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# Microwave-submillimeter wave double-resonance spectrometer for the investigation of van der Waals complexes

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A double-resonance spectrometer, suitable for the investigation of low lying intermolecular vibrational modes and of tunneling transitions of van der Waals complexes, is described. The instrument utilizes a pulsed molecular beam Fourier transform microwave spectrometer (frequency range 4–26 GHz) for signal detection, and a high frequency, phase stabilized, backward wave oscillator (258–375 GHz), as well as a millimeter wave synthesizer (78–118 GHz), as pump radiation sources. A brief description of the Fourier transform microwave spectrometer and of the phase stabilization system of the backward wave oscillator is given. The experimental arrangement is such that the molecular ensemble travels through the submillimeter radiation field prior to the pulsed excitation microwave experiment, in which the resulting population changes are detected. The sensitivity and the resolution capabilities of the new technique are illustrated with double resonance spectra of the van der Waals complexes Ar–CO and CO–N<sub>2</sub>. © 1998 American Institute of Physics. [S0034-6748(98)01312-4]

## I. INTRODUCTION

Weak intermolecular interactions, such as van der Waals or hydrogen bonding, are responsible for a multitude of phenomena and may affect the properties of dense phases of matter significantly. Examples are condensation and biological recognition, and the lattice structures of solid rare gases. High resolution spectroscopic investigations of van der Waals complexes have become one of the richest experimental sources for quantitative descriptions of potential energy surfaces of weak intermolecular interactions. Numerous studies of rotational spectra in the microwave (MW) and radio frequency (rf) ranges, van der Waals vibrational and tunneling spectra in the far-infrared (FIR), and near-infrared (IR) spectra associated with monomer vibrations have been published. Some of the first MW and rf studies were done using the method of molecular beam electric resonance spectroscopy.<sup>1</sup> Fourier transform (FT) MW spectrometers of the Balle–Flygare type<sup>2–5</sup> have become a powerful tool for the investigation of rotational transitions. In the IR region, FT techniques<sup>6</sup> and laser absorption-modulation techniques<sup>7,8</sup> are used on static gas samples and pulsed and continuous molecular beams.

Use of spectroscopic techniques in the millimeter,<sup>9</sup> submillimeter,<sup>10</sup> and FIR ranges<sup>11</sup> has been less widespread, mainly because of the difficulties in providing coherent and tunable radiation sources. High resolution spectra of van der Waals complexes in these frequency ranges, however, depend in the most sensitive way on the interaction potential energy surfaces, because they probe the characteristic intermolecular large amplitude motions. These spectra are therefore a rich source of detailed information for the construction of the corresponding potential energy surfaces.

The difficulties associated with spectroscopic investigations of van der Waals complexes in the range from the millimeter waves to the FIR concerns both the radiation sources and the detectors. An account of the state of the art of FIR spectrometers has been given in an article by Blake *et al.*<sup>12</sup> The availability of tunable and coherent radiation sources is essential for high resolution and high sensitivity spectroscopy. Several types of such sources that differ in complexity and in their specifications, such as output power, frequency stability, spectral purity, are in use in FIR and submillimeter spectrometers.<sup>12</sup> However, some of the most commonly used techniques, such as harmonic generation from tunable MW sources and generation of tunable FIR laser sideband radiation, produce only output powers in the  $\mu$ W range. This is sufficient for spectroscopy of molecular systems with relatively large transition dipole moments. The relatively low power of these sources, however, is a significant drawback for the investigation of species with small transition dipole moments. It was only recently that tunable coherent backward wave oscillators (BWOs) with output powers in the mW range could be phase stabilized and thus utilized for high precision spectroscopy in the Terahertz frequency range.<sup>13</sup>

In this article we present a double-resonance technique that can be used for the detection of, for example, intermolecular low frequency van der Waals vibrations or tunneling motions in weakly bound complexes. The double-resonance signal is detected in the MW range, using a pulsed molecular beam FTMW spectrometer.<sup>2–5</sup> This type of spectrometer is particularly sensitive for the detection of rotational transitions of van der Waals complexes with small dipole moments. Studies of rare gas hetero dimers<sup>14,15</sup> and of larger rare gas hetero clusters<sup>16,17</sup> are testimony to this. An additional advantage of the FTMW spectrometer is its modulation free operation, and, as a result, relatively simple line

