Rotation commensurate echo of asymmetric molecules—Molecular fingerprints in the time domain

E. N. Chesnokov, V. V. Kubarev, and P. V. Koshlyakov

Articles you may be interested in

Photodissociation of N 2 O: Energy partitioning
J. Chem. Phys. **135**, 024311 (2011); 10.1063/1.3602324

Unveiling the nonadiabatic rotational excitation process in a symmetric-top molecule induced by two intense laser pulses
J. Chem. Phys. **134**, 224302 (2011); 10.1063/1.3598962

Quantum control of molecular vibrational and rotational excitations in a homonuclear diatomic molecule: A full three-dimensional treatment with polarization forces
J. Chem. Phys. **124**, 014111 (2006); 10.1063/1.2141616

Rotational line-integrated photoabsorption cross sections corresponding to the δ (0 , 0) band of NO:A molecular quantum-defect orbital procedure
J. Chem. Phys. **123**, 114305 (2005); 10.1063/1.2018799

Photodissociation of laboratory oriented molecules: Revealing molecular frame properties of nonaxial recoil
J. Chem. Phys. **121**, 11645 (2004); 10.1063/1.1812756

Rotation commensurate echo of asymmetric molecules—Molecular fingerprints in the time domain

E. N. Chesnokov,[1,2,a)] V. V. Kubarev,[3,2] and P. V. Koshlyakov[1]

[1]*Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia*
[2]*Novosibirsk State University, Novosibirsk 630090, Russia*
[3]*Budker Institute of Nuclear Physics, Novosibirsk 630090, Russia*

Using the pulses of terahertz free electron laser and ultra-fast Schottky diode detectors, we observed the coherent transients within a free induction decay of gaseous nitrogen dioxide NO_2. The laser excited different sub-bands of rotation spectra of NO_2 containing about 50–70 lines. The free induction signal continued more than 30 ns and consisted of many echo-like bursts duration about 0.2 ns. Unlike the similar effect observed previously for linear and symmetric top molecules, the sequence of echo bursts is not periodic. The values for delay of individual echo are stable, and the set of these delays can be considered as a "molecular fingerprint" in the time domain. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4905205]

The analysis of chemical compositions is a typical task in molecular spectroscopy. In the last decade, the Terahertz time-domain spectroscopy (THz-TDS) has developed into a versatile characterization tool in the far-infrared spectral region.[1] This technique exploits the changes in the temporal structure of the short pulses of broadband terahertz radiation after passing through a test medium. These changes can be described in terms of free induction decay (FID) of the medium.[2] The spectrum of test media then can be evaluated from the FID signal and then can be used in a usual way. Mittleman and co-workers[2] suggested another approach that implies the use of the FID waveform for analysis instead of using the spectrum. They discuss the chemical-recognition system based on linear digital filter for FID signal. Since the FID waveform has an oscillating character, the analogy with speech recognition systems was used.

Such approach might be good for automatic control systems, which operate without human assistance. For qualitative analysis, to determine the specific chemical component, it is better to use the characteristic features of the experimental signal. Typically, the FID signal consists of various oscillations and does not contain such characteristic features, in contrast with molecular spectrum. But in some cases, the FID signal looks like a sequence of short spikes, repeated with period, which is specific for a certain molecule. Such signals occur in the excitation of the rotational spectrum of a linear molecule by a short broadband pulse of terahertz radiation. This phenomenon was called commensurate echo.[3] The origin of these THz pulses (echoes) is a periodic rephasing, during the free-induction decay, of many coherently excited rotational lines with commensurate transition frequencies. The rotational spectrum of linear molecules contains several tens absorption lines, with approximately equal spacing. The frequency spacing between lines is 2B, where B is rotation constant. That means that with the period $\tau = 1/2B$, the phases of all emitters, related to different absorption lines, have to coincide. In the experiment with nitrous oxide N_2O molecule, approximately fifteen echo signals were observed[4]

with a period of 39.81 ps (B = 12.561 GHz). For carbonyl sulfide COS molecule,[5] the period of the echo signals was 82.65 ps. Analogous echo signals were observed for nonlinear molecule[6] of methyl chloride CH_3Cl, which is symmetric top type. The rotation spectrum of a symmetric top is similar to the rotation spectra of linear molecule, therefore, the same signals are expected.

