Doppler-Free Two-Photon Millimeter Wave Transitions in OCS and CHF_3

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Doppler-free two-photon rotational transitions $J = 13 \leftarrow\leftarrow 11$ and $J = 12 \leftarrow\leftarrow 10$ of OCS and $J = 8 \leftarrow\leftarrow 6$ and $J = 7 \leftarrow\leftarrow 5$ of CHF_3 were detected in the frequency range 134–156 GHz, using a novel, highly sensitive intracavity-jet technique. The sub-Doppler narrowing of the observed peaks (down to 40 kHz full width at half maximum as compared to 300 kHz of the Doppler width) demonstrates the potential of this new technique for high precision millimeter wave spectroscopy. The possibilities of the further reduction of the two-photon absorption line widths are considered.

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The possibility of using two-photon absorption in a standing electromagnetic wave by molecular or atomic gases for removing Doppler broadening of the absorption lines was first discussed by Vasilenko *et al.* [1]. The idea of the method is that, for a particular velocity group of the absorbing particles in a gas, the first order Doppler shift has an opposite sign for two counterpropagating electromagnetic waves. Therefore, if one quantum of radiation is absorbed from each of the two counterpropagating waves, the resulting frequency of the two-photon transition does not depend on the velocity of the particle; i.e., the Doppler effect will not influence the absorption linewidth. This effect has been used for Doppler-free laser spectroscopy in the infrared or optical regions, involving electronic or vibrational transitions of atoms or molecules (see, for example, [2]).

As far as we know, there have been no observations of Doppler-free two-photon absorption lines in the microwave or millimeter wave regions on pure rotational molecular transitions. Carrington *et al.* observed two-photon microwave transitions in the electron-resonance spectra of NO, ClO, BrO, and SO [3]. Microwave two-photon transitions in CD_3CN and PF_3 were observed by Oka and Shimizu using a microwave-microwave double resonance technique [4]. Martinache *et al.* detected two-photon absorption in CF_3CCH by using a microwave pulsed beam Fourier transform crossed-cavity spectrometer [5]. In the present paper, we report an experimental observation of Doppler-free two-photon transitions in the OCS and CHF_3 molecules, placed in the resonator of a millimeter wave generator called OROTRON. The width of the two-photon absorption lines was reduced by 1 order of magnitude in comparison with the normal Doppler width, allowing an extension of the nonlinear Doppler-free two-photon spectroscopy to the microwave and millimeter wave ranges.

The standing wave arrangement of the radiation necessary for the Doppler-free two-photon excitation was achieved by placing investigated molecules inside the resonator of the millimeter wave generator OROTRON [6]. The intracavity arrangement also enabled the high sensitivity required for the detection of the weak two-photon absorption. In the following, we describe briefly the operation and detection principle of the spectrometer, emphasizing those features which are essential for understanding the analysis of the experimental results.

The semiconcentric resonator of the millimeter wave generator OROTRON (Fig. 1) consists of a plane and a spherical mirror. The resonator is divided in two parts by a mica window. In the high vacuum part, the electrons are emitted by a cathode and accelerated by the high voltage applied to the plane mirror. A periodic structure fabricated on the surface of the plane mirror enables interaction of the electrons with the electromagnetic field in the resonator. This interaction causes the generation of millimeter wave radiation. For the generation to occur, the time the electrons need to cross one period of the structure has to be equal to the time period of one of the modes of the resonator. Hence, at a given period of the slow wave structure, the millimeter wave radiation frequency is determined by the accelerating voltage. For a chosen voltage, the generation conditions could be fulfilled by tuning the length of the resonator. Most of the electrons emitted by the cathode arrive at the anode, i.e., they reach the plane mirror. However, a small fraction of about 1% of the electronic beam passes through the slotted slow wave structure and reaches the collector, which is placed beyond the plane mirror. The collector is maintained at a potential close to that of the cathode. As the electrons are interacting with the electromagnetic field, their velocity distribution and, hence, the collector current depend on the radiation power in the resonator. Therefore, an absorption in the resonator can be very sensitively detected by measuring changes of the collector current. Part of the millimeter wave radiation was taken out of the resonator through coupling openings in the spherical mirror and mixed on a Schottky diode with the fundamental of a microwave synthesizer in order to measure the generation frequency.

