Hydrogen Stretching Band of Hydrogen Bonded Complex: Molecular Dynamics Approach

D. Pumpernik, B. Borštnik, and A. Ažman
Chemical Institute Boris Kidrič, Ljubljana, Yugoslavia

Z. Naturforsch. **33a**, 505–506 (1978);
received February 23, 1978

The molecular dynamics is used to evaluate the hydrogen stretching band in the hydrogen bonded system. The vibrational relaxation is the main mechanism influencing the band profile.

Rahman et al. [1] have recently reported a molecular dynamics study of water. This seems to be the first calculation avoiding the assumption of rigidness of the molecules by explicitly introducing the vibrational degree of freedom.

The purpose of this note is to show a new kind of information available through the molecular dynamics simulation. As a model compound we studied the $(CH_3)_2SO-HF$ complex where we have been interesting in the band shape of the stretching vibration ν(HF).

The potential of the system was composed from pair-wise additive atom-atom potentials. Three kinds of potentials were used. Within $(CH_3)_2SO$ we used harmonic potentials derived from infrared data [2]. The Lippincott-Schroeder potential [3] was used for atoms which are directly involved in hydrogen bonds (O, H, F). The parameters of this potential were obtained by fitting Lippincott-Schroeder potential to ab-initio calculated quantities such as equilibrium distances, dissociation energies and vibrational frequencies of the hydrogen bonded dimers $(CH_3)_2SO-HF$ and HF–HF. The potential between $(CH_3)_2SO$ molecules has been composed from Lennard-Jones potentials [4]. We have studied 54 molecules of both kinds ($(CH_3)_2SO$, HF), at the concentration ratio 1:1, density 1 g/cm^3 and room temperature. More details about the potentials and the strategy used in the molecular dynamics simulation may be found elsewhere [5].

The intensity $I(w)$ of an infrared absorption is given by

$$I(w) \sim \int_{-\infty}^{\infty} G(t)\, e^{iwt}\, \mathrm{d}t \tag{1}$$

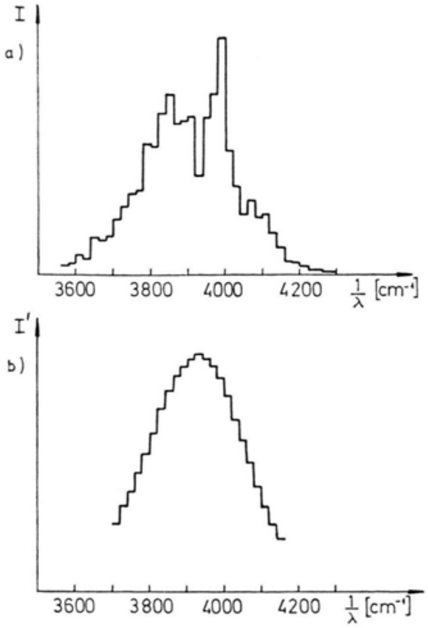

Fig. 1. a) Band profile determined by Equation (1). b) Band profile calculated with the assumption of uncorrelated rotational and vibrational motions.

with $G(t) = \langle (\boldsymbol{r}(0) - \boldsymbol{r}_0)(\boldsymbol{r}(t) - \boldsymbol{r}_0) \rangle$ as an autocorrelation function of the vector distance $\boldsymbol{r}$ in the molecule HF, where $\boldsymbol{r}_0$ is the equilibrium distance. Figure 1a gives the stretching bands ν(HF). The band at higher frequency corresponds to unbonded HF molecules while the band at lower frequency belongs to HF molecules bonded into complexes. If r is taken as a scalar quantity, the autocorrelation function (called vibrational correlation function G_{v}) does not include the rotational degree of freedom. The stretching band ν(HF) calculated with G_{v} does not differ significantly from the band in Figure 1a. This seems to be a reasonable result since one expects that in hydrogen bonded systems the vibrational relaxation is the predominant mechanism in determining the band profile.

Very often it is claimed that rotational and vibrational motions are uncorrelated. With this assumption the intensity is

$$I'(w) \sim \int_{-\infty}^{\infty} G_1(t)\, G_{\mathrm{v}}(t)\, e^{iwt}\, \mathrm{d}t\,, \tag{2}$$

where $G_1(t)$ is the autocorrelation function

$$\langle \boldsymbol{u}(0)\ \boldsymbol{u}(t) \rangle$$

Reprint requests to Dr. A. Azman, Chemical Institute Boris Kidric, Hajdrihova 19, 61001 Ljubljana, Jugoslawien.

(**u** is the unit vector) and G_V is the vibrational correlation function. Figure 1 b gives the hydrogen stretching band deduced with the mentioned assumption. From the results it is obvious that the supposition of uncorrelated motions can not be valid. The motion of the hydrogen bonded complex is complicated to such an extent that any trivial separation between the vibrational and the rotational degrees of freedom is impossible. Such a separation is also avoided in more advanced theories [6].

Acknowledgements

This work was suported by RC of Slovenia.

[1] A. Rahman, F. H. Stillinger, and H. L. Lemberg, J. Chem. Phys. **63**, 5223 (1975).

[2] M. F. Forel and M. Tranquille, Spectrochim. Acta **26 A**, 1023 (1970).

[3] E. R. Lippincott and R. Schroeder, J. Chem. Phys. **23**, 1099 (1955).

[4] J. O. Hirschfelder, Ch. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley 1954). H. A. Scheraga, Advances Physical Organic Chemistry, Vol. 6., Ed. V. Gold (Academic Press, 1968), p. 103.

[5] D. Pumpernik, B. Borštnik, D. Janežič, and A. Ažman, to be published.

[6] S. Bratos, J. Chem. Phys. **63**, 3499 (1975). S. Bratos and J. P. Chestier, Phys. Rev. **A 9**, 2136 (1974).

Nachdruck — auch auszugsweise — nur mit schriftlicher Genehmigung des Verlags
Verantwortlich für den Inhalt: A. Klemm
Satz und Druck: Konrad Triltsch, Würzburg