

CCA-632

530.145:541

Note

## Studies in Hydrogen Bond Systems: g-Factor and Infra-red Intensity

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Received June 19, 1970

It is well known that the hydrogen bond has a pronounced influence on infra-red<sup>1</sup> intensity and on g-factor<sup>2</sup>. In this work we report a CNDO calculation of the changes in g-factor and IR intensity when the hydrogen bond is formed.

g-factor was calculated for H<sub>2</sub>NO radical unbonded and bonded with water. The geometry of the latter was taken as in Fig. 1 and of the former

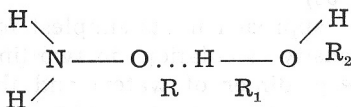


Fig. 1. Geometry of (H<sub>2</sub>NO + H<sub>2</sub>O) radical R = 1.7 Å, R<sub>1</sub> = 1 Å, R<sub>2</sub> = 0.96 Å.

from ref.<sup>5</sup>. The parametrization of the CNDO method was due to Sichel and Whitehead<sup>3</sup> and the g-factor (Table I) was calculated using well known

TABLE I  
Δg Factors (× 10<sup>-5</sup>)

	Δg <sup>xx</sup>	Δg <sup>yy</sup>	Δg <sup>zz</sup>	Δg <sub>average</sub>
H <sub>2</sub> NO	163	210	0	124
H <sub>2</sub> NO + H <sub>2</sub> O	226	5	15	82

Stone's<sup>4</sup> expression. The calculated Δg of H<sub>2</sub>NO radical is lower than that calculated by Kikuchi<sup>5</sup> although the main excitations which contribute to Δg<sup>xx</sup> or Δg<sup>yy</sup> are the same as in his calculation. When H<sub>2</sub>NO radical forms a hydrogen bond with H<sub>2</sub>O it is not possible within the CNDO method to isolate which excitations mainly contribute to the Δg factor. In the united molecule treatment of hydrogen bond system excitations which contribute to Δg come from molecular orbitals extending over H<sub>2</sub>NO radical and water. The predicted change of Δg factor is in an agreement with the experiment. Fukui *et al.*<sup>1</sup> have observed change in Δg factor of 64.10<sup>-5</sup> for diphenyl nitric oxide radical measured in CCl<sub>4</sub> and water, respectively.

The changes of IR intensities of stretching vibrations were calculated for dimers of water and acetic acid. The calculated quantity which is proportional

to the IR intensity is  $|\Delta\mu/\Delta Q|^2$  (Table II) where  $\mu$  is the dipole moment and  $Q$  is the normal coordinate. Stretching vibrations are well separated from all others so we introduce instead of  $Q$  the distance  $R$  between O—H or symmetry combination of  $R$ 's for calculation in acetic acid cyclic dimer. The geometry of acetic acid was taken from ref.<sup>6</sup> and for water dimer from ref.<sup>7</sup> (linear conformation).

TABLE II  
The Calculated Ratios of  $|\Delta\mu/\Delta Q|^2$

	$\frac{ \Delta\mu ^2}{ \Delta Q ^2}$ dimer	$\frac{ \Delta\mu ^2}{ \Delta Q ^2}$ monomer	experiment
H <sub>2</sub> O	6.2		—
HCOOH	8.2		~ 30

The calculated value for water is close to that of Kollman and Allen's<sup>7</sup> *ab-initio* calculation but the value for acetic acid is much lower than the experimental one (about 30).

The molecular orbital approach in its simplest form (one Slater determinant) is useful for IR intensity calculations in two limiting cases: in the weak hydrogen bond system (*e. g.* dimer of water) and the very strong one. The second conclusion is based on the *ab-initio* calculation done on HF<sub>2</sub><sup>-</sup> with the calculated wave functions at the Hartree-Fock level that certainly predict the correct IR intensities. For the intermediate range of the hydrogen bond strength the molecular orbital approach used in this study is not adequate<sup>8</sup>.

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#### IZVLEČEK

#### Študija vodikove vezi: g-faktor in intenziteta infra-rdeče absorbcije

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S semiempirično SCF metodo sta izračunani spektroskopski količini g-faktor in intenziteta infra-rdeče absorbcije. Metoda molekulskih orbital v najenostavnejši obliki (ena Slaterjeva determinanta) je primerna za izračun omenjenih spektroskopskih podatkov za sisteme ki tvorijo šibke vodikove vezi.

KEMIČNI INŠTITUT »BORIS KIDRIČ«

IN

ODDELEK ZA KEMIJO  
UNIVERZE V LJUBLJANI

Sprejeto 19. juna 1970.