Investigated molecules were injected into the low vacuum part of the resonator by a pulsed wave (General

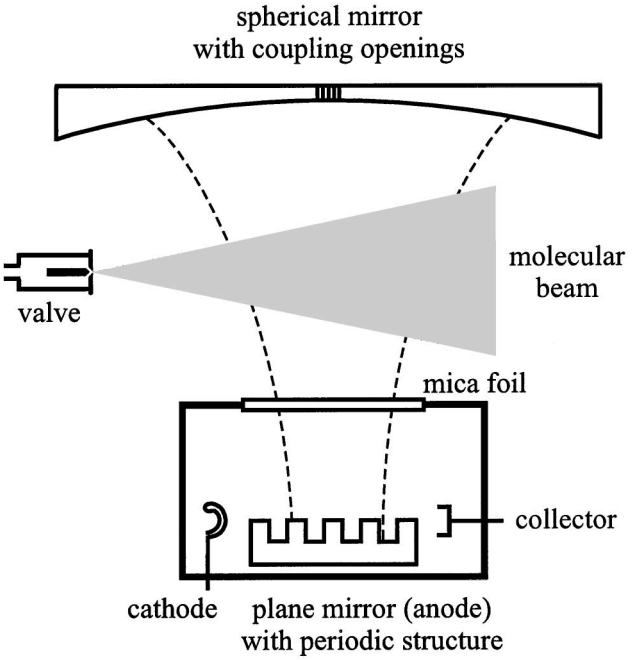

FIG. 1. Schematic representation of the intracavity jet arrangement of the OROTRON spectrometer. The geometry of the electromagnetic field in the resonator is shown by dashed lines. The periodic structure with the period of 120 μm is shown schematically on the surface of the plane mirror.

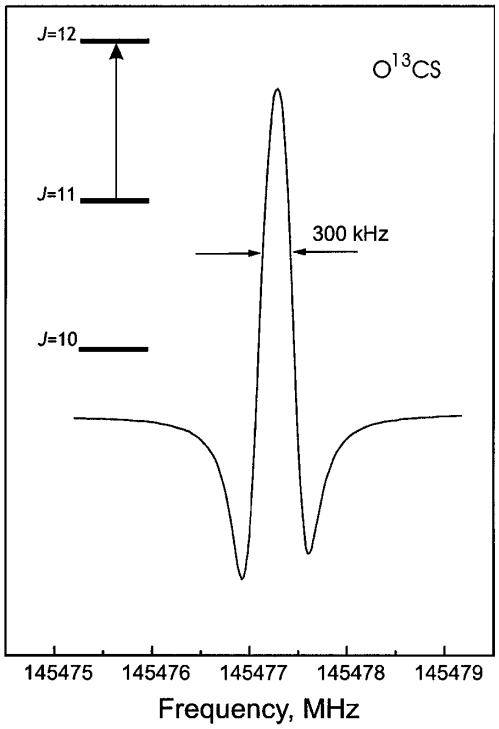

FIG. 2. The $J = 12 \leftarrow 11$ transition of $O^{13}CS$ measured in natural abundance of 1% with the intracavity jet millimeter wave spectrometer. The width of the absorption line is determined by Doppler broadening in the free jet.

Valve, 1 mm opening diameter, 5–10 Hz repetition rate) and evacuated by a diffusion pump. Typically, backing pressure of 1 bar of the gas under investigation was used for the supersonic expansion. In order to increase the sensitivity, the double modulation technique was used for the signal detection. The OROTRON frequency was modulated at a $f = 25$ kHz sinewave. The source modulation amplitude was chosen to optimize the signal without additional broadening of the line. The $2f$ detection of the collector signal by a lock-in amplifier was followed by a gated detection with a boxcar integrator. The two gates of the boxcar were set shortly before and during the gas pulse. Subsequently, a subtraction was performed within the boxcar. The total integration time for all recorded single- and two-photon spectra was a few minutes, with the time constant of the registration system 1 s.

