

Precise lamb-dip studies of monodeuterated Methanol

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We report on the results of precise frequency and hf constants measurements of CH₂DOH and CH₃OD molecules performed with the sub-Doppler spectrometer of the the IAP RAS, N.Novgorod [1]. Due to Lamb dip technique, the experimental accuracy of the transition frequencies in the range 44–520 GHz is improved by more than two orders in comparison with conventional spectroscopy [2–5]. The obtained data are of great interest both in the studies of physical parameters in the regions of star formation, as well as in a search for possible m_e/m_p variations from comparison of laboratory and radio astronomical frequencies.

All laboratory measurements were performed thanks to the Russian Foundation for Basic Research (project 16-02-00761). Their analysis was supported by the Russian Science Foundation (project No.17-12-01256).

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State-to-state rotational rate coefficients for $\text{NH}_3\text{-NH}_3$ collisions obtained with pump-probe chirped-pulse experiments

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Relaxation of rotational state populations of ammonia is studied in the laboratory by pump-probe experiments and observing its inversion doublets in the ground vibrational state using a broadband chirped pulse Fourier transform microwave spectrometer. The thermal distribution of states is altered by a resonant pump pulse that changes the population of an inversion doublet of a single rotational state. The resulting deviation from equilibrium is then propagating to other states due to collisions and interrogated by a probe pulse. The bandwidth of the spectrometer allows to probe the intensity of many inversion transitions within a single chirped pulse excitation on sub-microsecond timescales as a function of the pump pulse conditions. The relaxation time of the radiation-induced superposition state of the two level tunneling system (T2) is inferred from the free induction decays (FID) of the individual states. Also the collisional relaxation time (T1) for the population difference of the two-level system is determined. These values exhibit a linear pressure dependence, the slope of which agrees very well with previous measurements 1,2,3,4.

Analysis of collision induced transitions observed in these pump-probe experiments reveals the well known hierarchy of collisional relaxation in ammonia which was first found by Oka fifty years ago through steady state intensity measurements⁵. Collision-induced transitions with dipole selection rules ($\Delta J = 0$) are faster than $\Delta J = \pm 1$ transitions. Of those only $\Delta K = 0$ transitions could be detected and are thus much faster than those with $\Delta K \neq 0$. State-to-state rates are obtained by simulations of all coupled states fitted to the temporal behavior of the complete pump probe experiments where many individual (J,K) rotational states can be addressed step by step by separate pump pulse sequences.

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Chirped-pulse millimetre-wave spectrometer for the 140–180 GHz region

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A chirped-pulse millimetre-wave spectrometer working in the 140–180 GHz range has been developed for spectroscopic investigations of molecules and clusters in pulsed supersonic expansions. Its sensitivity is illustrated by a measurement of the relative intensities of pure rotational transitions in $^{14}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ and $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ in a natural N_2O sample and of pure rotational transitions of the carbon monoxide dimer ($^{12}\text{C}^{16}\text{O}$)₂.

Wave-packet imaging spectroscopy of the nitrogen dimer

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Irradiation of a molecular system by a short pulse of electromagnetic wave creates a non-stationary state of motion, which is commonly termed quantum wave packet (WP). Since a WP is a coherent superposition of several eigenstates, the time-dependent observable provides information on the energy intervals between the constituent eigenstates. Several spectroscopic methods working in such a time domain have been developed and applied extensively so far.

Here we present another variation of time-domain molecular spectroscopy. In our approach, molecular WPs are created via impulsive Raman excitation by intense nonresonant ultrashort laser pulses. Then, another time-delayed (more) intense ultrashort pulse is irradiated onto the molecular system to induce "Coulomb explosion", which multiply ionizes the system and makes its prompt rapture into charged fragments. The resultant fragments are detected by a 2D ion-imaging setup newly constructed in the present laboratory [1,2]. By successively changing the delay between the excitation and the explosion, time-dependent kinetic-energy and angular distribution of the fragments is taken as a series of ion-image records.

For demonstrating the capability of the present experimental method, we have examined the dimer of nitrogen molecules. Since this cluster possesses no appropriate optical transition from MW to UV region, spectroscopic investigation so far reported is so scarce [3]. The adiabatically cooled cluster produced in a supersonic expansion was excited by a linearly polarized pulse, and N_2^+ fragments created by Coulomb explosion of the dimer were monitored. Signal of N_2^+ from much abundant monomer can be differentiated since the exploded N_2^+ has substantial kinetic energy and gives images well separated. The time-dependent fragment angular distribution shows complex oscillatory change in $\sim ns$ regime. This observed feature is attributed to WP propagation pertinent to overall cluster rotation. Fourier-transformation of the data shows several regular series of peaks in the power spectrum. They are assigned to rotational-level intervals for different internal-rotation manifolds. The assignment has been confirmed by conducting the measurement of the $^{15}N_2$ isotopic species. Rotational constants are obtained, yielding to the experimental determination of the intermolecular distance between the two nitrogen molecules. By examining with higher time resolution, faster ($\sim sub$ ps) oscillation has been identified in angular distribution. This is most probably due to WP propagation pertinent to intermolecular vibration (or internal rotation). The present results will be valuable experimental input for elucidating geometry and internal dynamics of this cluster with fundamental importance.

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