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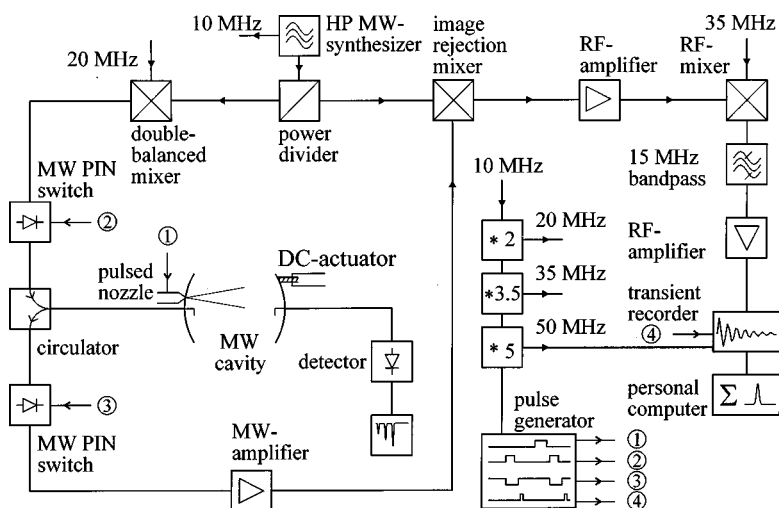


FIG. 1. Schematic diagram of the FTMW spectrometer.

shapes. (See, however, Ref. 18 for a discussion of line shapes.) A high frequency BWO is used as pump radiation source in the double-resonance scheme. This source combines relatively high output power (up to 60 mW) with broadband tunability in a phase-stabilized mode. A brief description of the main features of the FTMW spectrometer will be given, followed by a short discussion of the operation of the BWO tube. Spectra of two molecular systems, Ar-CO and CO-N<sub>2</sub>, serve to demonstrate the sensitivity and resolution achieved with the double-resonance technique.

## II. FTMW SPECTROMETER

A short description of the FTMW spectrometer used has been given previously.<sup>19</sup> For completeness, however, a brief discussion of the details of this instrument follows here. The measurement principle is that of coherent pulsed excitation of a molecular ensemble with subsequent detection of the spontaneous coherent molecular emission signal ("free induction decay" FID) as a function of time. A block diagram of the spectrometer is shown in Fig. 1. The sample cell of the spectrometer is a MW cavity that is formed by two spherical aluminum mirrors (diameter 260 mm, radius of curvature 380 mm). One of the mirrors is fixed and mounted into the flange cover of a cylindrical stainless-steel vacuum chamber (diameter 50 cm, length 70 cm). The other mirror is mounted on two linear bearings and can be positioned with a computer controlled Motor Mike drive (Oriol). A 12 in. diffusion pump (Diffstack 250/2000 M, Edwards), backed by a 800  $\ell$ /min rotary pump (E2M40, Edwards), is used to evacuate the chamber.

A MW synthesizer (Hewlett Packard, HP 83711 B) with operating range from 1 to 20 GHz is used as the radiation source. The MW excitation pulses typically have pulse lengths of a few  $\mu$ s and are generated with two *p-i-n* diode MW switches (Sierra Microwave Technology, SFS 0526-001). The pulse frequency is up-converted to (synthesizer frequency + 20 MHz) by selecting the upper sideband from a double balanced mixer (Miteq, DB 0218 LW2). For molecular systems with relatively small transition dipole moments, such as Ar-CO and CO-N<sub>2</sub>, solid state power amplifiers (Miteq, AMF-8B-081800-2TP, 8–18 GHz, and Mini Cir-

cuits, ZVE-8G, 4–8 GHz) are used to produce MW pulse powers in the order of 0.5–1.0 W, depending on the frequency range. The radiation is fed through a circulator (Sierra Microwave technology, SMC 6018) into the MW cavity through a wire hook antenna. The molecular emission signal is detected with the same antenna, and then fed through the circulator into a heterodyne detection circuit. This circuit consists of a low noise MW amplifier (Miteq, AMF-4F-080180-18-10P), and two mixing stages in which the molecular signal is down-converted to radio frequencies around 15 MHz. A single sideband mixer (Miteq, IR 0618 LC3A) is used in the MW mixing stage in order to avoid the accumulation of noise from the unwanted sideband. The FID is then digitized in a personal computer based transient recorder card (Gage, CS 225) at sample intervals of 20, 60, or 120 ns, depending on the desired spectral resolution. 4k data points are stored in the computer for signal averaging. A fast FT algorithm produces the frequency spectrum; the transition frequencies are obtained from a three-point interpolation procedure. Prior to the experiment the MW cavity is tuned into resonance with the excitation pulse frequency. For this purpose, the cavity throughput is monitored with a detector attached to an antenna in the moveable MW mirror. The procedure of scanning through larger frequency ranges is automated in a similar fashion as described in Ref. 5. The internal 10 MHz standard of the MW synthesizer is used as the reference for phase synchronous spectrometer control and data acquisition.

