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10 μm High-resolution spectrum of *trans*-acrolein: Rotational analysis of the ν_{11}, ν_{16}, ν_{14} and $\nu_{16} + \nu_{18} - \nu_{18}$ bands ☆

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ABSTRACT

High-resolution Fourier transform spectra of *trans*-acrolein, $H_2C{=}C(H){-}C(H){=}O$, have been recorded in the 10 μm region at both room and cooled temperatures on the modified Bomem DA3.002 at the National Research Council of Canada and the Bruker IFS 125HR spectrometer at the far infrared beam line of the Canadian Light Source in Saskatoon. Vibrational fundamentals analyzed so far include the ν_{11}, ν_{16} and ν_{14} bands centered at 911.3, 958.7 and 992.7 cm^{-1} corresponding respectively to the A' in-plane $=CH_2$-rocking mode, the A'' out-of-plane $=CH_2$-wagging mode, and the A'' wagging mode highly mixed between the $\geqslant C{-}H$ vinyl and $\geqslant C{-}H$ formyl groups [Vibrational mode descriptions are based on Y.N. Panchenko, P. Pulay, F. Török, J. Mol. Spectrosc. 34 (1976) 283–289.] As well, the $\nu_{16} + \nu_{18} - \nu_{18}$ hot band centred at 957.6 cm^{-1} has been analyzed, where ν_{18} is the low-frequency (157.9 cm^{-1}) A'' $\geqslant C{-}C\leqslant$ torsional mode. The ν_{11} band is *a*/*b* type while the ν_{16}, ν_{14} and $\nu_{16} + \nu_{18} - \nu_{18}$ bands are *c*-type. The assigned transitions of each band have been fitted to a Watson asymmetric rotor Hamiltonian, with ground state parameters fixed to values obtained from rotational analyses in the literature. As well, a combined 3-state fit for ν_{11}, ν_{16} and ν_{14} was carried out including Coriolis and Z_1 constants which account for J and ΔK interactions. Transition dipole moments have been calculated for each of the fundamentals using the *ab initio* B3LYP method and 6-311++G** basis set. For the A' vibrational modes, we have also evaluated transition dipole *a*- and *b*-components in the principal axis system from vibrational displacements and dipole moment derivatives. Our *ab initio* results predict that the ν_{11} in-plane $=CH_2$ rocking mode has an *a*-type transition strength about three times greater than the *b*-type, which is consistent with our observations. Our *ab initio* force field analysis gives vibrational mode descriptions consistent with previously published work for all 13 A' modes. However, for the five A'' vibrational modes, our *ab initio* results disagree with two of the descriptions of Panchenko et al. and three of the descriptions of Hamada et al. [Y. Hamada, Y. Nishimura, M. Tsuboi, Chem. Phys. 100 (1985) 365–375].

1. Introduction

Acrolein, or propenal, plays an important role in environmental pollution [1–3] and may be present in interstellar molecular clouds [4]. It is principally used as a chemical intermediate in the production of acrylic acid and its esters. Combustion of fossil fuels and tobacco smoke contribute to the environmental prevalence of acrolein, which is a byproduct of fires and is one of several acute toxicants posing risks for firefighters. The American Environmental Protection Agency (EPA) has recently compiled a list of 188 Hazardous Air Pollutants formed from 32 main compounds and their derivatives. Acrolein is one of those 32 compounds and is also considered as one of the six priority mobile source air toxics [5,6] by the US Federal Highway Administration.

Spectroscopically, acrolein, $H_2C{=}C(H){-}C(H){=}O$, is among the first few medium size molecules containing several heavy atoms for which rotationally resolved high-resolution studies have been carried out in the mid-infrared region. The lower energy *trans* rotamer [7] has been the subject of most of the reported investigations of the rotational [8–10], vibration–rotation [11–14], and electronic [15–19] spectra. Most recently, there have been very

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detailed high-resolution studies [20–22] of the ν_{18}, ν_{13}, ν_{12} and ν_{17} fundamentals and their associated hot and combination bands, leading to a comprehensive energy map of the 10 states below 700 cm^{-1} shown in Fig. 1 of Ref. [22], using 1-state, 2-state, 3-state and 5-state treatments. These papers [20–22] have laid a strong foundation for further infrared (IR) studies in the region above 700 cm^{-1}.

The present paper reports analysis of several strong vibrational bands in the 10 μm region, as labeled in Fig. 1, to support detection of acrolein in a smoke environment using a tunable diode laser (TDL) spectrometer [23]. The bands include the ν_{11} $=\mathrm{CH_2}$ in-plane rocking mode (A') centred around 911.3 cm^{-1}, the ν_{16} $=\mathrm{CH_2}$ out-of-plane wagging mode (A'') centred around 958.7 cm^{-1} plus its associated $\nu_{16}+\nu_{18}-\nu_{18}$ hot band red-shifted by about 1.1 cm^{-1} from the fundamental, and the ν_{14} wagging mode (A'') that is highly mixed between the $\geqslant$C—H vinyl and $\geqslant$C—H formyl groups and is centred around 992.7 cm^{-1} [7]. The energy levels in Fig. 1 are computed under the harmonic approximation, using fundamental frequencies from [14], and staged in order of vibrational fundamentals, 1st overtones and higher order bath states. The ν_{15} fundamental is predicted to be very weak and has not yet been analyzed in high resolution.

In the present paper, the experimental conditions and the measurement procedure are presented in Section 2, then features of the spectra and assignments are discussed for each of the vibrational bands in Section 3. Modeling of the spectra, determination of the upper state molecular parameters and comparison of the parameters for the vibrational states are considered in Section 4. The *ab initio* analysis for the harmonic frequencies and vibrational mode descriptions is given in Section 5, and the calculation of the dipole derivative components and band intensities in Section 6. The paper concludes with discussion in Section 7.

