

Fourier-transform infrared and jet-cooled diode-laser spectra of the 867 cm^{-1} ν_9 band of acetaldehyde

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(Received 31 March 1994; accepted 27 June 1994)

The spectrum of the ν_9 A' C—C stretching fundamental band of acetaldehyde (CH_3CHO) at 867 cm^{-1} has been recorded in a slit-jet nozzle expansion using a diode-laser spectrometer and in a room-temperature gas cell using a Fourier-transform infrared spectrometer. The spectrum exhibits a-type transitions which have been assigned for $J' \leq 19$ and $K'_a \leq 5$ for the A state and $J' \leq 19$ and $K'_a \leq 4$ for the E state. The transitions show a large tunnelling splitting of $\approx 0.5\text{ cm}^{-1}$ for $K_a = 0$, attributed primarily to an anharmonic interaction of the ν_9 vibration with the $\nu_{14} + \nu_{15}$ torsional combination vibration at 920 cm^{-1} . Evidence is also presented for an additional interacting vibration(s) affecting the ν_9 tunnelling splitting.

1. Introduction

As one of the simplest molecules with a methyl internal rotor, acetaldehyde (CH_3CHO) can be used potentially as a model system for complex internal rotation effects in spectroscopy. As a result, it has been the subject of extensive study by high-resolution spectroscopy; its microwave spectrum has been well characterized in the ground, first and second torsional excited states, and the torsional modes have been studied directly by high-resolution far-infrared spectroscopy [1–4]. These data have been fitted globally by Kleiner *et al.* to near experimental precision using an internal rotation Hamiltonian to determine a V_3 barrier term of $\approx 407.9\text{ cm}^{-1}$ and a V_6 barrier term of $\approx -12.9\text{ cm}^{-1}$ in the Fourier series expansion of the internal rotation potential [4].

More recently, high resolution studies of the mid-infrared bands have been undertaken. Belov *et al.* have reported on the 2 MHz resolution molecular-beam microwave-sideband CO_2 laser spectrum of the 920 cm^{-1} $\nu_{14} + \nu_{15}$ torsional combination band which is coupled anharmonically with the ν_9 band at 867 cm^{-1} [5]. Kleiner and Herman have reported on the assignment and partial fitting of a high resolution, room-temperature Fourier-transform infrared spectrum of the 763 cm^{-1}

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ν_{14} band [6]. We have studied the spectra of the ν_4 and $2\nu_4$ C=O stretching fundamental and overtone bands using the diode-laser spectrometer described here for the fundamental band at 1750 cm^{-1} and a molecular-beam colour-centre laser spectrometer for the 3480 cm^{-1} overtone [7]. The spectrum of the fundamental is complex and remains largely unassigned while that of the overtone is mostly assigned through the use of microwave-infrared double resonance.

From low-resolution infrared spectra of acetaldehyde, Walters *et al.* have suggested that in the C=O stretching fundamental and overtone bands significant coupling occurs between the 'bright' C=O stretching mode and background combination and overtone states [8]. This is inferred from the observation of spectral congestion and broad featureless absorptions. It has been suggested also from studies of *p*-fluorotoluene that methyl groups can promote intramolecular vibrational-energy redistribution (IVR) [9]. In an attempt to quantify the effect of increasing torsional excitation on IVR, Kleiner, Hougen and others have undertaken a systematic study of the acetaldehyde system. One of the objectives of the study is to understand the spectroscopy of acetaldehyde at lower energy in detail and then use that understanding as a base to explore the spectroscopy in the higher energy regions where state densities are larger and intermode couplings will be more prevalent.

The 867 cm^{-1} ν_9 band is of particular interest for a study of intermode coupling in acetaldehyde. High-resolution spectroscopy has confirmed the conclusion of Hollenstein and Günthard that the 920 cm^{-1} band is the $\nu_{14} + \nu_{15}$ combination vibration which interacts through a Fermi resonance with the 867 cm^{-1} ν_9 vibration [10]. The observed splittings are consistent with the 21 cm^{-1} interaction matrix element calculated from low-resolution work, but analysis of the ν_9 band is required to allow a detailed characterization of this strong interaction. Further, the first overtone of the ν_9 band has been suggested as playing a significant role in the complicated spectrum seen for the ν_4 C=O stretch at 1745 cm^{-1} , making the complete characterization of the ν_9 fundamental necessary for understanding the apparently complex dynamics exhibited in the ν_4 band and its overtone [8]. Here we investigate the rotationally resolved jet-cooled diode-laser and room-temperature Fourier-transform infrared spectra of the 867 cm^{-1} band, and discuss the effect of rovibrational couplings on the observed torsional tunnelling splittings.