The molecular sample is prepared in a pulsed molecular expansion through a nozzle (General Valve, Series 9, orifice diameter 0.8 mm) into the MW cavity. The nozzle is mounted near the center of the fixed mirror, such that the expansion travels parallel to the cavity axis.<sup>20</sup> As a result, all lines appear as Doppler doublets in the MW spectra. For the generation of van der Waals complexes, we typically use 1% of the constituent gases (e.g., 1% Ar and 1% CO) in Ne at backing pressures of up to 10 atm. The experiment repetition rate is about 2 Hz, limited by the capacity of the diffusion pump. Typical linewidths are 7 kHz (full width at half height) and measurement accuracy is believed to be better than  $\pm 1$  kHz.

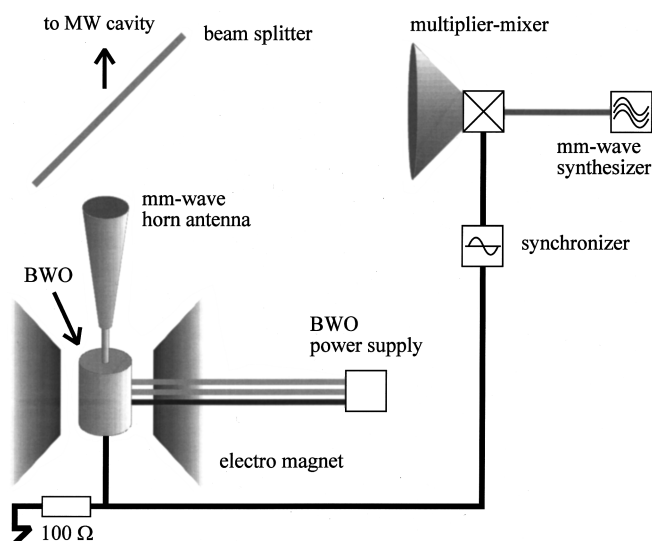


FIG. 2. Schematic diagram of the BWO stabilization scheme.

### III. BWO OPERATION

The type of BWOs used in the current experiment was developed by the State Research and Production Corporation "Istok" (Fryazino, Moscow Region, Russia).<sup>21</sup> Operation of the first phase-lock loop (PLL) stabilization system for these BWOs in the frequency range up to 350 GHz was demonstrated in 1970.<sup>22</sup> The operating range of the system was then extended in several stages up to 820 GHz.<sup>23</sup> The next important step towards the high frequency range was made after the development of a series of commercial millimeter wave synthesizers by the Institute of Electronic Measurements "Kvarz" (Nizhny Novgorod, Russia), covering the frequency range from 35 to 178 GHz.<sup>24</sup> The synthesizers are based on "Istok" BWOs that are stabilized by a PLL system against a radio reference signal. Phase stabilization of high frequency BWOs up to 970 GHz was then achieved in the Cologne laboratory by Winnewisser *et al.*<sup>13</sup> in a collaboration with the Institute of Applied Physics at the Russian Academy of Sciences (IAP RAS) using the millimeter wave synthesizer as reference for the PLL. The frequency range was subsequently extended up to 1267 GHz.<sup>25</sup> A detailed description of the Cologne submillimeter absorption spectrometer can be found in Ref. 10. A similar BWO phase stabilization scheme was employed in this work.

Figure 2 shows a schematic diagram of the BWO phase stabilization circuit. The BWO tube (Istok, OB30) is positioned between the poles of an electromagnet (Bruker, B-E 10) and can be fine adjusted with a translation-rotation stage for collimation of the electron beam. A high voltage (500–6000 V), high stability (output voltage stabilization coefficient  $>100\,000$ , alternating part of output voltage  $<10$  mV,  $<0.1$  V/h drift) power supply with a high stability filament current (heating current stabilization coefficient  $\approx 50\,000$ ) is used. Incorporated into the power supply is a BWO tube protection circuit that drops the output voltage within  $10\ \mu\text{s}$  after tripping. The BWO unit has an oversized waveguide (waveguide dimensions  $1.2\text{ mm} \times 2.4\text{ mm}$ ) as output that is connected to a millimeter wave horn antenna. A beam splitter (Teflon sheet, 0.5 mm) reflects part of the radiation onto