Commensurate echo is a linear effect and can be observed at low energies of optical pulse. Recently, the similar effect was studied with two time-delayed moderate energy THz pulses.[7] It was shown that two properly delayed THz pulses can significantly enhance coherence of rotational levels of the COS molecule relative to that induced by a single THz pulse.

The existence of such echo-like coherent transients for the asymmetric molecules that have three different moments of inertia is not clear. Up to this time, only the study of methanol molecule is published.[8] A few transients were observed, following with a period of 21 ps, which is equivalent to the rotation constant 23.8 GHz. Methanol molecule is a slightly asymmetric top with two almost equal rotation constants B = 24.68 GHz and C = 23.77 GHz.[9] Therefore, its rotation spectrum has some features that are typical for symmetric top and linear molecule.

The question is whether a similar phenomenon can be observed for large asymmetric molecules, their rotational spectra have no obvious periodicity. The structure of the spectrum of such molecules is much more complex than for linear molecules. Usually, it contains many overlapped sub-bands. For this reason, one should not expect the existence of the periodic structure of lines for the whole spectrum. A better way to find a periodic line structure is to use separate sections of the spectrum. Rotational spectra of complex molecules often have the condensation regions of absorption lines, such as Q-type sub-bands[10] or heads of the sub-bands. If the experimental source of short laser pulse can be tuned to such regions, the possibility of getting echo-like signals will be greater.

Another feature of the rotational spectra of asymmetric molecules is the higher density of absorption lines. The interval between rotational lines for large molecules is smaller

a)Electronic mail: chesnok@kinetics.nsc.ru

than for linear molecules. Hence, for large molecules such echo signals should appear with longer delay, and therefore can be detected in real time experiment without using scanning technique.

In this letter, we report the observation of such echo-like signals in the free induction decay in gaseous NO_2 using the short pulses of tunable free-electron laser. The observed signals differ from those observed in literature for linear molecules. Like a previously observed commensurate echo in linear molecules, echo signals in NO_2 contain short spikes, but this is not simple periodic sequence on time. Each signal can be characterized by several values of time, showing the moments when different spikes arise. The set of these values is stable for the specific region of the spectra (sub-band) and can be considered as a "fingerprint" of the molecule in the time scale.

Experiments were performed on Novosibirsk Free Electron Laser (NovoFEL).[11] This laser is continuously tunable in the range of 42–90 cm^{-1} with a spectral width of 0.12–0.25 cm^{-1}. It emits a sequence of pulses at repetition frequency of 5.6 MHz with the energy of 5–20 μJ and FWHM duration about of 100 ps.

The experiment is very simple in essence.[12] The laser radiation passes through the gas sample to the detector. The response of the detector is proportional to the radiation power, so the phase information of the FID is not available in the experiment. Self-made ultra-fast Schottky diode detectors with rise time of less than 20 ps were used.[13] Signals were accumulated by a 30 GHz LeCroy digital oscilloscope. Before entering the sample, a small fraction of the laser beam was reflected by a flat 30 μm polypropylene film to the second Schottky diode detector, which was used to trigger the oscilloscope. Signals were measured in real time in contrast to the slow scanning in a typical time-domain spectroscopy. Two gas cells 20 and 100 cm long with polypropylene windows were used.

Due to the large value of the rotational constant $A = 8.00236 \, cm^{-1}$,[14] the pure rotation spectra of NO_2 stretch over a large spectral interval up to 100 cm^{-1}. In the low resolution spectra, different Q_R bands are clearly visible. Each Q_R band contains many absorption lines corresponding to different $(J, K_a + 1) \leftarrow (J, K_a)$ transitions. The internal structure of each Q_R band is rather complicated. It contains sub-bands of two spin-rotation components and hyperfine structure.[15] Figure 1 shows the rotation spectra of NO_2 in 35–130 cm^{-1} region, recorded by a conventional FTR spectrometer. The internal structure of Q_{R5} band is shown in the inset. This structure was calculated using the data of line frequencies and intensities from Ref. 16. The total width of Q_R branches roughly coincides with the spectral width of the laser pulse. There are three Q_R branches in the tuning range of the laser, from Q_{R3} to Q_{R5}. For each of these branches, the laser can be tuned to excite most of the lines in the branch.

