MEASUREMENTS OF THE DEUTERATED WATER VAPOR ABSORPTION LINE SHIFTS IN THE N₁ BAND CAUSED BY NITROGEN PRESSURE

N.F. Borisova, V.M. Osipov, and V.V. Tsukanov

All-Union Scientific Center "S.I. Vavilov State Optical Institute,"
Sosnovyi Bor of Leningrad Region
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The results of measurements of the nitrogen pressure-induced shift coefficients of the $HD^{16}O$ *and* $D_2^{16}O$ *lines in the* ν_1 *band are presented. The obtained data are compared with the line shift coefficients in the* H_2O *absorption bands and with each other. The results obtained are of interest for the calculation of atmospheric transmission in the* 3.5—4.1 μm *atmospheric window.*

Pressure-induced spectral line shift, like line broadening, is the manifestation of intermolecular interaction in the gas phase. However, in contrast with broadening, the spectral line center shift, being a consequence of frequency redistribution of the line intensity, proves to be strongly dependent on the character of intermolecular interaction. It has been just this phenomenon which has led to the fact that its character is determined to a considerable degree by isotopic composition of not only absorbing but also exciting particles. Special-purpose investigations of this effect were not conducted. However, it is known that in case of polar molecules such as HCl and DCl, the isotope meter type may change even the line shift sign.[1] Our measurements for lines of the 0—1 band of the $^{12}C^{16}O$ and $^{13}C^{16}O$ molecules showed that for the $R12$ and $R13$ lines their shifts in absolute values were by two-three orders of magnitude higher in the case of the first isotope meter than in the case of the second isotope meter. For the molecules of deuterated water $HD^{16}O$ and $D_2^{16}O$, a noticeable change of the shift value also may be expected in comparison with its value for the $H_2^{16}O$ molecule. Moreover, these measurements are of interest for applied problems of atmospheric optics, because the $HD^{16}O$ molecule is one of the main absorbing components in the 3.5—4.1 μm atmospheric window.[2]

The data about the shift coefficients of absorption lines of the $HD^{16}O$ and $D_2^{16}O$ molecules in the ν_3 band were presented in Ref. 3, and about the shift coefficients of the main isotope meter $H_2^{16}O$ in the ν_1 and ν_3 bands in Ref. 4. Here, we pose the problem of measuring the line shifts of the $HD^{16}O$ and $D_2^{16}O$ molecules in the ν_1 band excited by nitrogen molecules and of comparing the obtained results with the line shifts of the $H_2^{16}O$ and deuterated water molecules in other absorption bands.

In the present paper, all measurements were performed by the differential technique described earlier in Ref. 5 with a step scanning of spectrum and two gas cells using a high-resolution automated spectral complex built around a diffraction monochromator based on Littrov's scheme with a collimating parabolic mirror having the 5-m focal distance. A source of

infrared radiation was a platinum-ceramic radiator stabilized with accuracy of 1% on the light flux in the visible spectral range with a brightness temperature near 1500 K. It was fabricated considering the geometrical factor of the light source and the preliminary monochromator. A diffraction grating with 100 lines per mm and area of lined part 300×200 mm² and a brightness angle of 51.5° was used capable of recording the investigated spectrum range in the 4th order of diffraction, which was selected by a preliminary monochromator with a prism fabricated from calcium fluoride. A germanium photodetector cooled by liquid nitrogen and alloyed with aurum was used to receive radiation. The spectral resolution was 0.05—0.07 cm⁻¹ and the signal-to-noise ratio was on a level of 200.

As noted by a number of investigators of the absorption spectrum of heavy water,[2,6–8] the problem of its "purity" exists, because the intensive exchange by the hydrogen atoms between the D_2O and H_2O molecules adsorbed on the walls of gas cells takes place resulting in the superposition of the absorption spectrum of semiheavy water (HDO) on the absorption spectrum of D_2O. Therefore, the cells were filled with deuterated water vapor in several steps. First, the cell was evacuated to a pressure of 2.5 Pa and was filled with the $D_2^{16}O$ vapor (with a degree of purity of 99.7%) and a buffer gas (N_2); after that, some hours later, the cell was evacuated and filled ones more with the same mixture, and so on. The purity of heavy water vapor in the cell was controlled by recording of the absorption spectrum. In spite of such measures, the lines were recorded in the absorption spectra belonging to the HDO molecules; therefore, the choice of lines whose shifts were measured was based on an analysis of literature data about positions and integral intensities of the $HD^{16}O$ (Ref. 9) and $D_2^{16}O$ lines.[7] To record the line shifts of the semiheavy water, the cells were filled with the mixture of H_2O and D_2O vapor in the 1:4 proportion. The pressure in the cell filled with the D_2O and HDO vapor without buffer gas was 6—10 hPa for the absorbing layer 60 m long. The partial pressure in the cell with the buffer gas (nitrogen) was 10.5—11.0 hPa for

lengths of the absorbing layer of 4 and 8 m and total pressure of mixture between 1000–1040 hPa.

The results of measurements of the absorption line shifts of the deuterated water vapor in the ν_1 band induced by the nitrogen pressure are given in Table I.