The performance of the spectrometer was tested by recording single-photon absorption transitions of OCS and CHF_3. As an example, the $J = 12 \leftarrow 11$ absorption line of a linear molecule $O^{13}CS$ is shown in Fig. 2. Here, J denotes the rotational angular momentum of a molecule. The intensity of the radiation in the resonator was kept at a low level, i.e., near the generation threshold, in order to avoid saturation of the absorption signal. The recorded "second-derivative" line shape is a consequence of the $2f$ detection technique. The linewidth is 300 kHz if measured as the full width at half maximum (FWHM) of the central peak.

In order to observe two-photon transitions in OCS, the generation power was increased to a higher level, which was estimated to be about 1 W/cm^2. At this power level, two-photon absorption signals were detected for the $J = 13 \leftarrow\leftarrow 11$ and $J = 12 \leftarrow\leftarrow 10$ transitions of OCS. A recording of the $J = 12 \leftarrow\leftarrow 10$ transition is shown in Fig. 3. The line profile is presented as a function of the OROTRON frequency. The width (FWHM) of the central peak is about 40 kHz, which is 7–8 times smaller than the normal Doppler width of a single-photon absorption line. The center frequencies of the recorded transitions $J = 13 \leftarrow\leftarrow 11$ and $J = 12 \leftarrow\leftarrow 10$ are 152 027.076 (8) MHz and 139 866.364 (4) MHz, which coincide within the estimated uncertainty to the values 152 027.086 (4) MHz and 139 866.356 (4) MHz obtained in the previous Lamb dip and molecular beam studies [7,8].

For a symmetric top molecule CHF_3, the $K = 0$ and $K = 1$ components of the two-photon transitions $J = 7 \leftarrow\leftarrow 5$ and $J = 8 \leftarrow\leftarrow 6$ were measured. Here, K is the projection of the rotational angular momentum J on the symmetry axis of the molecule. At Doppler limited resolution, the closely spaced $K = 0$ and $K = 1$ components of CHF_3 usually remained unresolved. However, the reduction of the linewidths caused by two-photon absorption allows these two K components to be resolved, as shown in Fig. 4 for the $J = 8 \leftarrow\leftarrow 6$ spectrum. As can be seen from this spectrum, the width (FWHM) of

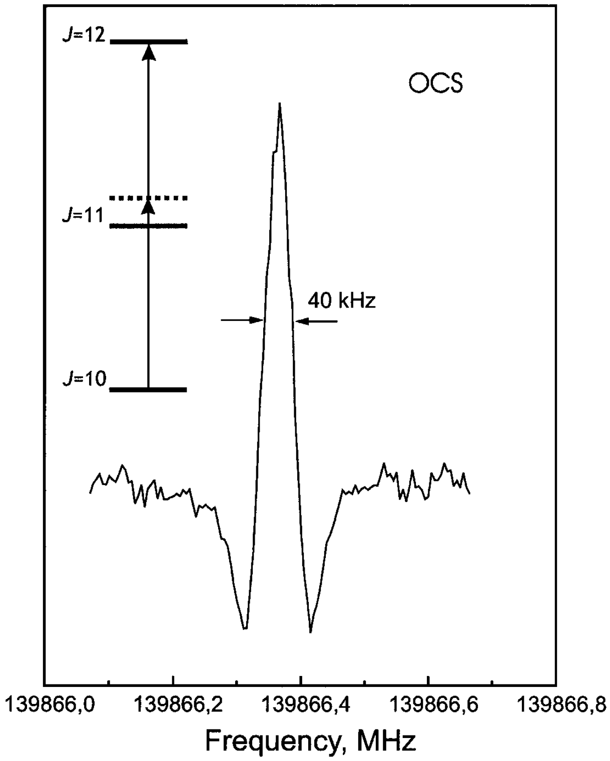

FIG. 3. The Doppler-free two-photon $J = 12 \longleftarrow\!\longleftarrow 10$ transition of OCS. The linewidth is reduced by an order of magnitude in comparison with the Doppler width.