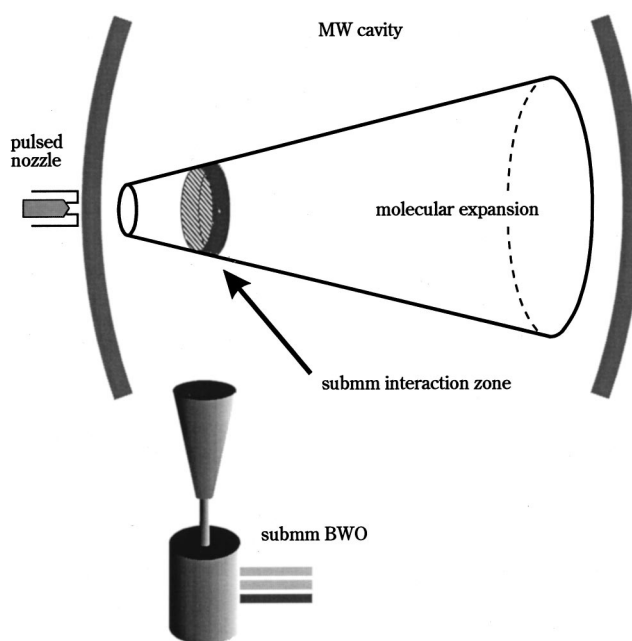


FIG. 3. Experimental arrangement of the submillimeter source in the FTMW spectrometer.

the parabolic mirror of a harmonic mixer unit that utilizes a planar Schottky-barrier diode. The local oscillator of the mixer is a millimeter wave synthesizer (78–118 GHz), connected to the mixer with a 30 cm long waveguide ( $1.2\text{ mm} \times 2.4\text{ mm}$ ). The intermediate frequency (IF) of 350 MHz from the mixer is amplified, divided by 10, and fed into a synchronizing unit for phase locking to the seventh harmonic of a 5 MHz reference. The correction signal for frequency phase stabilization is applied to a  $100\ \Omega$  resistor which connects the BWO anode to ground. Tuning of the high frequency BWOs is achieved by changing the frequency of the millimeter wave synthesizer that is used as the local oscillator in the PLL. The synthesizer is computer controlled via IEEE bus. The internal 5 MHz standard of the millimeter wave synthesizer is currently used as the reference for the PLL.

BWO power supply, translation-rotation stage, horn antenna, phase synchronizer, and harmonic mixer were purchased from the IAP RAS. The millimeter wave synthesizer is from the Institute of Electronic Measurement, "Kvarz."

### IV. EXPERIMENTAL ARRANGEMENT AND PROCEDURE

The BWO source is incorporated into the MW spectrometer as shown schematically in Fig. 3, similar to an arrangement used in a previous MW-millimeter wave double-resonance study of *b*-type rotational transitions of Ar-CO.<sup>26</sup> The BWO radiation enters the vacuum chamber through a Teflon window (7 mm thick, diameter 5 cm) that is mounted into the cover of a side looking flange at the height of the pulsed nozzle. The center of the submillimeter wave beam intersects the molecular beam approximately 12 cm downstream from the nozzle orifice. After traversing the MW cavity in a perpendicular fashion, the BWO radiation is reflected

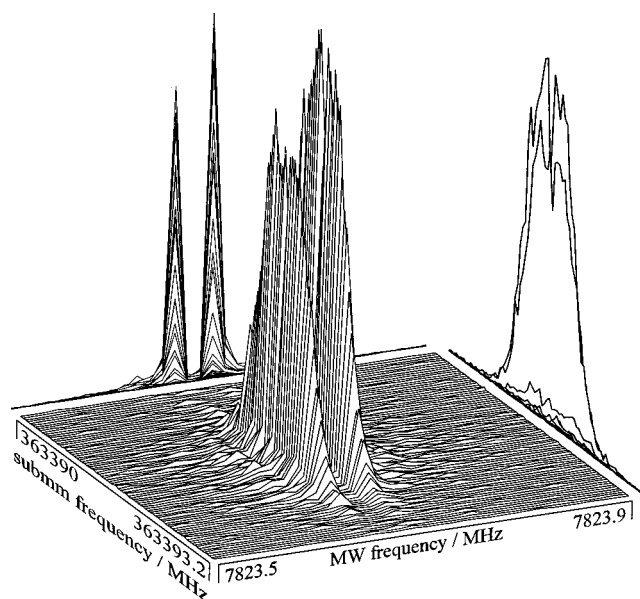


FIG. 4. Three-dimensional view of a double-resonance spectrum of the Ar-CO van der Waals complex. Signal transition:  $J_{K_a K_c} = 2_{02} - 1_{01}$ ,  $\nu_{\text{bend}} = 1$ ; pump transition:  $J_{K_a K_c} = 1_{01} - 0_{00}$ ,  $\nu_{\text{bend}} = 1 - 0$ . The total accumulation time for this spectrum was 4 min.

back by a copper mirror (diameter 17.6 cm, radius of curvature 54.8 cm) to intersect the molecular beam again.