Figure 2 shows the FID signal observed for the Q_{R5} branch at 82 cm^{-1}. The laser pulse was accumulated separately with empty cell and subtracted from the signal. The FID signal consists of many echo signals that look like a short burst; some of them are repeated periodically over time, some are not periodic. The initial fast decay of the FID signal at $t < 0.5$ ns is associated with dephasing of the individual emitters with different frequencies. Due to overload of the detector by laser pulse, this part of the FID is not registered accurately.
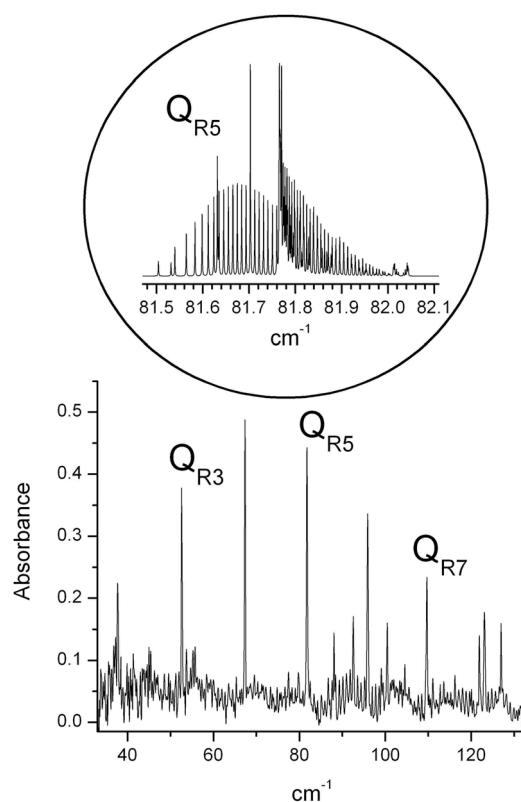

FIG. 1. Low resolution rotation spectra of NO_2. (L = 50 mm, 70 Torr). Inset—The internal structure of Q_{R5} band, calculated based on spectroscopic data.

Subsequent short bursts occur at the moments when the phases for a large number of emitters coincide.

Fig. 3 shows the FID signals observed in two other Q_R branches in the tuning range of the laser. Unlike the previous case, these signals do not contain periodically repeating echo signals at all.

All of the observed FID signals were very stable in shape. With increasing gas pressure, the positions of individual echoes on a time scale do not change. Only the total duration of the FID signal becomes shorter. Signal shapes were also stable at a detuning of the laser relative to the center of the Q_R band. At detuning of the laser, we observed a change in the relative intensities of individual echoes. The position of the echoes on a time scale has not changed. Each signal can be characterized by a set of delays, which correspond to main echo signals with the highest amplitude. For example, the FID signal for Q_{R4} branch has characteristic peaks at 2.96, 4.79, 5.63, 9.23, 9.53, 11.56, 13.71, 15.33 ns, and so on. Due to stability, such set of delays can be considered as a "fingerprint" of the molecule.

Fig. 2 also shows FID signal calculated using the literary data of $Q_{R(5)}$ branch of the NO_2. In calculations, we used 354 absorption lines of NO_2 with intensity more than $10^{-27} \, cm$.[16] Each absorption line was considered as a Lorentz with a width of 0.0005 cm^{-1} that corresponds to collision broadening at 1–2 Torr. Doppler broadening is about $10^{-4} \, cm^{-1}$ and was neglected. Real and imaginary parts of the refractive index were calculated by summing the contributions from each of the absorption line. The laser spectra were assumed to be Gaussian of 0.25 cm^{-1} width. FID signal was obtained by Fourier transformation.
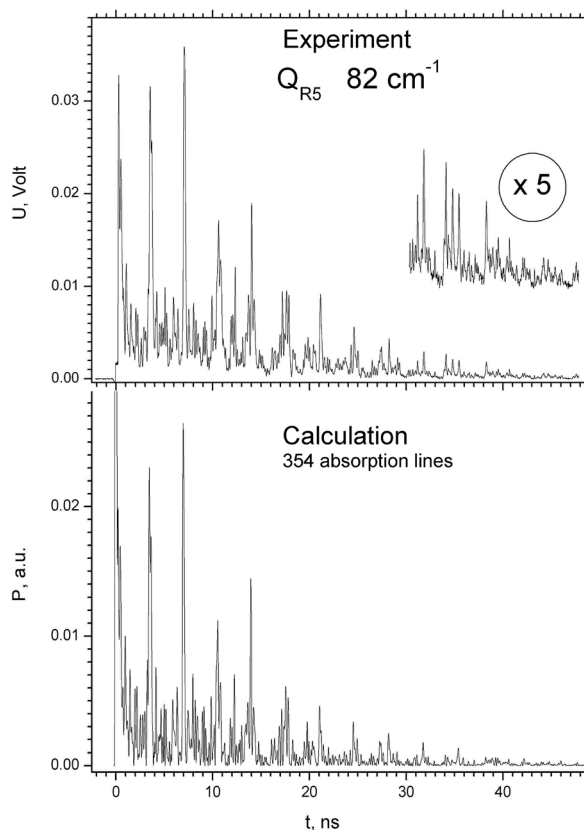
FIG. 2. (Upper panel) intensity of experimental FID. Laser is tuned to Q_{R5} branch in rotation spectra of NO_2. The laser pulse at t = 0 was accumulated separately with empty cell and then was subtracted from the experimental signal. Experimental conditions: length 100 cm, P NO_2 1 Torr, number of accumulated pulses 1000. Part of the experimental signal at t > 30 ns is magnified by a factor of 5. (Lower panel) intensity of the calculated FID. Calculations were made by Fourier transform of the molecular spectrum in the Q_{R5} region, consisting of 354 Lorentz lines, weighted by the laser spectrum.