2. Experimental

The slit-jet diode-laser spectrometer has been described previously [11]. Briefly, the frequency of the laser is repetitively swept at 800 Hz over a frequency window of $\approx 0.2\text{ cm}^{-1}$ by applying a voltage ramp to the diode laser controller. The laser beam is collimated with an off-axis parabolic mirror and passes through a monochromator for single-mode selection. Small samples of the beam are sent through a germanium etalon ($\text{FSR} = 0.016\text{ cm}^{-1}$) for relative frequency markers, and a reference gas for absolute frequency calibration. The main part of the beam makes six passes across the output of a $25\text{ }\mu\text{m} \times 10\text{ cm}$ slit-jet nozzle. All three beams are detected using HgCdTe detectors and simultaneously digitized in a four-channel 8-bit digital oscilloscope; the section of the beam probing the nozzle output is also sent to a separate 10-bit transient recorder. For each spectral window 100 sequential sweeps of the laser are co-added. The files are linearized on a computer and the windows are merged by overlapping on a common acetaldehyde transition.

For the acetaldehyde spectrum, the jet was formed by passing about 120 kPa (900 Torr) of Ar over liquid acetaldehyde at room temperature. About 60% of the region from 853 cm^{-1} to 874 cm^{-1} was covered. Transitions typically had a full width at half height of 0.0015 cm^{-1} and line positions are estimated to be accurate to $\pm 0.0004\text{ cm}^{-1}$ (1σ); for an unperturbed band, transitions are typically fitted to a standard deviation of about 10 MHz. Carbonyl sulphide was used as a calibration gas [12].

The ν_9 band was also recorded in a room-temperature gas cell using the Bruker IFS 120HR Fourier-transform spectrometer in Brussels with a resolution of 0.00186 cm^{-1} .† A pressure of 40 Pa (300 mTorr) of acetaldehyde and a path length of 42 m were used. Acetylene, which was in the gas cell with the acetaldehyde as an impurity, was used for frequency calibration [13]. The Fourier-transform spectrum was later calibrated against the acetaldehyde diode laser spectrum.

3. Results

The 867 cm^{-1} band of acetaldehyde, assigned by Hollenstein and Günthard to the ν_9 predominantly C—C stretching vibration [10], is expected to be primarily an *a*-type spectrum. This band has been shown to interact through a Fermi resonance with the $\nu_{14} + \nu_{15}$ torsional combination band at 920 cm^{-1} , so it is further expected that the 867 cm^{-1} band will exhibit torsional tunnelling splittings which are large compared with the ground state splittings ($+0.07\text{ cm}^{-1}$). Assuming the 21 cm^{-1} interaction matrix element of Hollenstein and Günthard between the ν_9 and $\nu_{14} + \nu_{15}$ vibrations, the ν_9 torsional splitting is predicted to be $\approx -0.2\text{ cm}^{-1}$, with the E state below the A state [5].

Figures 1 and 2 show sections of the diode-laser spectrum in the low-*J* region of the P branch. *a*-Type transitions terminating on levels up to $J' = 10$ and $K'_a = 3$ were assigned in the jet spectrum. Where possible, the transitions were assigned using ground-state combination differences between the P and the R branches. The Q branch region, which is very crowded, was not considered a good test of an assignment since the likelihood of a fortuitous combination difference was quite high. One additional series of transitions with an appropriate B value was identified in the jet spectrum. This series arose from one of the higher K_a stacks, but we were unable to distinguish among them; the P and R branch combination differences were the same within the experimental precision for the different K_a series at low *J* and the corresponding Q branches were in gaps in the diode-laser coverage. This series and several others were identified positively in the Fourier transform infrared (FTIR) spectrum, a section of which is shown in figure 3, where assignments were made for transitions terminating on levels up to $K'_a = 5$ for the A state and $K'_a = 4$ for the E state. Also, assignments of the lower K_a series were extended to the gaps in the diode laser coverage and up to $J' = 19$. A total of 558 transitions have been assigned and are available as supplementary material (5 pages) from the British Library, Lending Division by quoting the number SUP 16108 according to the procedure described at the end of this issue. The resulting ν_9 term values are listed in the table. Some strong lines remain unassigned in the Q branch region; combination differences show that these transitions do not originate from monomer acetaldehyde states with $K_a \leq 6$.