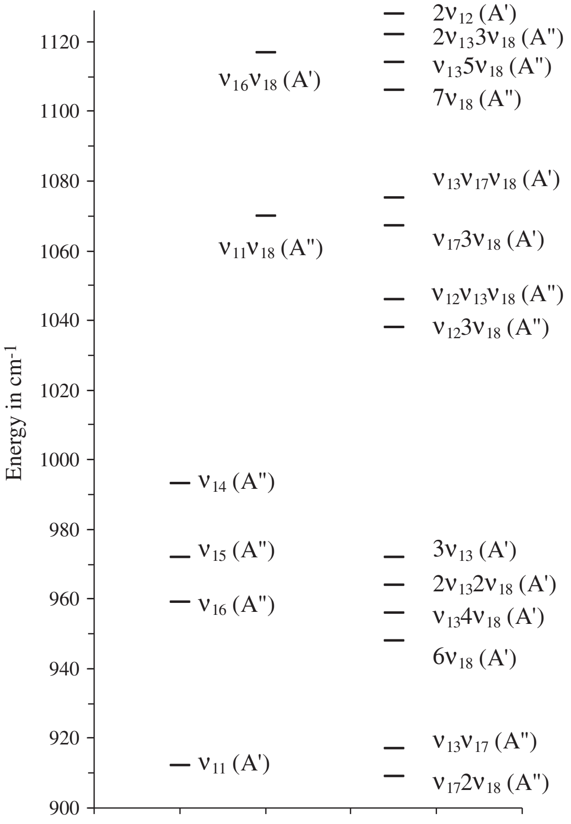

Fig. 1. Vibrational fundamentals, first overtones and bath states in the 10 μm region based on the harmonic approximation.

2. Fourier transform spectra

Initially, acrolein spectra from 878 to 1081 cm^{-1} were recorded at the National Research Council of Canada (NRC) in Ottawa on a modified Bomem DA3.002 Fourier transform spectrometer at 0.002 cm^{-1} resolution under both room and cooled temperature conditions. The room temperature spectrum was taken with a 29-cm multi-pass cell set to 4 transits at ~500 mTorr sample pressure with 196 scans co-added, and the cooled spectrum was recorded at an estimated temperature of ~180 K in a 2-m multi-pass cell set to 4 transits at ~60 mTorr sample pressure with 205 scans co-added. The latter spectrum was calibrated against the room temperature spectrum using ~200 selected strong acrolein lines. The simplification and reduced crowding in the cooled spectrum greatly assisted the rotational analysis. A third spectrum from 650 to 1549 cm^{-1} was later recorded on the Bruker IFS125HR spectrometer at the Canadian Light Source (CLS) synchrotron facility using the internal globar radiation source. The spectrum was recorded at a nominal resolution of 0.0012 cm^{-1} at room temperature with a 29-cm multi-pass cell set to 24 transits, 164 scans co-added and a sample pressure of ~0.47 Torr. Residual CO$_2$ lines could be recognized near 670 cm^{-1} and water lines near 1270 cm^{-1}. Our peak frequencies for these lines agreed with the standard reference values for CO$_2$ and water [24] to the 4th decimal place in cm^{-1} with the signs of the residuals randomly distributed, indicating that further frequency calibration was not necessary.

Spectral peak finding was performed using GRAMS and OPUS software packages [25,26], both of which gave consistent peak positions. Blended spectral features were analyzed using a multi-line fitting routine, built into the software. On average, the measurement uncertainty is believed to be within ±0.0005 cm^{-1}, with extensive overlapping and a high density of weak lines in the background contributing to frequent asymmetric line shapes and a relatively high uncertainty in line positions. Fig. 2 shows a comparison plot from 889 to 890 cm^{-1} of the (a) NRC room temperature, (b) NRC low temperature and (c) CLS room temperature spectra. We used the NRC spectra for initial analysis of the ν_{16} and ν_{14} bands, while the analysis of the ν_{11} and $\nu_{16}+\nu_{18}-\nu_{18}$ bands was based on the CLS spectrum.

3. Rotational analysis and vibrational band structures

3.1. ν_{11} (A') CH$_2$ in-plane rocking mode centred at 911.3 cm^{-1}

Acrolein is a planar near-prolate ($A > B \approx C$) asymmetric rotor belonging to the C_s point group, with both μ_a and μ_b permanent dipole components. In-plane vibrations with A' symmetry give rise to bands with a- and/or b-type transitions, while out-of-plane fundamentals with A'' symmetry give rise to bands with c-type transitions. Fig. 3 shows a medium resolution plot of the ν_{11} band from 908 to 911.5 cm^{-1} where a-type Q branches of different K_a values are illustrated. Each individual Q branch is relatively compact, indicating little change in the B and C rotational constants from ground to excited state. On the other hand, distinct shading of the Q-branch origins towards lower wavenumber with increasing K_a value indicates a reduced A constant in the upper state. The $|\Delta A|$ value can be estimated to be of order 0.02 cm^{-1} from the Q branch spacing seen in Fig. 3. With the small $(B+C)/2$ value of about 0.15 cm^{-1} [10] and the wide K_a spacing, compact a-type J-multiplet patterns are not seen for the R and P branches. Instead, as shown in the sample plot from 905 to 906 cm^{-1} in Fig. 4, P transitions ranging from $J = 11$ for high K_a to $J = 21$ for lower K_a all appear in the same spectral window. For $K_a \geqslant 11$, the P transitions are below 905 cm^{-1}. Other interesting features in this spectral