Although the numerical calculation shows a very good agreement with experiment, it can not explain the nature of the echo bursts. In order to understand their origin, we use a simple qualitative approach. Each short echo in the FID signal indicates a partial regularity in the rotation spectra. This regularity can be clarified in the following way. To make a phase of many emitters coincide in the time, t = τ, their frequency must obey the condition
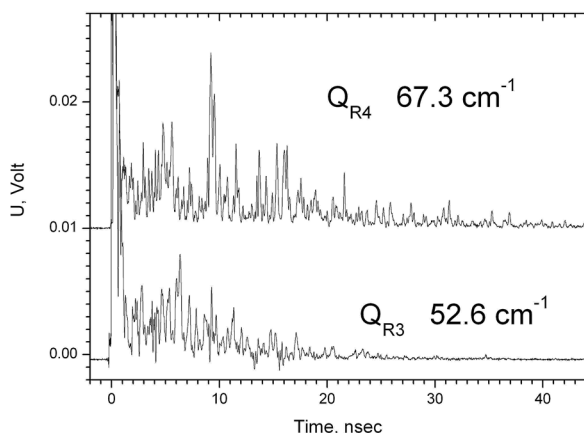

FIG. 3. The FID signal of NO_2 at Q_{R4} and Q_{R3} branch. Length 100 cm, P 1 Torr and 1.9 Torr.

$$\nu_n^{gr} = F + 2\pi n/\tau, \qquad (1)$$

where n is an integer number. Constant F is a frequency offset that does not affect the signal, because the signal is insensitive to the total phase of the wave. Equation (1) forms a grid in the frequency scale. In fact, the exact match of the frequencies is not necessary for spike behavior of a signal. If many of the actual absorption lines are close to this frequency grid, the phases of many emitters will be close to each other at t = τ, and the intensity of the FID arises at that point.

The frequency and intensity of the absorption lines of NO_2 are known with a high accuracy.[16] Therefore, for each echo of the FID, one can find the real absorption lines that form it. In order to find the lines that are located close to the grid nodes, we varied frequency offset in (1). Specifically, the value of F was chosen to maximize the following expression which is proportional to echo power

$$S = \left(\sum A_i \cos\left(2\pi(\nu_i - \nu_n^{gr})\tau\right)\right)^2. \qquad (2)$$

Summation in formula (2) was made over absorption lines which are close enough to the grid nodes. A_i denotes the amplitude of the corresponding emitter and was derived from the intensity of the absorption line. The absorption line was considered as "close enough," if $|\nu_i - \nu_n^{gr}|\tau < 0.1$.

The FID signal of Q_{R5} branch has several intense echoes. The first one has a doublet structure and consists of two peaks at t = 3.54 ns and t = 3.72 ns. Fig. 4(a) shows the results of the search of absorption lines which are involved in the formation of the echo at t = 3.72 ns. Thin blue lines show the frequency grid defined by formula (1). Below the internal structure of this rotation branch is shown. The thick red segments at the top indicate the contribution of the absorption line into the echo signal according to the formula (2). The length of the segment is proportional to the term in the sum (2).