† Reference to this product by name is not to be construed as an endorsement by NIST.

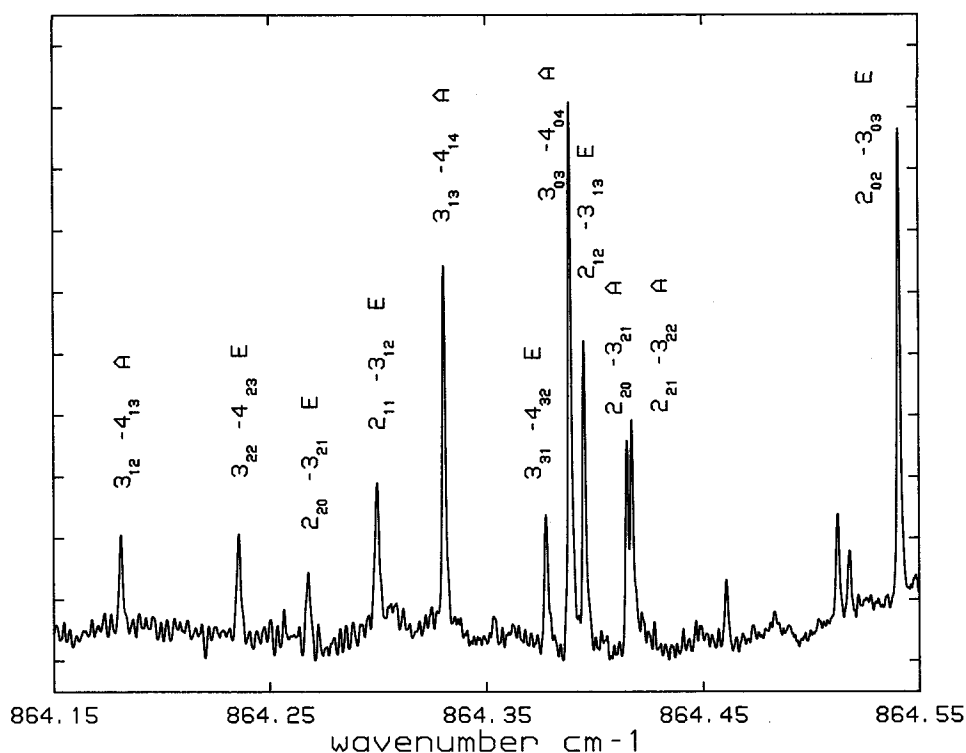


Figure 1. Diode laser spectrum of the acetaldehyde ν_9 band $864.15\text{--}864.55\text{ cm}^{-1}$ showing a region of the P branch. The unlabelled peaks are presently unassigned. The structured noise is caused by interference fringes arising from the multipass cell.

As detailed by Belov *et al.* in their study of the $\nu_{14} + \nu_{15}$ band [5], a strong *a*-type Coriolis interaction between K_a rotation and the internal rotation angular momentum allows the observation of intense ‘forbidden’ transitions in the E state for $K > 1$, which more closely follow the selection rules of a symmetric top than of an asymmetric top. Such forbidden transitions are also observed in the ν_9 band, where transitions of the type $4_{31} \leftarrow 3_{31}$ are observed for the E state, but the corresponding $4_{31} \leftarrow 3_{30}$ ‘allowed’ transitions are not observed. As noted by Belov *et al.*, these forbidden transitions may be the cause of some of the spectral congestion at high energy previously attributed to intermode couplings.

