \nu_{15}$ and ν_9 states are found to be -1.49 cm^{-1} and -0.19 cm^{-1} , respectively. The calculated $\nu_{14} + \nu_{15}$ splitting is in good agreement with the observed value of -1.4535 cm^{-1} , suggesting that the ν_9 state is the principal perturber of the $\nu_{14} + \nu_{15}$ tunnelling splittings. We note that in this type of analysis the tunnelling splittings are sensitive only to perturbors which have a different number of torsional quanta than the $\nu_{14} + \nu_{15}$ state. Perturbing states with the same number of torsional quanta as the $\nu_{14} + \nu_{15}$ state (i.e., one) will affect both tunnelling components of the $\nu_{14} + \nu_{15}$ state nearly equally.

The strong interaction between $\nu_{14} + \nu_{15}$ and ν_9 will play a role in the vibrational dynamics of acetaldehyde at higher energies. Vibrational states of the form $p\nu_i + \nu_{14} + q\nu_{15}$ are expected to interact via a large anharmonic matrix element with the $p\nu_i + \nu_9 + (q - 1)\nu_{15}$ states, where p and q are integers > 0 . The extent of mixing will depend on the separation between the coupled levels and the vibrational dependence of the interaction matrix element, both of which vary due to vibrational anharmonicity. For example, as the number of quanta in the ν_{15} mode increases, the torsional vibration is expected to become more free rotor in nature. Since the leading term in the anharmonic coupling term has a $\sin 3\alpha$ torsional angular dependence for hindering potential of the form $V_3(1 - \cos 3\alpha)/2$, the torsional selection rules on the coupling term change from those of a harmonic oscillator with $\Delta v_{15} = \pm 1$ to those of a free rotor with $\Delta m = \pm 3$, where m is the free rotor quantum number.

3.2. Fit to an internal rotation Hamiltonian

We have attempted to fit the term values of the $\nu_{14} + \nu_{15}$ state to obtain effective spectroscopic constants to compare with the $\nu_{15} = 1$ state. In this analysis we have used a computer program written by Godefroid and Kleiner [30] which is based on

the internal axis method as described by Herbst *et al.* [31]. The program allows the A and E states to be fitted simultaneously.

The Hamiltonian matrix is set up in a product basis of symmetric rotor wavefunctions and torsional wavefunctions, where the torsional wavefunctions are obtained from solution of the pure torsional problem using a free rotor basis of 21 functions. We have truncated the torsional basis to 7 functions, giving a rotational-torsion basis set of $[7 \times (2J + 1)]$ functions.

To fit the term values of the $\nu_{14} + \nu_{15}$ state we started with the best set of constants available for the $\nu_{15} = 0, 1$, and 2 state [10] and floated the rotational constants (A, B, C), the nondiagonal constant (D_{ab}), the barrier to internal rotation (V_3), and the dimensional constant ρ , and some of the centrifugal distortion constants. The distortion constants were, in general, poorly determined, and we finally chose a model which includes only the D_{JK} and H_{KJ} constants. Attempts to determine some of the other constants which describe interactions between torsion and rotation failed, so we have fixed these constants at the $\nu_{15} = 0, 1$, and 2 values. In the fit we treated the $\nu_{14} + \nu_{15}$ state as a vibration with one quantum of torsional excitation. The resulting fit yielded a standard deviation of 0.04 cm^{-1} , which is several orders of magnitude larger than the experimental uncertainty. Attempts to fit just the A state data or just the E state data also failed. The fit for the A state is slightly better than that of the E state ($\sigma_A = 0.02 \text{ cm}^{-1}$ compared with $\sigma_E = 0.03 \text{ cm}^{-1}$), but is still not close to the experimental uncertainty.

The inability to fit the spectrum by using a standard internal rotation Hamiltonian is most likely the consequence of the strong interaction between $\nu_{14} + \nu_{15}$ and ν_9 . Additional perturbations may also be arising from the A torsional component of the A'' $\nu_{10} + 3\nu_{15}$ vibration predicted near 917 cm^{-1} , which can Coriolis couple to the A internal rotor state of the $\nu_{14} + \nu_{15}$ vibration. A more complete analysis and spectroscopic fitting of the $\nu_{14} + \nu_{15}$ band requires high resolution data on the ν_9 band to allow complete treatment of the $\nu_{14} + \nu_{15}/\nu_9$ anharmonic interaction.