The presented data demonstrate some features of echo formation in our experiment. First, not all absorption lines are involved in echo formation. The number of lines with the matched phases, which are marked at the top of the picture, is $N_{match} \approx 25$ while the total number of absorption lines in this branch $N_0 \approx 70$. The second feature of echo formation in our experiments is that the regularity of absorption lines is not connected with any spectroscopic parameter. This is completely different from the formation of commensurate echo for linear molecules, for which the interval between the absorption lines is defined by rotational constants. As follows from Fig. 4, in our case the set of lines with commensurable frequencies is formed even from different sub-branches. This set originates likely due to some statistical law, rather than due to spectroscopic regularities.

The set of rotation lines that forms echo signal at t = 3.54 ns is shown in Fig. 4(b). In this case the grid in frequency scale has a 5% wider step than the previous one. Although the grid was stretched only slightly, the set of absorption lines that forms echo is completely different. We found a similar behavior for other echoes. Despite the fact that the total set of rotation lines is not periodic, some subsets of them can make periodic structures and create echo signal. The value of echo delay for this subset is determined
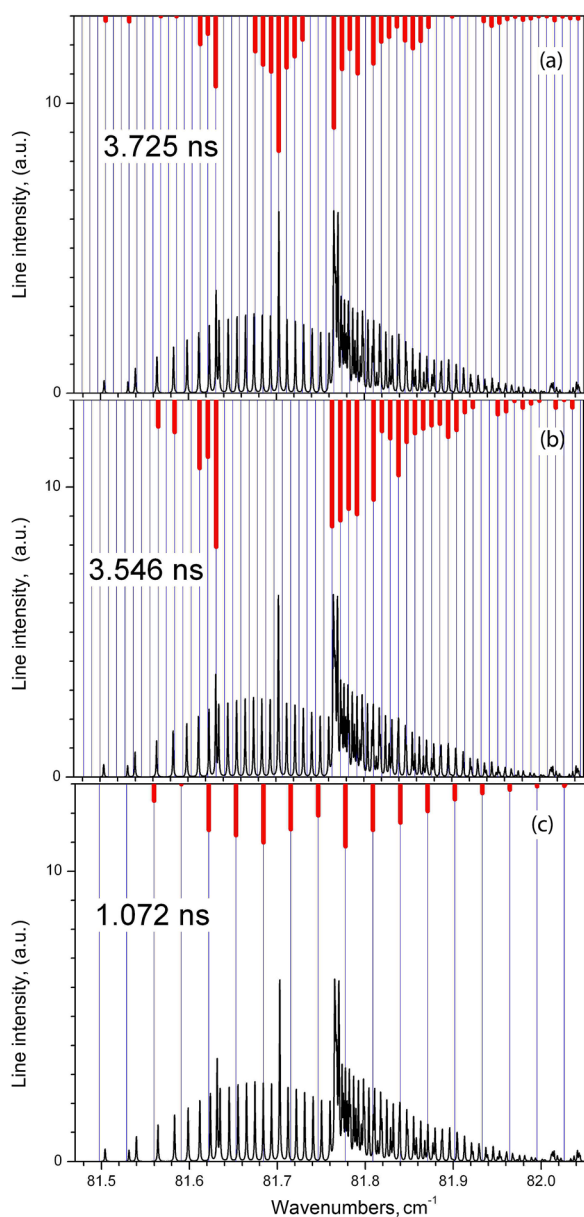
FIG. 4. Frequency grids that form the echo at different delays in experiment at Q_{R5} sub-band. Grid nodes are shown by narrow vertical blue lines. Period of the grid corresponds to the time delay of the echo. The spectrum of NO_2 in the region of Q_{R5} sub-band is shown near the bottom of each panel. Molecular lines that are close to the grid nodes form the echo signal. Thick red segments at the top of the panel show the contribution of the absorption line into the echo signal.

by its period. One can expect that this value is characteristic of the molecule as the line frequencies in this subset are characteristic.

We found similar patterns for forming echo spikes in other Q_R sub-branches of rotation spectra. In all cases, commensurate subset of the absorption lines looks like a random sampling from the entire set of rotational lines. If the number of the lines in this subset N_{match} is large enough, it forms a short echo in the time domain. For the required number of lines, one can make a simple estimate. The intensity of echo is expected to depend on the number of lines as $(N_{match})^2$, while the intensity of total FID with random phases of emitters is proportional to the total number of excited lines N_{tot}. If we want the intensity of the echo signal to be 10 times

larger than the average FID intensity, the following condition is required: $N_{match} > \sqrt{10 N_{tot}}$. If $N_{tot} \approx 10^2$, about 30% of absorption lines have to participate in this periodic structure. This imposes some restrictions on the statistics for the frequency intervals in the spectrum.

