Does the Stark Effect Cause Anomalies in the (02^20) State of HCO^+ and DCO^+?

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The HCO^+ ion has been studied so extensively both in the laboratory and in space by microwave and infrared spectroscopies that one might think that no more experiments would be needed for this species. Yet compared with an isoelectronic stable species HCN, crucial information is missing, in particular for the excited vibrational states. Hirota and Endo reported observations of the rotational transitions of HCO^+ and DCO^+ in excited vibrational states, (100), (001), (010), and (020), in the frequency range of 210 to 360 GHz.[1] The lowest three rotational transitions of (02^20) could not be detected in their experiment, while the lines in (02^00) were observed apparently with no difficulty. They ascribed this non-observation of the $\ell = 2$ lines to the Stark broadening caused by the electric field in a hollow cathode discharge. More recently Dore and coworkers[2] also did not see the $\ell = 2$ lines in an extended negative glow discharge and interpreted this result in terms of the Stark effect. However, symmetric top ions such as CH_3CNH^+ [3] and SD_3^+ [4] were observed with no difficulty. Also no anomalies were observed for similar lines for HCN [5] and HNC [6] produced in an extended negative glow discharge.

In the present investigation, we extended the measurements up to 800 GHz. The HCO^+ and DCO^+ ions were produced in an extended negative glow discharge in a gas mixture of H_2 or D_2 and CO (about a mTorr each) in Ar buffer (12 mTorr). The measurements were done mostly at liquid nitrogen temperature. For HCO^+, the rotational lines in the excited vibrational levels up to (040) and (002) which are located at about 4300 cm^{-1} above the ground state have been measured. The measurements for DCO^+ are not as extensive so far. Our observations confirm that the low-J lines in (02^20) are much weaker than what is expected from thermal equilibrium, and different ℓ stacks of the (021), (030), (031) and (040) states carry non-thermal populations. However, a most notable result obtained in the present investigation is that some low-J lines of (02^20) and (04^20) have been detected as induced emission for both HCO^+ and DCO^+. Also the originally claimed systematic deviations of the fit that were cited as evidence of the Stark effect have been fitted very well in the present analysis. These observations clearly lead to a conclusion that the previous non-observation of low-J lines in (02^20) is not due to the Stark effect.

Upon protonation of CO to form HCO^+ or DCO^+, collinear approach of H (or D) from H_3^+ (or D_3^+) to the C side of CO is likely to be more favorable. If so, the stretch vibrations are predominantly excited at the initial stage. The energy transfer from the stretch vibrational modes to bending modes may not be efficient process. If the electric dipole interaction is a dominant process, $\Delta\ell = \pm 1$ is a major process and therefore only the $\ell = 1$ levels of odd-v states can be populated at initial stage. Moreover parity selection rule limits the transitions only to either the e- or f-levels. Energetically the bending excited states of as high as $v_2 \sim 20$ can be excited. However, transition probability from high v_1 and v_3 states to high v_2 states is small and inefficient. Therefore at initial stage of the relaxation they would be cascading down within the stretch modes, then gradually transfer to the bending mode. Once bending excited levels are populated, cascading process within the bending mode will populate the $\ell = 2, 3, \cdots$ levels. The selection rules for the collisional transitions are not as strict as the radiative transitions, and in particular in the highly excited states vibration-rotation interactions may induce rather heavy mixing among the stretch and bending modes. Definitely more quantitative theoretical considerations are needed. However, our observation of the population inversion among several low lying rotational levels strongly suggests that the collinear approach is the favorable reaction path in protonation of CO.

In this talk, in addition to this notable observation, we also present detailed analysis of the rotational lines in excited vibrational states for both HCO^+ and DCO^+.

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