TABLE I. *Coefficients of shifts of the* $HD^{16}O$ *and* $D_2^{16}O$ *absorption lines in the* ν_1 *band.*

Molecule	Position of line center, cm⁻¹	Transition		Shift coefficient, cm⁻¹·atm⁻¹
$D_2^{16}O$	2500.268	616	725	$-(0.015 \pm 0.002)$
	2512.297	542	651	$-(0.004 \pm 0.002)$
		541	652	
	2520.279	633	744	$-(0.005 \pm 0.001)$
	2525.496	440	551	$-(0.003 \pm 0.001)$
		441	550	
	2531.573	532	643	$-(0.019 \pm 0.009)$
	2595.203	606	717	$-(0.015 \pm 0.001)$
	2532.547	202	313	$+(0.007 \pm 0.002)$
$HD^{16}O$	2546.992	927	1028	$-(0.008 \pm 0.002)$
	2562.298	918	1019	$+(0.004 \pm 0.001)$
	2644.465	423	524	$-(0.015 \pm 0.002)$
	2675.195	220	321	$-(0.000 \pm 0.001)$

The comparison of these results with the available literature data demonstrates the following. First, only two positive shifts were recorded for the line transitions 202–313 of $D_2^{16}O$ and 918–1019 of $HD^{16}O$. Second, the abnormally large absolute values of shifts of line transitions 616–725, 532–643, and 606–717 of $D_2^{16}O$ and 423–524 of $HD^{16}O$ have engaged our attention. They are close to line shifts belonging to composite and overtone absorption bands of the $H_2^{16}O$ molecule in visible and near-infrared spectral ranges.[10–11] Thus, for the 532–633 line of the $\nu_1 + 3\nu_3$ band of $H_2^{16}O$ the shift coefficient was -0.017 cm⁻¹·atm⁻¹ (see Ref. 10), that is, very close to the value of the shift coefficient for the 532–643 line of $D_2^{16}O$ found by us and equal to -0.019 ± 0.009 cm⁻¹·atm⁻¹. It should be noted that in the ν_2 band of $H_2^{16}O$, the shift coefficient of the 542–633 line had the opposite sign and was 0.002 cm⁻¹·atm⁻¹ (see Ref. 10).

The value of the line shift coefficient for the 927–1028 transition of $HD^{16}O$ was close to the corresponding value for the same transition in the ν_3 band of D_2O (-0.005 ± 0.002 cm⁻¹·atm⁻¹, see Ref. 3). The doublet line shift coefficient (542–651 and 541–652) of $D_2^{16}O$ also was close to the value for the transition line 523–624 of $HD^{16}O$ (0.005 ± 0.001 cm⁻¹·atm⁻¹, see Ref. 3), but markedly increased its value for the transmission line 532–633 of $D_2^{16}O$ with the same principal quantum numbers (-0.0018 ± 0.0002 cm⁻¹·atm⁻¹, see Ref. 3).

The shift coefficient for doublet (440–551 and 441–550) of the $D_2^{16}O$ molecule, according to our measurements, was -0.003 ± 0.001 cm⁻¹·atm⁻¹. At the same time, for the transition lines 431–532 and 432–533 of the $HD^{16}O$ molecule it was 0.0015±0.0002 and -0.0008 ± 0.0001 cm⁻¹·atm⁻¹, respectively (see Ref. 3). And finally, for the transition 542–651 in the ν_2 band of $H_2^{16}O$, a theoretical shift value of -0.012 cm⁻¹·atm⁻¹ was reported in Ref. 10, which is by 3 orders of magnitude higher then our result for the doublet (542–651 and 541–652) in the ν_1 band of $D_2^{16}O$.

The observed pattern of absorption line shifts of water vapor including deuterated water was chaotic in character and gave us no change of observing the simple correlation between their values for various vibrational-rotational bands and isotope meters. It is seen, for example, that even for one and the same ν_1 band of the $HD^{16}O$ molecule the line shifts for 927–1028 and 918–1019 transitions with identical principal rotational quantum numbers differ even in signs. In this case, the effect of isotopic molecular composition not only on the shift of vibrational frequency of transition (vibrational dephasing), but also on the character of the dependence of the absolute value of shift on the principal and secondary rotational quantum numbers may be expected, which is explained by the specific character of dynamics of inter- and intramolecular interactions. In case of collisions between water and nonpolar molecules, the full consideration is required of vibrational excitation and intramolecular forces (centrifugal distortion, anharmonic vibrations, resonances of various types, and so on). If various factors are taken into account, the shift coefficient, as was pointed out in Ref. 10, may vary by an order of magnitude and may change the sign.

In conclusion, we note that the shifts of the absorption lines of deuterated water vapor measured by us in the ν_1 band are of interest for solving the problem about the propagation of DF-laser radiation through the atmosphere,[2] because in a number of cases the lasing frequencies are close to the centers of the corresponding absorption lines. This is true for the following lasing lines:

$P_2 11$ (2553.97 cm⁻¹), $P_3 7$ (2570.51 cm⁻¹),
$P_3 8$ (2546.37 cm⁻¹), $P_3 10$ (2596.61 cm⁻¹),
$P_4 7$ (2486.83 cm⁻¹), $P_4 9$ (2439.29 cm⁻¹).

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