DETERMINING THE TUNNELING PATH OF THE CHF_3-Ar COMPLEX

L. H. COUDERT, *LISA, CNRS/Universités Paris 12 et 7, 61 Avenue du Général de Gaulle, 94010 Créteil, France*; W. CAMINATI, A. MARIS, AND P. OTTAVIANI, *Dipartimento di Chimica "G. Ciamician," Università di Bologna, Via F. Selmi, 40126 Bologna, Italy*; AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol BS8 1TS, England*.

Using high-resolution data in order to qualitatively understand the potential energy surface of weakly bound species and to determine the large amplitude motions executed by them has always been a challenge. This is well illustrated by the case of the CHF_3-Ar complex.
In this complex, for symmetry reasons, there are three equilibrium configurations with C_s symmetry corresponding to three equivalent minima of the multidimensional potential energy surface. The complex tunnels between these minima and this gives rise to a tunneling splitting of the rotational levels: nondegenerate A-type and doubly degenerate E-type sublevels arise. Although this result is fairly obvious, the determination of the tunneling path used by the complex is not straightforward. The nature of this tunneling motion depends on whether the C_{3v} configuration in which the CH bond points towards the argon atom is a local maximum or a saddle point of the potential energy surface. In the former case the tunneling motion is a usual internal rotation. In the latter case it is an internal rotation combined with a rotation of the CHF_3 molecule about an axis perpendicular to its 3 fold axis of symmetry.
In the paper, this will be discussed and we will attempt to determine the tunneling motion taking place in the complex by examining the rotational dependence of the tunneling splitting. The parameters describing this rotational dependence will be retrieved with the help of an IAM-like approach[a] which will be used to fit the millimeter wave and FTMW data available of the complex.[b] Comparing these experimental values with calculated ones, we hope to unambiguously establish the nature of the large amplitude motion taking place in the complex.

[a]Hougen, *J. Molec. Spectrosc.* **114,** 395 (1985) *and* Coudert and Hougen, *J. Molec. Spectrosc.* **130,** 86 (1988).
[b]Caminati, Maris, Melandri, Favero, and Ottaviani, *57th Int. Symposium on Molecular Spectroscopy,* Paper MI09, June 17–21, 2002.