The spectra obtained (see Sec. V) can be interpreted in the following way. The molecular ensemble travels on its way from the nozzle to the opposite MW mirror through the beam of submillimeter wave radiation. The molecules see, in effect, a submillimeter radiation pulse that affects population changes in the energy levels involved in the pump transition in the case of resonance or near resonance. These population changes can then be monitored with the subsequent MW experiment, that involves one of the pump transition energy levels. In this simplified view the experiment is thus a two-pulse experiment consisting of a submillimeter pump pulse followed by a MW signal excitation pulse.

If the frequency of the signal (MW) transition is known, recording of the double-resonance spectrum is relatively straightforward. The FTMW spectrometer is tuned to, and kept fixed at, the MW signal transition frequency. Individual MW spectra are then recorded as a function of pump (submillimeter) frequency. The result can be represented as a stack of MW spectra, as shown in Fig. 4 for the case of the Ar-CO van der Waals complex. In this particular case, the signal (MW) transition energy levels are only sufficiently populated for the MW transition to be seen, if the pump frequency is near resonant [see energy level diagram in Fig. 5(a)]. The projection of the three-dimensional view onto the MW axis gives the spectrum of the signal transition, the projection onto the submillimeter axis gives the spectrum of the pump transition. If the frequency of the signal transition is not known, a two-dimensional search procedure has to be employed in which the MW excitation frequency has also to be varied systematically. This procedure is automated and can be run without operator intervention.

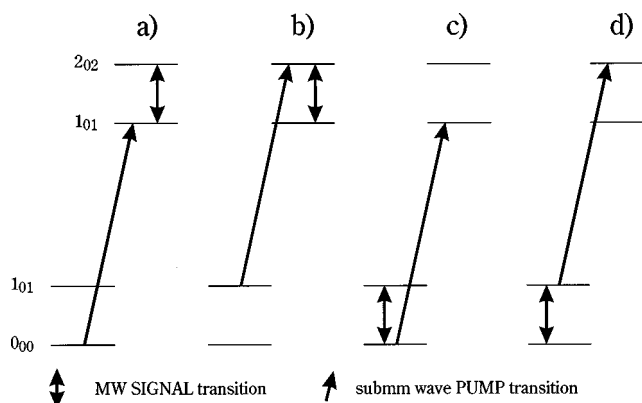


FIG. 5. Four possible three-level double-resonance connections. Experiments were successful using schemes (a) and (b). For an explanation of the failure to observe double-resonance effects with schemes (c) and (d), see the text.

## V. MOLECULAR EXAMPLES AND SPECTROMETER PERFORMANCE

The Ar-CO van der Waals complex has been studied extensively spectroscopically in the infrared,<sup>7,27-31</sup> submillimeter,<sup>10,32,33</sup> millimeter wave,<sup>26,34</sup> and MW<sup>35</sup> ranges. In particular, Xu and McKeller<sup>31</sup> have measured infrared transitions that originate in the first excited van der Waals bending state, and were able to determine the band origin of this state from combination differences. Subsequently, Winnewisser and co-workers have measured directly transitions from the ground state to the first excited bending state, using a Terahertz absorption spectrometer.<sup>10,32</sup>

Shown in Fig. 4 is a three-dimensional view of a low resolution double-resonance spectrum of the Ar-CO complex. The signal transition is  $J_{K_a K_c} = 2_{02} - 1_{01}$ , at 7 823.6675 MHz, in the excited van der Waals bending state ( $\nu_{\text{bend}} = 1$ ). This transition cannot be detected in a single resonance FTMW experiment as a result of the low populations of the energy levels corresponding to the low rotational temperatures ( $T_{\text{rot}} < 1$  K) achieved in the molecular expansion. However, the frequency of this transition could be predicted from combination differences involving the data given in Refs. 32 and 35. The pump transition is  $J_{K_a K_c} = 1_{01} - 0_{00}$ ,  $\nu_{\text{bend}} = 1 - 0$ , at 364 091.520 MHz. The difference in submillimeter frequency for adjacent MW spectra in Fig. 4 is 40 kHz. Each individual MW spectrum in Fig. 4 is a result of ten averaging cycles; the total accumulation time for the double-resonance spectrum was 4 min.

