LETTER TO THE EDITOR

The Doppler-Splitting Method for the Ground Vibrational State

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Received February 26, 1996; accepted April 20, 1996

A novel technique of high-resolution spectroscopy has recently been developed in our laboratory (1). We used a new version of the IR-mmwave double-resonance method to study the \( \nu_1 = 1 \) excited vibrational state of CH\(_3\)I and to measure the frequency of rotational and vibrational transitions at sub-Doppler resolution (2). In this letter we describe the first application of the same approach to studying the ground vibrational state of a molecule. The basic idea is similar: double resonance with collinear propagation of pump and probe beams, which causes velocity selection and allows sub-Doppler resolution; however, in this case, the laser is used to decrease the population of the ground state, instead of populating an almost empty excited state.

The intensity of the pump laser is modulated by a mechanical chopper. In the absence of the laser a certain fraction of the microwave power is absorbed by the sample, while when the laser is present, the absorption is smaller because part of the molecules are removed from the lower state of microwave transition. The transmission of the mmwave radiation through the gas sample is measured using a synchronous amplifier referenced to the pump modulation. By this approach it is possible to observe the rotational transition of interest at sub-Doppler resolution, with the additional bonus of isolating it from other interfering transitions not connected to the laser excitation.

Two qualitatively different conditions can be found when the double resonance signals are recorded. In the first ("resonant") case the pump laser is tuned at, or very close to the IR resonance so that only the molecules with a null velocity component along the laser beam are excited. In this way one obtains a linewidth narrower than the Doppler limit. In the second case the laser is appreciably detuned, say by an amount \( \Delta \nu_{\text{IR}} \), from the exact center \( \nu_{\text{IR}} \) of the rovibrational transition, so a splitting of the rotational line is observed into two narrow components which correspond to counter- and copropagating radiations (see Figs. 2, 3 of Ref. 2). This Doppler-induced splitting amounts to \( \Delta \nu_{\text{rot}} = 2 \nu_{\text{rot}} \Delta \nu_{\text{IR}} / \nu_{\text{IR}} \) and can easily be changed by careful tuning of the laser frequency. As discussed in Ref. (2) for the case of an excited vibrational state, this approach allows the determination of the frequency \( \nu_{\text{IR}} \) with sub-Doppler accuracy. Here we prove that it is possible to use it also in the ground state.

The experimental setup has been described in Refs. (1, 2). We use a cavity spectrometer operating in the frequency region near 150 GHz to observe the rotational spectrum of CH\(_3\)I, and in Fig. 1 we summarize the principle of the experiment. In Fig. 1a we show what is observed in a traditional experiment, without using a laser. The power transmitted by the resonator is plotted versus the mmwave frequency: when the sample gas is present three lines (labelled as X, Y, and Z) appear, superimposed on the frequency scan of the sample transmission is displayed in (a) and shows two qualitatively different conditions can be found when the double resonance signals are recorded. In the first ("resonant") case the pump laser is tuned at, or very close to the IR resonance so that only the molecules with a null velocity component along the laser beam are excited. In this way one obtains a linewidth narrower than the Doppler limit. In the second case the laser is appreciably detuned, say by an amount \( \Delta \nu_{\text{IR}} \), from the exact center \( \nu_{\text{IR}} \) of the rovibrational transition, so a splitting of the rotational line is observed into two narrow components which correspond to counter- and copropagating radiations (see Figs. 2, 3 of Ref. 2). This Doppler-induced splitting amounts to \( \Delta \nu_{\text{rot}} = 2 \nu_{\text{rot}} \Delta \nu_{\text{IR}} / \nu_{\text{IR}} \) and can easily be changed by careful tuning of the laser frequency. As discussed in Ref. (2) for the case of an excited vibrational state, this approach allows the determination of the frequency \( \nu_{\text{IR}} \) with sub-Doppler accuracy. Here we prove that it is possible to use it also in the ground state.

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An example of the "resonant" case is shown in Fig. 1c, which displays the measurement of the absorption spectrum as recorded when the laser is chopped and tuned very close to the IR resonance of line Y. The frequency scale and the pressure are the same as in Fig. 1b: it is evident that the linewidth is smaller than before and, in addition, line Z is almost canceled, being reduced to a weak residual background. Last, but not least, the signal-to-noise ratio is very good as well. So this technique is a powerful tool for singling out a specific line in a crowded spectrum and allows accurate measurements which are otherwise impossible, e.g., lineshape and broadening studies.

FIG. 1. The mmwave spectrum of CH\(_3\)I near 149.95 GHz. A traditional frequency scan of the sample transmission is displayed in (a) and shows three lines superimposed on the resonator mode; trace (b) is an expanded version of its central part, where line Y is visible only as a shoulder of the stronger line Z. The third spectrum (c) is recorded by the double resonance method, using a CO\(_2\) laser operating on the 10-P(8) line at a small detuning (\(\Delta \nu_{\text{IR}}\)) from the infrared resonance of the \(^6R_0(9)\) line.
We report here the measurements of the rotational frequency $\nu_{\text{rot}}$ of line Y, which has never been directly measured, and of the rovibrational frequency $\nu_{\text{IR}}$ for the $^5\text{R}_d(9)$, $F = 25/2 - 23/2$ hyperfine transition, which was previously reported in Ref. (3). These results have been obtained from several data, taken with both resonant and nonresonant IR frequency, and the preliminary values are: $\nu_{\text{rot}} = 149,952.4516 \pm 20$ MHz and $\nu_{\text{IR}} = 28,616,560.3 \pm 4$ MHz. The rotational frequency is in good agreement with the value that can be computed using the available molecular constants (4), while the infrared frequency is slightly different from that in the literature data (3).

In conclusion, we have demonstrated that the method of Doppler splitting can be used for transitions in the ground vibrational state, the accuracy of the measurements is comparable to that of other Doppler-free techniques, and the method can be particularly appealing in cases of crowded spectra.

REFERENCES