From fitting the $K_a = 0$ series for the A and E states to a linear-molecule Hamiltonian, band centres are calculated as $866.9629(10)\text{ cm}^{-1}$ and $866.4725(2)\text{ cm}^{-1}$ for A and E, respectively. In energy space, this translates to state energies above the A ground state of 866.9629 cm^{-1} for the A state and 866.4036 cm^{-1} for the E state, and a tunnelling gap $\nu_0(\text{E}) - \nu_0(\text{A})$ of -0.5593 cm^{-1} for ν_9 . While this difference falls between the tunnelling gap for the ground state of 0.0698 cm^{-1} and that for the first torsionally excited state of -1.750 cm^{-1} [4], it is quite different from the -0.2 cm^{-1} gap predicted from a 21 cm^{-1} Fermi resonance with the $\nu_{14} + \nu_{15}$ torsional combination vibration [5]. As can be seen in the energy level diagram in figure 4, there are a number of additional states in the $700\text{--}1100\text{ cm}^{-1}$ region with which both the ν_9 and $\nu_{14} + \nu_{15}$ levels can interact. No evidence for

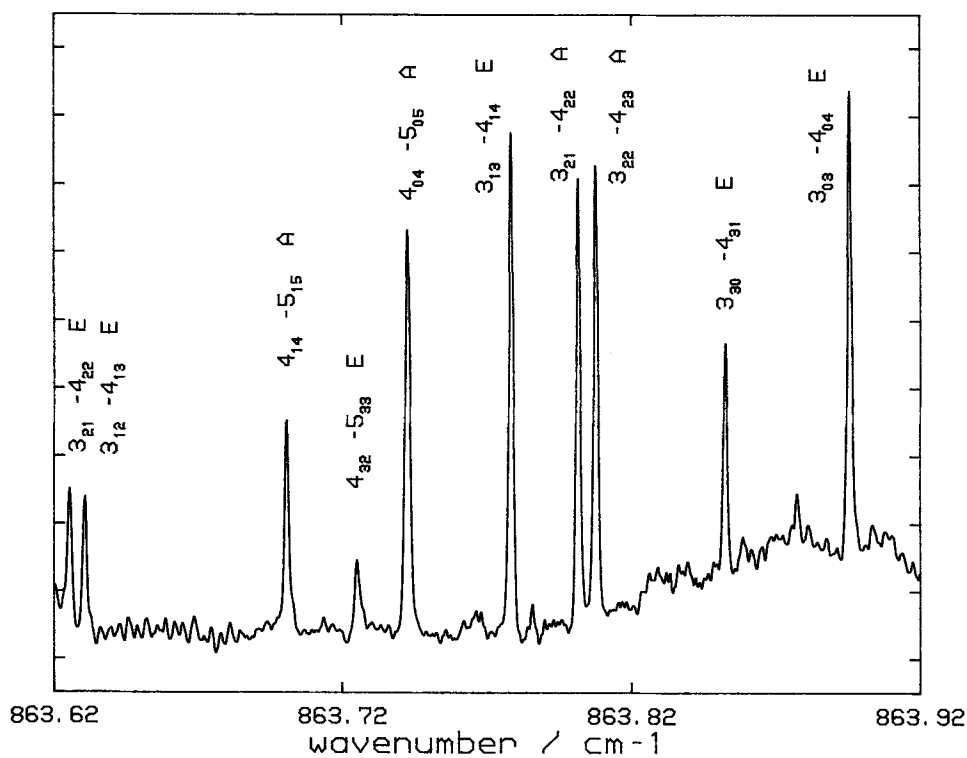


Figure 2. Diode laser spectrum of the acetaldehyde ν_9 band $863.62\text{--}863.92\text{ cm}^{-1}$ showing the corresponding E state transitions for several of the A state transitions shown in figure 1. The magnitude of the tunnelling splitting for $K_a = 0$ is approximately 0.56 cm^{-1} .

transitions to an additional perturbing state was seen in the ν_9 or $\nu_{14} + \nu_{15}$ spectra, making positive identification of the additional interacting state or states difficult. A differential perturbation of the A or E levels could arise from a single additional perturbing state or from the sum of interactions from several perturbing states.

No significant effort has been made at a simultaneous fit of the A and E states of the ν_9 band. The tunnelling splittings were expected to be contaminated from the interaction with the $\nu_{14} + \nu_{15}$ vibration at 920 cm^{-1} , which could not be fitted to an internal rotation Hamiltonian; however, the large discrepancy between the predicted and observed tunnelling splittings indicates that still other interactions must be considered in any attempt to model these interacting bands. The E state subbands for $K_a = 0$ and $K_a \geq 2$ and the A state $K_a = 0$ subband were each found to fit independently to a linear molecule expression, and the A state subbands for $K_a > 0$ were each found to fit independently to a Watson Hamiltonian. However, attempts to fit the A state subbands together were not successful, resulting in root-mean-square errors of the order of 0.1 cm^{-1} , which is several orders of magnitude greater than the experimental precision of 0.0004 cm^{-1} . The A ground state term values for $J \leq 18$, $K_a \leq 5$ were found to fit to $\approx 0.0001\text{ cm}^{-1}$ with this model. Figure 5 shows a plot of the subband origins calculated for the A state series versus K_a^2 . Because the fits were done for each K_a subband independently, the A rotational constants for the excited state could not be determined and were held fixed at the ground state value.