The spectrum in Fig. 6 is a high resolution spectrum of the  $J_{K_a K_c} = 1_{01} - 0_{00}$ ,  $\nu_{\text{bend}} = 1 - 0$ , transition at 364 091.520 MHz. This spectrum was obtained by recording only the maximum amplitude of each MW spectrum after ten averaging cycles as a function of submillimeter frequency. Five scans through the pump transition were averaged. The submillimeter step-size was 15 kHz. The resulting full width of the line at half height is 360 kHz. Visible at the top of the line in the high resolution spectrum is a Lamb dip caused by saturation effects<sup>36</sup> (see Sec. VI). The full width of this dip at half height is about 40 kHz, resulting in a much improved measurement precision.

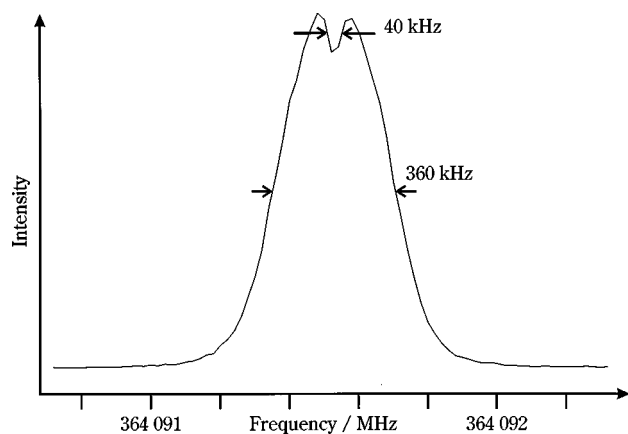


FIG. 6. High resolution spectrum of the  $J_{K_aK_c} = 1_{01} - 0_{00}$ ,  $\nu_{\text{bend}} = 1 - 0$  transition of Ar-CO. For this spectrum, the maximum amplitude of the MW spectra of the  $J_{K_aK_c} = 2_{02} - 1_{01}$ ,  $\nu_{\text{bend}} = 1$  transition at 7823.6675 MHz was recorded as function of submillimeter frequency. Five scans over the resonance were coadded. The step size in the submillimeter range was 15 kHz.

The only previously published reports about the second molecular example, namely, the van der Waals complex CO-N<sub>2</sub>, are the recent IR studies by Kawashima and Nishizawa<sup>37</sup> and by Xu and McKeller.<sup>38</sup> Subsequently, the Cologne group has measured pure rotational, *b*-type, transitions in the millimeter wave frequency range using an Orotron spectrometer.<sup>39</sup> Shown in Fig. 7 is a three-dimensional view of one of these *b*-type transitions (pump transition:  $J_{K_aK_c} = 2_{12} - 1_{01}$ , signal transition:  $J_{K_aK_c} = 3_{13} - 2_{12}$ , using asymmetric rotor notation), measured with the new double-resonance technique. In this case, the KVARZ millimeter wave synthesizer was used directly as the pump radiation source. The observed hyperfine structure of the rotational transition is caused by a coupling of the angular momenta of the <sup>14</sup>N nuclei with the overall rotational angular momentum of the CO-N<sub>2</sub> complex (<sup>14</sup>N nuclear quadrupole hyperfine structure). It should be noted that not only the

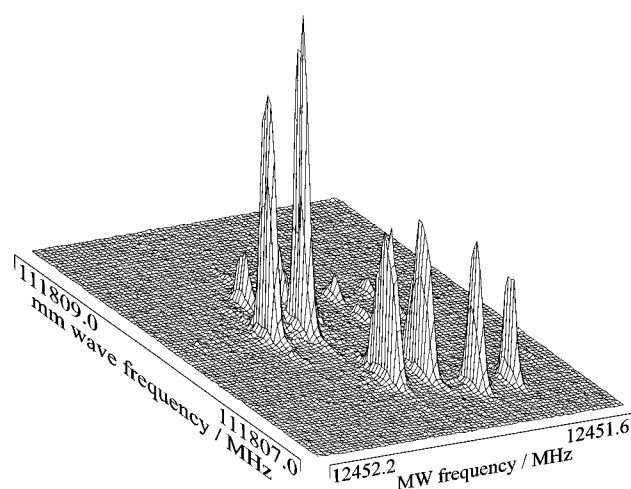


FIG. 7. Three-dimensional view of a double-resonance spectrum of the van der Waals complex CO-N<sub>2</sub> (signal transition:  $J_{K_aK_c} = 3_{13} - 2_{12}$ ; pump transition:  $J_{K_aK_c} = 2_{12} - 1_{01}$ , using asymmetric rotor notation).

pump frequency was varied in obtaining this spectrum, but also the signal MW frequency. For each MW transition frequency, a set of spectra with varied pump frequency was recorded. All these sets were added in a two-dimensional array in order to obtain the spectrum in Fig. 7.

