

## Fourier transform microwave spectroscopy of the N<sub>2</sub>-ethylene oxide and N<sub>2</sub>-dimethyl ether complexes: Intramolecular motion

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We have carried out a systematic study on complexes, which consist of either CO or CO<sub>2</sub> attached to one of ethylene oxide (EO), ethylene sulfide (ES), dimethyl ether (DME), and dimethyl sulfide (DMS), etc. by using Fourier transform microwave spectroscopy supplemented by quantum chemical calculations, in order to understand the dynamical behavior of van der Waals complexes and to obtain information on the potential function to internal motions in complexes [1]. In the present study, we focus attention to the N<sub>2</sub>-EO and N<sub>2</sub>-DME complexes. We have detected two sets of strong-weak pairs rotational spectra for the two complexes including either N<sub>2</sub> or <sup>15</sup>N<sub>2</sub>. In the case of the N<sub>2</sub>-EO, both *a*-type and *b*- or *c*-type transitions were observed and were definitely assigned using the sum rule of transition frequencies. In the case of the N<sub>2</sub>-DME, only *a*-type transitions have been identified for species containing either N<sub>2</sub> or <sup>15</sup>N<sub>2</sub>, while many lines remained to be assigned and some of them were probably ascribed to *c*-type transitions. The relative intensities of the four sets of the N<sub>2</sub>-EO and N<sub>2</sub>-DME spectra were consistent with the assignment that the four sets were due to the four eigenstates created by the exchange of the two nitrogen atoms of the N<sub>2</sub> and the two methylene or two methyl groups of the EO or DME. We have analyzed the observed spectra using the asymmetric-rotor program of *S*-reduction and *A*-reduction for the N<sub>2</sub>-EO and the N<sub>2</sub>-DME, respectively. We have observed an interesting correlation among some of the molecular parameters: *A*, *D*<sub>*J**K*</sub>, and *D*<sub>*K*</sub>, for two pairs of the spectra of the N<sub>2</sub>-EO complex and a large difference in the *A* rotational constant between the *ortho* and *para* states of the N<sub>2</sub>-DME complex. These observations are not explained by the first-order Coriolis interaction between the two lowest states under consideration, but are caused by that of these states with the excited states, where exchanges of the equivalent atoms and/or groups were treated as the two-fold internal rotations. The potential barrier height to the internal rotation of the N<sub>2</sub> moiety in N<sub>2</sub>-DME was estimated to be nearly half that in N<sub>2</sub>-EO, and in fact the rotational spectra observed for the N<sub>2</sub>-DME appeared deviated considerably from the rigid rotor pattern. We will discuss the structure at the potential minima and the internal motion of the N<sub>2</sub>-EO and N<sub>2</sub>-DME complexes, in comparison with the results predicted by quantum chemical calculations.

[1] Y. Kawashima, A. Sato, Y. Orita, E. Hirota, *J. Phys. Chem. A* **2012**, *116*, 1224.