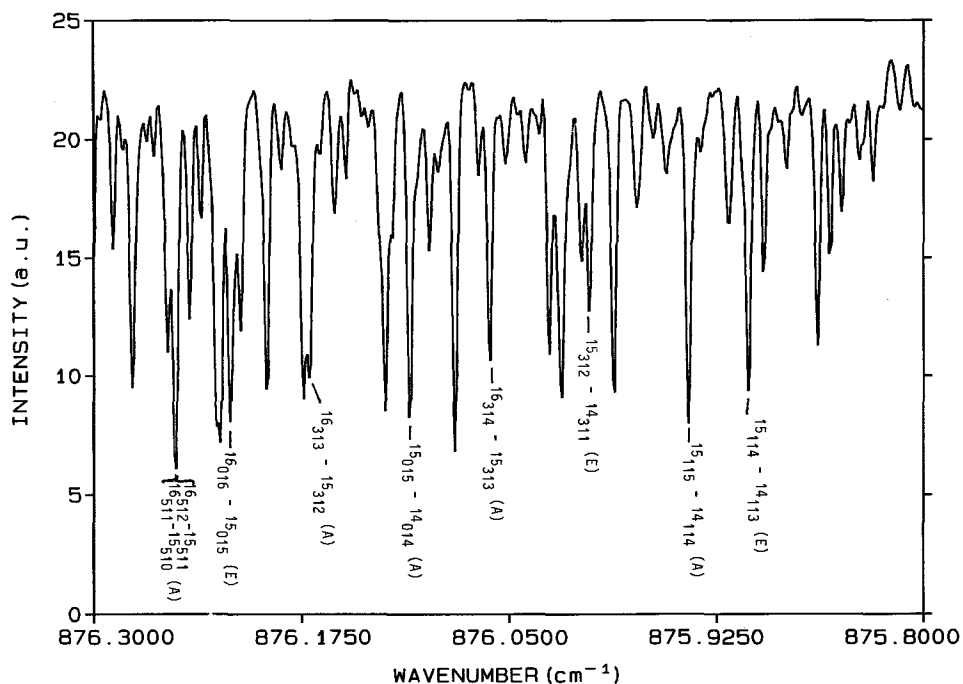


Figure 3. FTIR spectrum of the acetaldehyde ν_9 band taken on a Bruker IFS 120 HR Fourier-transform spectrometer from 876.3 cm^{-1} to 875.8 cm^{-1} , showing a region of the R branch. Unlabelled peaks are presently unassigned.