The contour plot of the same double-resonance spectrum in Fig. 8 serves to demonstrate the potential resolving power of the method. In particular, if two closely spaced hyperfine components have different double-resonance connections, it is possible to record the two components separately, by choosing the matching signal or pump frequencies. For example, the line in the MW spectrum marked with an arrow corresponds to two hyperfine components that are separated by approximately 5 kHz. Splittings of this order are usually difficult to resolve with a FTMW spectrometer. By recording, however, the MW spectrum with two different pump

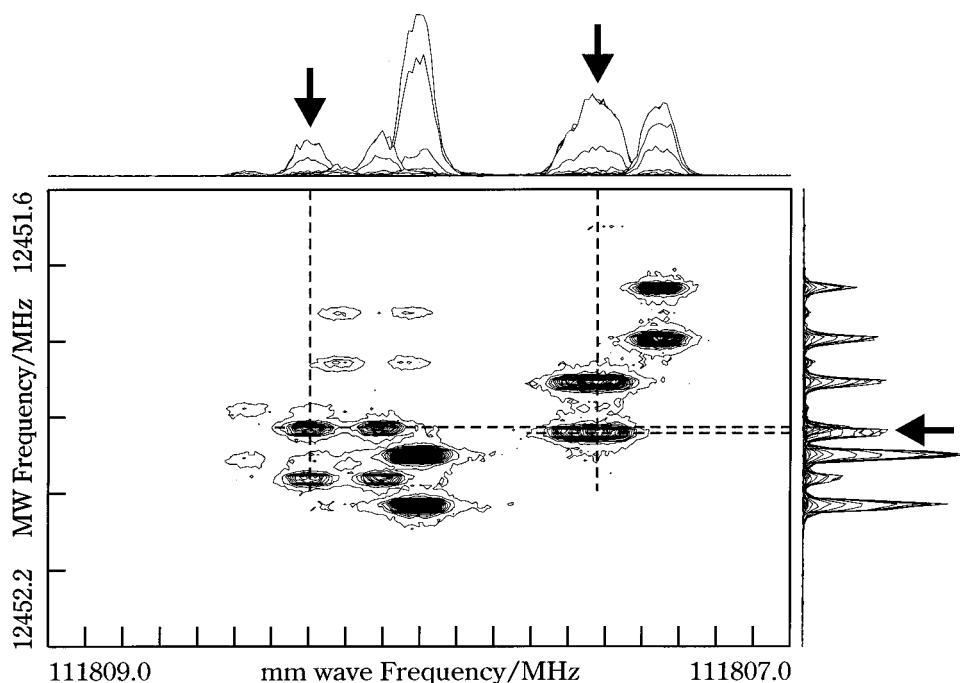


FIG. 8. Contour plot of the double-resonance spectrum of CO-N<sub>2</sub> in Fig. 7 (signal transition:  $J_{K_aK_c} = 3_{13} - 2_{12}$ ; pump transition:  $J_{K_aK_c} = 2_{12} - 1_{01}$ ). An arrow indicates two overlapping MW transitions that can be recorded individually by choosing appropriate pump frequencies (marked by arrows in the millimeter wave spectrum) as described in the text.

frequencies, for example, those marked with an arrow in the millimeter wave spectrum, one can simply record the two close components separately and determine their frequencies individually. The resolution is in such case limited by the measurement precision. In a similar fashion, very narrow splittings in the millimeter range can be resolved by observing the appropriate signal transitions. A detailed analysis of the observed hyperfine structure in the rotational transitions of CO-N<sub>2</sub> will be given elsewhere.<sup>40</sup>

## VI. DISCUSSION

The double-resonance technique presented here combines two powerful systems, a FTMW spectrometer and broadband tunable and phase-stabilized backward wave oscillators. The FTMW instrument was used in the described setup to detect population changes in the upper levels of the pump transitions as function of the pump frequency. It should be noted that the initial populations of these upper energy levels were essentially zero in both examples due to the low temperatures achieved in the molecular expansion. Experiments were done successfully where the common energy level of signal and pump transition was the lower [Fig. 5(a)] or the upper [Fig. 5(b)] level of the same MW signal transition. This served as an internal consistency check and confirmed the assignments of the double-resonance connections. It proved not possible, however, to detect the population changes of the lower level of the pump transition [see energy level diagrams in Figs. 5(c) and 5(d)]. The reason is that the pump radiation causes only relatively small changes in the initial populations of the lower levels which are commonly quite large in molecular expansions. As a result, the double resonance effect is the difference between two large signals. The corresponding intensity variations might be buried in fluctuations caused by instrument imperfections, such as unstable operation of the pulsed nozzle.