3.3. Forbidden transitions

The presence of a large number of intense forbidden transitions for the E state comes from the strong *a*-type Coriolis interaction between *a* axis rotation and the angular momentum of the rotor. The torsional degeneracy of the E state allows for a non-zero expectation value of the torsional angular momentum along the *a* inertial axis. For the A state this expectation value vanishes. The forbidden transitions have selection rules on K_a and K_c which differ from the normal *a, b*-type selection rules of a rigid acetaldehyde. The A state follows these rigid molecule selection rules. Some of the forbidden transitions are observed in the spectra of figures 2 and 3. Here, we see the $1_{10} \leftarrow 1_{10}$, $2_{12} \leftarrow 3_{12}$, $2_{12} \leftarrow 2_{12}$ and $1_{11} \leftarrow 1_{11}$ forbidden transitions for the E state.

The Coriolis term responsible for the forbidden transitions has the approximate form $-2AP_a p$, where P_a is the projection of the total angular momentum along the *a* inertial axis, A is a rotational constant, and p is the unquenched angular momentum of the internal rotor. This operator competes with the molecular asymmetry operator, $\frac{1}{2}(B - C)(J_b^2 - J_c^2)$, in determining whether the $K \neq 0$ wavefunctions will resemble those of an asymmetric top, where the degenerate pair of wavefunctions

takes the approximate form, $[|JKI\rangle + |J-KI\rangle]/2^{1/2}$ and $[|JK-l\rangle + |J-K-l\rangle]/2^{1/2}$, for the upper component of the asymmetry doublet, and $[|JKI\rangle - |J-KI\rangle]/2^{1/2}$ and $[|JK-l\rangle - |J-K-l\rangle]/2^{1/2}$ for the lower component of the asymmetry doublet, or of a symmetric top in a degenerate vibrational state, where the degenerate pair of wavefunctions takes the approximate form, $|J-KI\rangle$ and $|JK-l\rangle$, for the upper component of the 'asymmetry doublet', and, $|JKI\rangle$ and $|J-K-l\rangle$, for the lower component of the 'asymmetry doublet'. Here, l is a label used to designate the vibrational (i.e., torsional) angular momentum and l and K are taken to be positive.

If the asymmetry operator dominates, the selection rules for the E state resemble the asymmetric top selection rules of the A state; if the Coriolis term dominates, the E state selection rules resemble more those of a symmetric top in a degenerate vibrational state. In the ground state of acetaldehyde, the asymmetry term dominates for $K < 2$, while the Coriolis term dominates for $K \geq 2$, for low J . For the $\nu_{14} + \nu_{15}$ excited vibrational state, which has one quantum in the torsional mode, the Coriolis term also dominates for most of the $K = 1$ states studied.

The presence of these forbidden transitions may account for some of the spectral complexity observed in the infrared spectra of acetaldehyde and other molecules with partially hindered internal rotors. The high density of lines observed in room temperature and 80–130 K molecular beam spectra for such molecules have been attributed to strong mode coupling between the normal or local mode excited and the bath of background vibrational states. The presence of forbidden transitions for the E torsional species together with A–E torsional splittings and torsional hotbands can give a larger density of transitions over that expected for an asymmetric top. Upon deuteration, both the tunnelling splittings and number of forbidden transitions are reduced because of the larger effective tunnelling barrier for CD_3 internal rotation compared to CH_3 . These effects combined may be the source of the reduced spectral congestion reported [16] for the infrared spectra of the fundamental and first overtone CO stretches of CD_3CHO compared with CH_3CHO .

4. Conclusion

We have reported and assigned the high resolution infrared spectrum of the $\nu_{14} + \nu_{15}$ torsional combination band of acetaldehyde. These measurements when combined with future planned diode-laser molecular beam studies of the ν_9 band of acetaldehyde will allow detailed characterization of the strong anharmonic interaction between $\nu_{14} + \nu_{15}$ and ν_9 . Characterization of this Fermi interaction is importance since it has been suggested [16] that ν_9 is a 'doorway' state for coupling the carbonyl stretch to other vibrational modes.

We would like to thank Jon Hougen for initially suggesting this problem and Walt Lafferty for taking the Fourier-transform infrared spectrum of acetaldehyde shown in figure 1. We would also like to thank Jon Hougen and Isabelle Kleiner for furnishing us with the ground-state term values used in table 1. This study was partially supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, United States Department of Energy. J.O. is grateful to the Consejo Superior de Investigaciones Científicas of Spain for a post-doctoral fellowship.

