

Separation of Water into Its Ortho and Para Isomers

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Polyatomic molecules can exist as nuclear spin isomers. For example, the ortho and para hydrogen spin isomers are characterized by different values of specific heat, boiling point, heat of vapor formation, and so forth (1). Hydrogen has been the only substance whose spin modifications are well studied and available for practical use.

Like H_2 , a water molecule also has two alternative orientations of the hydrogen atom nuclear spins—either parallel (total spin $I = 1$, an ortho molecule) or antiparallel ($I = 0$, a para molecule)—and, correspondingly, it may have rotational energy spectra of two different types (Fig. 1A). The difference in I implies a nuclear statistical weight $2I + 1$ of the ortho levels (left set) that is three times larger than that of the para levels (right set).

As a result, in the high-temperature limit (>50 K), the equilibrium ratio of the ortho to para number densities (OP ratio) is 3:1. The OP ratio can be measured from the far-infrared spectra of water vapor.

Collisional and radiative transitions with change of I are strongly forbidden by theory, i.e., mutual conversion of the ortho and para H_2O molecules. Thus, water, like hydrogen, should readily be separable into the ortho and para components. Initial attempts to do so experimentally on the base of selective adsorption onto aluminum oxide surface have been described (2). Because the ground state is a nonrotation one, the strongly anisotropic water molecules in this state (para molecules) have the most chance to be trapped by the solid surface and extracted from the H_2O vapor.

We now show that selective absorption can lead to the accumulation of bulk amounts of metastable ortho- and para-enriched condensed water and estimate their lifetimes. Here we present results for charcoal adsorbent (3), but the phenomenon also occurs on alumina, silica gel, and zeolites.

The working gas was passed sequentially through the absorption column, quasi-optical test cell, and refrigerator. In the test cell, it was irradiated with a beam of frequency-tunable monochromatic radiation generated by the submillimeter backward

wave oscillator (4). The closely spaced doublet of the ortho and para H_2O absorption lines (36 to 38 cm^{-1} range) was used for the OP ratio measurement (Fig. 1B).

The OP ratio was notably time dependent (Fig. 1C). The leading edge of the working pulse (first 1 to 3 hours) was enriched by the ortho molecules and its trailing edge (after 4 to 5 hours) by the para molecules. The ortho enrichment to the 10:1 ratio and para enrichment to the 2:1 ratio instead of nominal 3:1 were achieved. The amplitude of the effect exceeded the instrumental error ($\pm 5\%$) by an order of magnitude.

Samples of metastable water were taken at the beginning (ortho) and the end (para) stages of the process. Productivity was 0.5 ml/

hour of ortho-enriched water and 0.1 ml/hour of para-enriched water. Samples of a few milliliters were frozen and stored at $-18^\circ C$.

The relaxation time needed to convert spin-modified ice to the 3:1 equilibrium state was estimated to be at least a few months long. The lifetimes of liquid metastable state were 26 ± 5 min for para and 55 ± 5 min for ortho water. These values are highly unexpected and their origin is unclear: They are 10^6 greater than what could be expected from the rate of proton exchange between H_2O molecules in liquid water (5). We conclude that fast proton exchange obviously does not lead to the fast OP conversion. The exchange without OP transitions, i.e., without change of energy (of resonance character), distinctly dominates.

Ortho and para water are expected to have notably different physical-chemical properties (6) and, like ortho and para hydrogen (7), have different magnetic properties. The absence of the magnetic moment in para modification implies its complete insensitivity to the magnetic field, which could be of use in magnetic resonance imaging. The OP separation procedure realized is quite straightforward and may occur in nature—in soil, atmosphere, living organisms, and cosmic objects. The scope and the role of this phenomenon are yet to be studied.

The occurrence of nonequilibrium ice offers insight into the OP ratio formation in comets (8). Along with equilibrium temperature 3:1 OP ratio variation at low temperatures, the nonequilibrium OP misbalance can be now considered as resulting, for example, from the contact of water molecules with dust.

References and Notes

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9. We thank V. K. Konyukhov, A. A. Vigasin, G. V. Kozlov, A. S. Prokhorov, A. V. Pronin, A. I. Ritus, B. P. Gorshunov, and G. A. Gousev for many stimulating discussions; V. B. Anzin, G. A. Komandin, and I. E. Spektor for technical help; Yu. G. Goncharov for software development; and S. A. Potekhin, A. I. Nadezhdensky, D. N. Basov, and V. G. Kozlov for their interest in this study and valuable consultations. This work was supported by a grant from the Russian foundation for fundamental research (grant 99-02-16860).

Supporting Online Material

www.sciencemag.org/cgi/content/full/296/5577/2363/DC1
Methods

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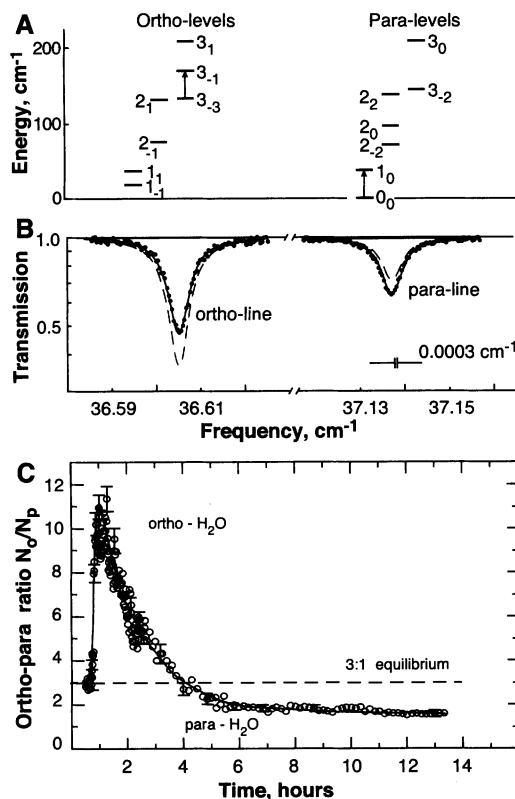


Fig. 1. (A) Rotational energy levels of an H_2O molecule. Arrows show the transitions used in the experiment. Notations for the levels meet HITRAN Database. (B) Transmission spectrum of the H_2O vapor in the test cell. Points: experiment, the case of 2:1 OP ratio. Solid lines show the fitting Lorentzians. Dashed lines show the equilibrium 3:1 OP ratio. The H_2O vapor layer thickness is 20 mm, and the gas pressure is ~ 1 torr. (C) Time dependence of the OP ratio at the exit of the chromatographic column (solid line is a guide for eye).