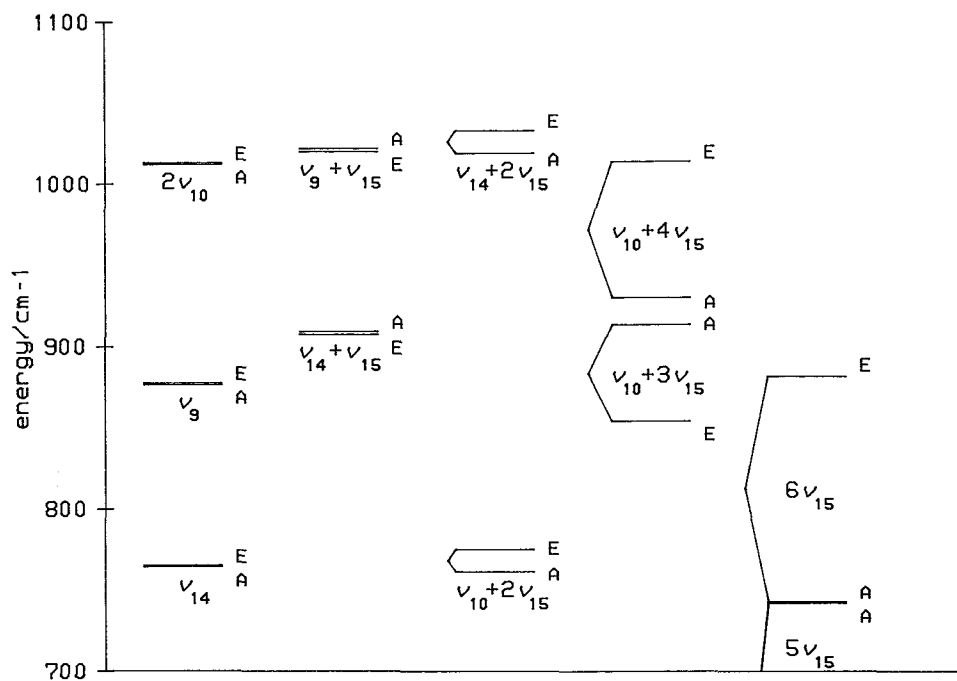


Figure 4. Energy level diagram for acetaldehyde in the region $700\text{--}1000\text{ cm}^{-1}$ showing predicted positions for ν_9 and $\nu_{14} + \nu_{15}$ and nearby combination and overtone vibrations.

Table 1. Term values relative to $v = 0$ A state 0_{00} level (cm^{-1}) for the ν_9 band of acetaldehyde.^a

J	K_p	K_o	A	E	J	K_p	K_o	A	E
1	0	1	—	867-1820	10	3	7	915-3679	916-3271
1	1	1	869-0388	—	10	4	7	926-6083	926-6220
1	1	0	869-0747	—	10	4	6	926-6084	—
2	0	2	868-8885	868-4621	10	5	6	940-6773	—
2	1	2	870-2854	869-7718	10	5	5	940-6773	—
2	1	1	870-3888	869-8944	11	0	11	908-8298	908-4055
2	2	1	874-5775	874-4816	11	1	11	909-4488	909-1067
2	2	0	874-5775	—	11	1	10	911-6789	911-2600
3	0	3	870-8059	870-3809	11	3	9	922-4151	923-0376
3	1	3	872-1553	871-6540	11	3	8	922-4363	923-3886
3	1	2	872-3610	871-8634	11	4	8	933-6785	933-6797
3	2	2	876-5382	876-4119	11	4	7	933-6792	—
3	2	1	876-5400	876-9453	11	5	7	947-7302	—
3	3	0	—	884-9064	11	5	6	947-7302	—
4	0	4	873-3607	872-9362	12	0	12	916-3649	915-9404
4	1	4	874-6458	874-1584	12	1	12	916-8884	916-5748
4	1	3	874-9921	874-4940	12	1	11	919-5082	919-1161
4	2	3	879-1612	878-9861	12	3	10	930-1263	930-7596
4	2	2	879-1702	879-5059	12	3	9	930-1619	931-0960
4	3	1	—	887-4690	12	4	9	941-3974	941-3834
4	4	1	897-7578	—	12	4	8	941-3969	—
4	4	0	897-7578	—	12	5	8	955-4269	—
5	0	5	876-5506	876-1255	12	5	7	955-4269	—
5	1	5	877-7605	877-2855	13	0	13	924-5078	924-0852
5	1	4	878-2740	877-7823	13	1	13	924-9427	924-6623
5	2	4	882-4536	882-2059	13	1	12	927-9742	927-6169
5	2	3	882-4724	882-7094	13	3	11	938-4838	939-1267
5	3	3	889-8853	890-2357	13	3	10	938-5438	939-4505
5	3	2	889-8858	890-6732	13	4	10	949-7607	949-7236
5	4	2	900-9624	901-0180	13	4	9	949-7615	—
5	4	1	900-9624	—	13	5	9	963-7665	—
6	0	6	880-3698	879-9476	13	5	8	963-7665	—
6	1	6	881-4939	881-0368	14	0	14	933-2554	932-8347
6	1	5	882-2144	881-7274	14	1	14	933-6096	933-3640
6	2	5	886-4155	886-0710	14	1	13	—	936-7597
6	2	4	886-4503	886-5575	14	3	12	947-4973	948-1384
6	3	4	893-6767	894-0936	14	3	11	947-5826	948-4467
6	3	3	893-6774	894-5184	14	4	11	958-7750	958-7320
6	4	3	904-8010	904-8343	14	4	10	958-7755	—
6	4	2	904-8010	—	14	5	10	972-7504	—
6	5	2	918-8963	—	14	5	9	972-7504	—
6	5	1	918-8963	—	15	0	15	942-6100	942-1895
7	0	7	884-8240	884-3974	15	1	15	942-8888	942-6813
7	1	7	885-8494	885-4089	15	1	14	—	946-5414
7	1	6	886-8065	886-3283	15	3	13	957-1530	957-7933
7	2	6	891-0320	890-5811	15	3	12	957-2780	—
7	2	5	891-0887	891-0359	15	4	12	968-4389	968-3525
7	3	5	898-1102	898-5938	15	4	11	968-4399	—
7	3	4	898-1108	899-0066	15	5	11	982-3798	—
7	4	4	909-2845	909-3154	15	5	10	982-3798	—
7	4	3	909-2845	—	16	0	16	952-5687	952-1507
7	5	3	923-3706	—	16	1	16	952-7790	952-6128