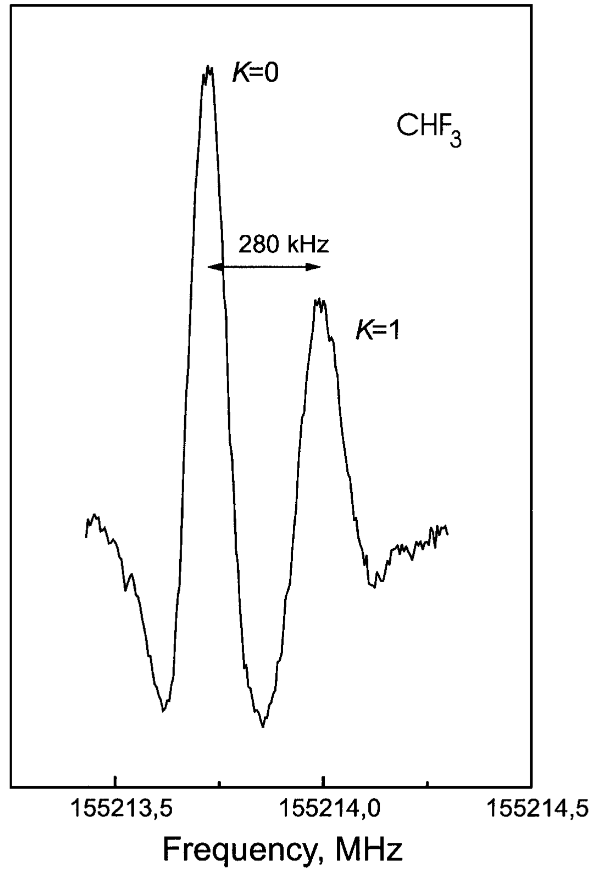

FIG. 4. The resolved $K = 0$ and $K = 1$ components of the Doppler-free two-photon transition $J = 8 \longleftarrow\!\longleftarrow 6$ of CHF_3. The width of the two components is mainly determined by the collisional homogeneous broadening in the jet.

each of the two components, i.e., $K = 0$ and $K = 1$, is about 70 kHz, and the splitting between the $K = 0$ and $K = 1$ components is 280 kHz.

Several factors influence the linewidth of the observed two-photon transitions. These are the limited time of flight of molecules through the millimeter wave radiation field, the radiation linewidth of the OROTRON generator, the frequency and the amplitude of the source modulation, and the collisional broadening in the jet. The time of flight $\tau = d/\nu$ can be estimated assuming the mean velocity of molecules in the jet to be $\nu = 500$ m/s and the diameter of the radiation beam to be $d = 2$ cm. The time of flight is $\tau = 40\ \mu$s, corresponding to the broadening of about 5 kHz. The measured radiation linewidth of the OROTRON generator was 10–15 kHz. The modulation broadening is caused by the source modulation $f = 25$ kHz, and is close to the value of the modulation frequency. All these broadening effects are smaller than the observed width of the two-photon absorption lines. We concluded, therefore, that the observed linewidths were mainly determined by collisional broadening in the supersonic jet conditions. The narrower two-photon linewidth observed for OCS as compared to CHF_3 confirmed this suggestion. The permanent dipole moment of the OCS molecule (0.71 D) is more than 2 times smaller than the dipole moment of the CHF_3 molecule (1.64 D). This difference results in the larger collisional broadening for CHF_3 as compared to OCS.

