ROTATIONAL SPECTRUM OF DIMETHYL METHYLPHOSPHONATE

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Dimethyl methylphosphonate [$(CH_3O)_2P(=O)CH_3$] is a relatively nontoxic chemical that is often used as a chemical weapons (CW) simulant to test the sensitivity of analytical techniques. We have undertaken a microwave investigation of its rotational spectrum in order that Fourier transform microwave (FTMW) spectroscopy can be used in conjunction with other analytical methods in test and analysis procedures. Analysis of the spectrum is complicated by several factors. First, there are a number of possible low energy conformational isomers. Second, the methoxy methyl groups have low barriers to internal rotation which causes large splittings in the transitions. And finally, in the observed spectrum, the two methoxy groups in the molecule are not equivalent and they undergo a concerted tunneling motion which adds additional splittings to the spectrum. Fortunately the third methyl top, which is attached directly to the phosphorous atom, has a high barrier to internal rotation and adds only small splittings to the transitions. The basic rotational spectrum is that of a rather asymmetric prolate top (κ = 0.41) with the dominant dipole selection rule along the cprincipal axis. Spectral splittings which arise from the internal rotation of the methyl tops and the concerted tunneling motion can, to a first approximation, be described using the Hamiltonian developed for the methanol dimer. (See the following paper.) In the present paper, only a rigid rotor analysis will be given and the structure of the observed conformational isomer will be presented. A comparison of the ab initio calculated structures and barriers to internal rotation will be made with the experimental results.