(continued)

Table 1. (*continued*)

<i>J</i>	<i>K_p</i>	<i>K_o</i>	A	E	<i>J</i>	<i>K_p</i>	<i>K_o</i>	A	E
7	5	2	923-3706	—	16	1	15	—	956-9580
8	0	8	889-9052	889-4721	16	3	14	967-4543	968-0997
8	1	8	890-8227	890-4031	16	3	13	967-6761	—
8	1	7	892-0513	891-5837	16	4	13	978-7519	978-6255
8	2	7	—	895-7365	16	4	12	978-7870	—
8	2	6	—	896-1573	16	5	12	992-6558	—
8	3	6	903-2020	903-7387	16	5	11	992-6559	—
8	3	5	903-2033	904-1366	17	0	17	963-1331	962-7227
8	4	5	914-4127	914-4408	17	1	17	963-2805	963-1587
8	4	4	914-4127	—	17	1	16	—	968-0044
8	5	4	928-4785	—	17	3	15	978-3994	979-0549
8	5	3	928-4785	—	17	3	14	978-7410	—
9	0	9	895-5950	895-1670	17	4	14	989-7140	989-5255
9	1	9	896-4139	896-0186	17	4	13	989-7695	—
9	1	8	897-9463	897-4921	17	5	13	1003-5783	—
9	2	8	902-0886	901-5530	17	5	12	1003-5787	—
9	2	7	902-2618	—	18	0	18	974-3035	—
9	3	7	908-9516	909-5272	18	1	18	974-3909	974-3213
9	3	6	908-9571	909-9099	18	1	17	—	979-6787
9	4	6	920-1875	920-2089	18	3	16	989-9872	—
9	4	5	920-1876	—	18	3	15	990-5075	—
9	5	5	934-2663	—	18	5	14	1015-1461	—
9	5	4	934-2663	—	18	5	13	1015-1467	—
10	0	10	901-9061	901-4739	19	0	19	986-0810	—
10	1	10	902-6234	902-2527	19	1	19	986-1132	986-0825
10	1	9	904-4903	904-0514	19	3	17	1002-2161	—
10	2	9	—	908-0312	19	5	15	1027-3599	—
10	3	8	915-3562	915-9605	19	5	14	1027-3609	—

^a Uncertainties in term values are $\pm 0.0004 \text{ cm}^{-1}$ (1σ).

Therefore, the plot is expected to be linear, with the slope giving the difference between the true and the assumed excited state A constant. The large scatter in the data points illustrates a strong K_a -dependent perturbation. This situation is not uncommon for vibrational bands of molecules with large A rotational constants, where the large difference in the A rotational constant between nearby combination/overtone vibrations and the normal mode vibration studied can allow K_a -dependent near-resonant interactions between different K_a stacks.

4. Conclusion

We present a rotationally resolved spectrum of the 867 cm^{-1} ν_9 band of acetaldehyde. These data are important to the characterization of the vibrational dynamics of acetaldehyde because of unusually strong interaction of this band with the nearby $\nu_{14} + \nu_{15}$ torsional combination band and the proposed role of the ν_9 overtone in driving the complex dynamics postulated for the ν_4 C=O stretch mode at 1750 cm^{-1} . It was hoped that this spectrum would furnish data to allow modelling of the Fermi interaction between ν_9 and the 920 cm^{-1} $\nu_{14} + \nu_{15}$ torsional combination vibration and a fitting of the energy levels of both vibrations. However, the A/E splittings in ν_9 indicate that one or both of ν_9 and $\nu_{14} + \nu_{15}$ are probably