The limited time of flight of the molecules through the millimeter wave cavity is the only broadening factor which cannot be improved in the present configuration of the intracavity-jet experiment. The radiation linewidth can be made well below 1 Hz by phase locking of the OROTRON generator to a frequency stabilized microwave synthesizer. The source modulation frequency can be reduced from 25 kHz to a few kHz without substantial losses in sensitivity. Finally, the collisional broadening can be reduced by using pulsed valves with smaller opening diameters in order to decrease the density of molecules in the cavity. We conclude that the linewidth of Doppler-free two-photon absorption lines can be reduced to 5–10 kHz by optimizing the spectrometer and the experimental conditions. However, the proposed refinements, which seem to be technologically straightforward, require quite a change of the existing experimental setup for their practical realization. They are beyond the scope of the present work.

The absorption coefficient of a two-photon $\Delta J = 2$ transition can be compared to that of a corresponding single-photon $\Delta J = 1$ transition. The probability of the two-photon transitions $\langle 2| \longleftarrow\!\longleftarrow \langle 0|$ in the presence of an intermediate state $\langle 1|$ is proportional [9] to the square of

the matrix element $\{[(\mu_{01}E)/\hbar][(\mu_{12}E)/\hbar]\}/(\Delta\omega)$. Here, μ_{01} and μ_{12} denote matrix elements of the dipole moment operator for the allowed transitions between the states $\langle 1| \leftarrow \langle 0|$ and $\langle 2| \leftarrow \langle 1|$, E is the strength of the electric field, and $\Delta\omega$ is the detuning of the pump radiation frequency from the $\langle 1| \leftarrow \langle 0|$ or $\langle 2| \leftarrow \langle 1|$ transition. For the corresponding single-photon transition $\langle 2| \leftarrow \langle 1|$, the probability is proportional to the square of the matrix element $(\mu_{12}E)/\hbar$. The ratio of the probabilities of the transitions $\langle 2| \leftarrow\leftarrow \langle 0|$ and $\langle 2| \leftarrow \langle 1|$ can be estimated as $[(\mu_{01}E)/\hbar\Delta\omega]^2$. For the two-photon $J = 12 \leftarrow\leftarrow 10$ and single-photon $J = 12 \leftarrow 11$ transitions of OCS, this expression is equal to 10^{-6} if we take the electric field E to correspond to the power density 1 W/cm^2. This value is equal to the experimentally determined ratio with an uncertainty factor of 2, which confirms the correct estimation of the power density inside the OROTRON resonator.

In conclusion, Doppler-free two-photon absorption spectroscopy was experimentally realized on pure rotational molecular transitions in the millimeter wave range. It is expected that the new millimeter wave two-photon absorption technique will enable precise measurements of molecular transitions with substantially improved accuracy and resolution.

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[1] L. S. Vasilenko, V. P. Chebotaev, and A. V. Shishaev, Pis'ma Zh. Eksp. Teor. Fis. **12**, 161 (1970).
[2] V. S. Letokhov and V. P. Chebotaev, *Springer Series in Optical Sciences* (Springer-Verlag, Berlin, 1970), Vol. 4.
[3] A. Carrington, D. H. Levy, and T. A. Miller, J. Chem. Phys. **47**, 4859 (1967).
[4] T. Oka and T. Shimizu, Phys. Rev. A **2**, 587 (1970).
[5] L. Martinache, I. Ozier, and A. Bauder, J. Chem. Phys. **92**, 7128 (1990).
[6] L. A. Surin, D. A. Roth, I. Pak, B. S. Dumesh, F. Lewen, and G. Winnewisser, J. Chem. Phys. **112**, 4064 (2000).
[7] R. S. Winton and W. Gordy, Phys. Lett. **32A**, 219 (1970).
[8] A. Dubrulle, J. Demaison, J. Burie, and D. Boucher, Z. Naturforsch. **35A**, 471 (1980).
[9] M. Göppert-Mayer, Ann. Phys. (Paris) **9**, 273 (1931).