There are some disadvantages associated with the fact that the signal transition has to be connected with the upper level of the pump transition. Often, ground state rotational MW transitions of van der Waals complexes are known from previous FTMW studies. Both van der Waals vibrational transition frequencies and the rotational transitions in the excited vibrational state, on the other hand, are not known in many instances. This requires a rather time consuming two-dimensional search procedure with frequency variation in both MW and submillimeter wave ranges. It is planned to substitute the single mirror configuration of the submillimeter setup with a cavity arrangement. This might enhance the double-resonance effects substantially and alleviate the search problem by making it possible to use double-resonance connections of the types (c) and (d) in Fig. 5.

For low  $J$  transitions, the sensitivity of the double-resonance method appears to be higher than that of direct absorption spectroscopy, as can be seen by comparison with the spectra presented in Ref. 32. The situation is reversed, however, for transitions with high  $J$  values, presumably because of the different characteristics of the molecular expansions used in these two types of experiments. The double-resonance method appears to be particularly powerful for the

detection of low dipole moment transitions of van der Waals complexes. The reasons are the high sensitivity of the FTMW spectrometer for the detection of rotational transitions of such complexes, and the relatively high output powers of the high frequency BWO tubes (30–60 mW for the OB-30 tube) which can generate significant changes in the population of the signal transition.

A very prominent feature in the high resolution recording of Ar-CO in Fig. 6 is the Lamb dip at the line center. This allows for very precise frequency measurements in the submillimeter range. For an explanation of this dip, we assume that the molecular expansion has a cone shape, as schematically shown in Fig. 3. Molecular species at the center of the cone have no velocity component in the direction of the submillimeter beam. The pump transition frequencies of those at the edges, however, are Doppler shifted to higher and to lower submillimeter frequencies, respectively. If, for example, the pump frequency is slightly lower than the transition frequency, the complexes with velocity component toward the horn antenna will be Doppler shifted into resonance with the pump radiation and those with velocity component in the opposite direction will see the radiation after reflection at the copper mirror. Two different groups of complexes are thus affected by the pump radiation. If the pump radiation is resonant, however, the same group of molecules, namely, that in the center of the expansion, will interact twice with the submillimeter radiation. Since the population of the respective energy levels had been depleted in the first pass already, there will be fewer molecules pumped into the higher energy level by the reflected submillimeter radiation, thus resulting in the dip at the center of the line. Removal of the submillimeter radiation mirror caused the dip to disappear, thus verifying the presence of saturation effects. The Lamb dip type effect results in a significant increase in the precision of the measurements, estimated to be  $\pm 5$  kHz. This estimate can be confirmed by using combination differences that involve the new high precision FTMW measurements (precision better than  $\pm 1$  kHz) of the rotational transitions within the excited bending state.

The total linewidths of the observed submillimeter wave transitions and the linewidths of the Lamb dips are consistent with the above interpretation. The variation of total linewidth with frequency (360 kHz for the Ar-CO transition at  $\sim 360$  GHz in Fig. 6, 110 kHz for the CO-N<sub>2</sub> hyperfine components at  $\sim 110$  GHz in Fig. 8) indicates Doppler broadening as a result of the cone shaped molecular expansion. An average velocity component of  $150 \text{ m s}^{-1}$  in directions perpendicular to the axis of the molecular expansion can be estimated from the line width. For comparison, the velocity in direction of the axis of the molecular expansion is  $\sim 780 \text{ m s}^{-1}$ , as calculated from the Doppler splitting in the MW spectra. The line width of the Lamb dip, on the other hand, is caused by time of flight broadening. The half power submillimeter beam width at the point of intersection with the molecular expansion can be estimated to be  $\sim 2 \text{ cm}$ .<sup>41</sup> The interaction time of the molecular ensemble with the submillimeter radiation is thus in the order of  $26 \mu\text{s}$ . The resulting corresponding homogeneous linewidth is 39 kHz, in agreement with experiment.

A considerable advantage of the method presented is the low sample consumption corresponding to a relatively low experiment repetition rate of 2 Hz and to the relatively dilute gas mixtures used. This makes it economically feasible to investigate isotopically labeled substances, such as Ar- $^{13}\text{CO}$  and CO- $^{15}\text{N}_2$ , using enriches samples. The spectra of such species contain, in general, significant additional information about structure and intermolecular dynamics of the complexes.

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