CAVITY RINGDOWN ABSORPTION SPECTRUM OF THE $T_1(n,\pi^*) \leftarrow S_0$ TRANSITION OF ACROLEIN: ANALYSIS OF THE 0_0^0 BAND ROTATIONAL CONTOUR

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Acrolein (propenal, CH_2=CH—CH=O) is the simplest conjugated enal molecule and serves as a prototype for investigating the photochemical properties of larger enals and enones. Acrolein has a coplanar arrangement of heavy atoms in its ground electronic state. Much of the photochemistry is mediated by the $T_1(\pi,\pi^*)$ state, which has a CH_2–twisted equilibrium structure. In solution, the $T_1(\pi,\pi^*)$ state is typically accessed via intersystem crossing from an intially prepared planar $S_1(n,\pi^*)$ state. An intermediate in this photophysical transformation is the lowest ${}^3(n,\pi^*)$ state, a planar species with adiabatic excitation energy below S_1 and above $T_1(\pi,\pi^*)$. The present work focuses on this ${}^3(n,\pi^*)$ intermediate state; it is designated $T_1(n,\pi^*)$ as the lowest-energy triplet state of acrolein having a planar equilibrium structure.

The $T_1(n,\pi^*) \leftarrow S_0$ band system, with origin near 412 nm, was first recorded in the 1970s at medium (0.5 cm^{-1}) resolution using a long-path absorption cell. Here we report the cavity ringdown spectrum of the 0_0^0 band, recorded using a pulsed dye laser with 0.1 cm^{-1} spectral bandwidth. The spectrum was measured under both bulk-gas (room-temperature) and jet-cooled conditions. The band contour in each spectrum was analyzed by using a computer program developed[a] for simulating and fitting the rotational structure of singlet-triplet transitions. The assignment of several resolved sub-band heads in the room-temperature spectrum permitted approximate fitting of the inertial constants for the $T_1(n,\pi^*)$ state. The determined values (cm^{-1}) are $A = 1.662$, $B = 0.1485$, $C = 0.1363$. For the parameters A and $(B+C)/2$, estimated uncertainties of ± 0.003 cm^{-1} and ± 0.0004 cm^{-1}, respectively, correspond to a range of values that produce qualitatively satisfactory global agreement with the observed room-temperature contour. The fitted inertial constants were used to simulate the rotational contour of the 0_0^0 band under jet-cooled conditions. Agreement with the observed jet-cooled spectrum was optimized by varying the homogeneous linewidth of the rovibronic transitions as well as the rotational temperature. The optimal FWHM was about 0.20 cm^{-1}, leading to an estimate of 25 ps for the lifetime of the $T_1(n,\pi^*)$ state of acrolein ($v = 0$) under isolated-molecule conditions.

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[a] R. H. Judge *et al.*, *J. Chem. Phys.* **103**, 5343 (1995).