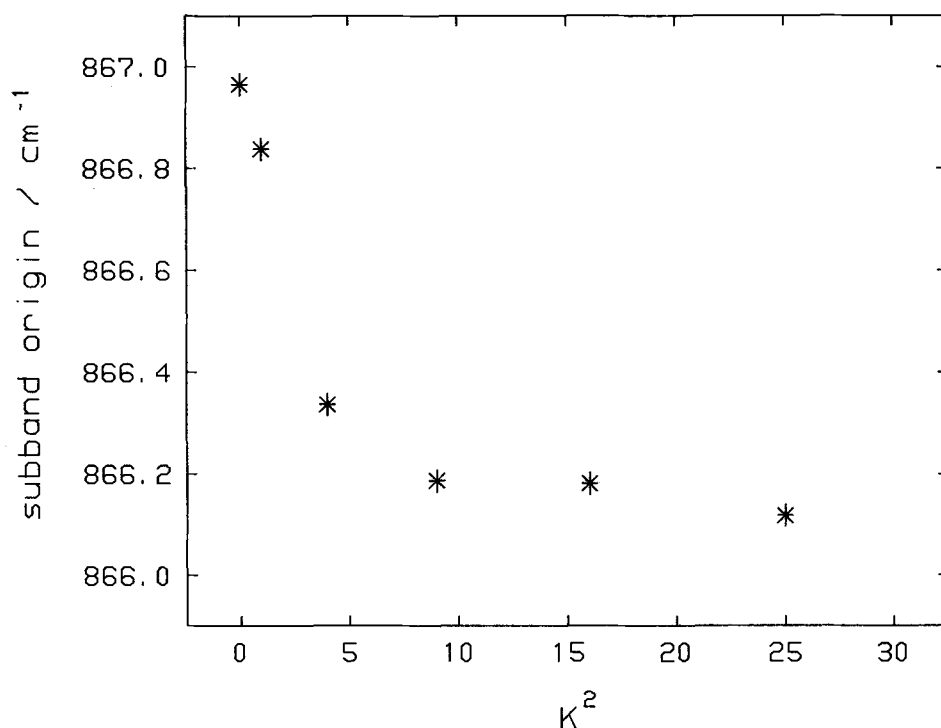


Figure 5. Plot of A state subband origins versus K_a^2 . The subband origins are calculated by fitting the transition frequencies for each K_a subband independently to a Watson A-reduction Hamiltonian, holding the excited state A rotational constant fixed at the ground state value (i.e., the band origins are the positions of 0_{00} level predicted from fitting each subband).

coupled to other nearby states and that a two-level treatment will not provide a sufficient model. Unfortunately, it is difficult to characterize a perturbing state which shifts the energy levels of a band but is too weak to be seen in the spectrum.

Evidence from recent high-resolution spectroscopic studies of a number of molecules suggests that 'contaminated' or perturbed tunnelling splittings in vibrationally excited states, even in low density-of-states regimes, are more the rule than the exception. For example, five normal-mode vibrations of propene, which is isoelectronic with acetaldehyde, were studied in the $900\text{--}1100\text{ cm}^{-1}$ region. It was found that the torsional tunnelling splittings for the excited states, $\nu_0(\text{E}) - \nu_0(\text{A})$, are -343.3 , -87.9 , -23.8 , $+189.1$ and $+279.7$ MHz, while the value for the ground state is $+102$ MHz [14]. It was shown that these large changes in tunnelling splittings are not attributable to changes in the barrier height, but arise from non-resonant coupling of the normal modes to background vibrations with excitation in the large amplitude motion. These observations combined with our current results on acetaldehyde and other recent results on methanol [15–18], ethane [19–21], CH_3SiH_3 [22], CH_3CF_3 [23], and NH_3 [24, 25] indicate that torsional tunnelling splittings are likely to contain contributions from anharmonic and Coriolis interactions with nearby background combination and overtone vibrations which contain several quanta in the low-frequency large amplitude vibrational mode, and thus alter the tunnelling splittings considerably.

We are grateful to J. T. Hougen for initially suggesting this problem and for providing ground-state energy levels. This work was funded partially by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, United States Department of Energy (grant number DE-FG05-90ER14161). In Brussels, we are indebted to Dr M. Herman, Dr M. Carleer and D. Hurtmans (ULB) for providing the FT Bruker spectrum used in the present analysis.

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