Each commensurate subset of lines forms an echo at $t = \tau$. The echo also can be formed at $t = 2\tau$, at $t = 3\tau$, and so on, but it requires more accurate match of the frequencies of absorption lines to periodic structure. We observed such periodic echoes only for $t = 3.54$ ns at $82\,cm^{-1}$. This echo is accompanied by the echo at $t = 7.09$ ns, at $t = 10.6$ ns, and so on up to $t = 35.46$ ns (Fig. 2). Most of the other echo spikes in our experiments are not periodic. This confirms the stochastic origin of the commensurate subset of lines, for which the phase matching is sufficient at the moment $t = \tau$, but not sufficient at $t = 2\tau$.

Based on this study, one can suggest that in the case of exciting a significant number of narrow rotation lines, the formation of short coherent transients within free induction decay is a common effect. For linear molecules with equidistant absorption lines, such transients form a periodic sequence on time. For asymmetric top type molecules, such echoes are not periodic, and the set of delays of the echoes reflect some regularities in the location of the absorption lines.

[1] M. C. Nuss and J. Orenstein, *Terahertz time-domain spectroscopy (THz-TDS) Millimeter and Sub-Millimeter—Wave Spectroscopy of Solids*, edited by G. Grüner (Springer, Heidelberg, 1998).

[2] R. H. Jacobsen, D. M. Mittleman, and M. C. Nuss, Opt. Lett. **21**, 2011 (1996).

[3] H. Harde, S. Keiding, and D. Grischkowsky, Phys. Rev. Lett. **66**, 1834 (1991).

[4] H. Harde and D. Grischkowsky, J. Opt. Soc. Am. B **8**, 1642 (1991).

[5] D. Bigourd, G. Mouret, A. Cuisset, F. Hindle, E. Fertein, and R. Bocquet, Opt. Commun. **281**, 3111 (2008).

[6] H. Harde, N. Katzenellenbogen, and D. Grischkowsky, J. Opt. Soc. Am. B **11**, 1018 (1994).

[7] S. Fleischer, R. W. Field, and K. A. Nelson, Phys. Rev. Lett. **109**, 123603 (2012).

[8] B. L. Yu, Y. Yang, F. Zeng, X. Xin, and R. R. Alfano, Appl. Phys. Lett. **86**, 101108 (2005).

[9] C. C. Pei, Q. Q. Gou, and Q. Zeng, Astron. Astrophys. Suppl. Ser. **76**, 35 (1988).

[10] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II: Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966).

[11] N. G. Gavrilov, B. A. Knyazev, E. I. Kolobanov, V. V. Kotenkov, V. V. Kubarev, G. N. Kulipanov, A. N. Matveenko, L. E. Medvedev, S. V. Miginsky, L. A. Mironenko *et al.*, Nucl. Instrum. Methods A **575**, 54 (2007).

[12] E. N. Chesnokov, V. V. Kubarev, P. V. Koshlyakov, and G. N. Kulipanov, Appl. Phys. Lett. **101**, 131109 (2012).

[13] V. V. Kubarev, V. K. Ovchar, and K. S. Palagin, "Ultra-fast Terahertz Schottky diode detector," in *Conference digest of the 34th international conference on infrared, millimeter and terahertz wave*, Busan, Korea, 21–25 September 2009.

[14] B. Carli, M. Carlotti, F. Mencaraglia, A. Mahmoudi, C. Camy-Peyret, and J. M. Flaud, Mol. Phys. **51**, 1505 (1984).

[15] A. Perrin, J. M. Flaud, C. Camy-Peyret, B. Carli, and M. Carlotti, Mol. Phys. **63**, 791 (1988).

[16] N. Jacquinet-Husson, L. Crepeau, R. Armante, C. Boutammine, A. Chédin, N. A. Scott, C. Crevoisier, V. Capelle, C. Boone, N. Poulet-Crovisier *et al.*, J. Quant. Spectrosc. Radiat. Transfer **112**, 2395 (2011).