References

- [1] LIN, C. C., and KILB, R. W., 1956, *J. chem. Phys.*, **24**, 631.
- [2] KILB, R. W., LIN, C. C., and WILSON, E. B., JR., 1957, *J. chem. Phys.*, **26**, 1695.
- [3] HERSCHBACH, D. R., 1959, *J. chem. Phys.*, **31**, 91.
- [4] IJIMA, T., and TSUCHIYA, S., 1972, *J. molec. Spectrosc.*, **44**, 88.
- [5] BAUDER, A. and GÜNTARD, H. H., 1976, *J. molec. Spectrosc.*, **60**, 290.
- [6] LIANG, W., BAKER, J. G., HERBST, E., BOOKER, R. A., and DeLUCIA, F. C., 1986, *J. molec. Spectrosc.*, **120**, 298.
- [7] BAKER, J. G. and PETTY, G. C., 1988, *J. molec. Struct.*, **189**, 227.
- [8] KLEINER, I., GODEFROID, M., HERMAN, M., and McKELLAR, A. R. W., 1990, *J. molec. Spectrosc.*, **142**, 238.
- [9] KLEINER, I., HOUGEN, J. T., SUENRAM, R. D., LOVAS, F. J., and GODEFROID, M., 1991, *J. molec. Spectrosc.*, **148**, 28.
- [10] BELOV, S. P., TRETYAKOV, M. YU., KLEINER, I., and HOUGEN, J. T., unpublished.
- [11] EVANS, J. C., and BERNSTEIN, H. J., 1956, *Can. J. Chem.*, **34**, 1083.
- [12] COSSEE, P., and SCHACHTSCHNEIDER, J. H., 1966, *J. chem. Phys.*, **44**, 97.
- [13] HOLLENSTEIN, H. and GÜNTARD, Hs. H., 1971, *Spectrochim. Acta A*, **27**, 2027.
- [14] WIBERG, K. B., WALTERS, V., and COLSON, S. D., 1984, *J. phys. Chem.*, **88**, 4723.
- [15] SHIMANOUCHI, T., 1972, *Table of Molecular Vibrational Frequencies*, Vol. I, NSRDS-NBS 39, (US Government Printing Office, Washington DC).
- [16] WALTERS, V. A., COLSON, S. D., SNAVELY, D. L., WIBERG, K. B., and JAMISON, B. M., 1985, *J. phys. Chem.*, **89**, 3857.
- [17] KIM, H. L., MINTON, T. K., RUOFF, R. S., KULP, T. J., and McDONALD, J. D., 1988, *J. chem. Phys.*, **89**, 3955.
- [18] FRASER, G. T., PINE, A. S., DOMENECH, J. L., and PATE, B. H., 1993, *J. chem. Phys.*, **99**, 2396.
- [19] AINETSCHIAN, A., FRASER, G. T., and PATE, B. H., unpublished.
- [20] FRASER, G. T., and PATE, B. H., unpublished.
- [21] AINETSCHIAN, A., FRASER, G. T., and PATE, B. H., *J. chem. Phys.*, in press.
- [22] GAMBOGI, J., FRASER, G. T., and PATE, B. H., unpublished.
- [23] PARMENTER, C. S., and STONE, B. M., 1986, *J. chem. Phys.*, **84**, 4710.
- [24] FRASER, G. T., SUENRAM, R. D., and COUDERT, L. H., 1989, *J. chem. Phys.*, **90**, 6077.
- [25] FRASER, G. T., and PINE, A. S., 1989, *J. chem. Phys.*, **91**, 637.
- [26] FRASER, G. T., PINE, A. S., and KREINER, W. A., 1991, *J. chem. Phys.*, **94**, 7061.
- [27] CHEO, P. K., 1984, *IEEE J. Quantum Electron.* **20**, 700.
- [28] MAGERL, G., SCHUPITA, W., FRYE, J. M., KREINER, W. A., and OKA, T., 1984, *J. molec. Spectrosc.*, **107**, 72.
- [29] Ground-state term values furnished by I. Kleiner and J. T. Hougen and were generated using the spectroscopic constants of reference [10].
- [30] KLEINER, I. and GODEFROID, M., private communication.
- [31] HERBST, E., MESSER, J. K., DeLUCIA, F. C., and HEMINGER, P., 1984, *J. molec. Spectrosc.*, **108**, 42.