

## NORMAL VIBRATIONS OF N, N-DIMETHYLPROPIONAMIDE

V. VENKATA CHALAPATHI AND K. VENKATA RAMIAH

*Department of Physics, College of Science, Osmania University, Hyderabad-7*

**E**XTENSIVE work has been done in regard to the spectroscopic studies and normal co-ordinate treatment of primary and secondary amides and their deuterated analogues.<sup>1-4</sup> Recently the authors<sup>5</sup> have recorded the Raman and infrared spectra of some tertiary amides and have carried out their normal co-ordinate treatment in order to assign the vibrational frequencies and investigated the mixing up of skeletal frequencies. The Raman and infrared spectra of N, N-dimethylpropionamide were recorded by the authors<sup>6</sup> and the assignments were reported.

The authors report in this paper the normal co-ordinate treatment of N, N-dimethylpropionamide treating it as a six-body problem and using general quadratic force field.

TABLE II

*Force constants of N, N-dimethylpropionamide*

$f_d = f_e = 5.3$	$f_{ad} = f_{ae} = 1.2$
$f_c = 3.8$	$f_{ca} = 1.2$
$f_b = 9.0$	$f_a^d = 0.1$
$f_a = 6.8$	$f_a^b = 0.8$
$f_{ab} = 1.2$	$f_b^c = 1.2$
$f_{bc} = 0.9$	$f_c^a = 1.2$
$f_{ca} = 0.8$	$f_c^{ea} = 0.4$
	$f_c^{bc} = 0.9$

TABLE I

*Symmetry co-ordinates for the in-plane vibrations of N, N-dimethylpropionamide*

Symmetry co-ordinates	Vibrational mode
$R_1 = 1/\sqrt{2} (\Delta d - \Delta e)$	N-CH <sub>3</sub> asymmetric stretching
$R_2 = 1/\sqrt{2} (\Delta d + \Delta e)$	N-CH <sub>3</sub> symmetric stretching
$R_3 = \Delta c$	C-C <sub>2</sub> H <sub>5</sub> stretching
$R_4 = \Delta b$	C=O stretching
$R_5 = \Delta a$	C-N stretching
$R_6 = 1/\sqrt{6} (2\Delta de - \Delta ad - \Delta ae)$	CH <sub>3</sub> -N-CH <sub>3</sub> bending
$R_7 = 1/\sqrt{2} (\Delta ac - \Delta bc)$	C-H deformation
$R_8 = 1/\sqrt{2} (\Delta ad - \Delta ae)$	CH <sub>3</sub> -N-CH <sub>3</sub> rocking
$R_9 = 1/\sqrt{6} (2\Delta ab - \Delta ac - \Delta bc)$	O=C-N bending

This molecule belongs to the point group C<sub>s</sub> and therefore the twelve fundamental frequencies are classified into 9 in-plane (A') and 3 out-of-plane (A'') vibrations. The orthonormalised set of symmetry co-ordinates for the in-plane vibrations are given in Table I.

The structure parameters used in these calculations are:  $r(C=O) = 1.23$  Å,  $r(C-N) = 1.29$  Å,  $r(C-C) = 1.55$  Å,  $r(N-C) = 1.47$  Å,  $\angle O=C-N = 123^\circ$ ,  $\angle N-C-C_2H_5 = 117^\circ$ ,  $\angle C_2H_5-C=O = 120^\circ$ ,  $\angle C-N-CH_3 = 120$  and  $\angle CH_3-N-CH_3 = 120^\circ$ .

The method of obtaining F-, G- and L-matrices and calculating the frequencies and potential energy distribution are same as reported earlier.<sup>5</sup> At the first instance the force constants of N, N-dimethylacetamide<sup>5</sup> were transferred and the values of a few constants were to be adjusted to obtain a close fit between the observed and calculated frequencies. They are given in Table II.

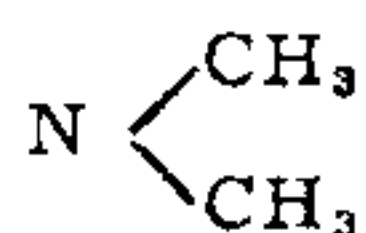
The observed and calculated frequencies, the potential energy distribution of each normal mode among the various symmetry co-ordinates are given in Table III.

TABLE III

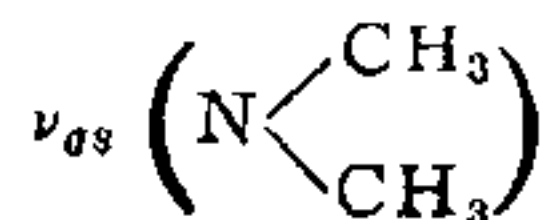
*Potential energy distribution of different modes of vibrations*

Frequencies in cm. <sup>-1</sup>		Symmetry co-ordinates									
Observed	Calculated	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>	R <sub>8</sub>	R <sub>9</sub>	
1280	1298	98	13	2	31	12	6	0	2	0	
760	734	3	45	13	7	10	2	3	3	3	
1014	1008	20	24	30	0	4	6	4	0	30	
1668	1683	6	1	3	58	17	1	0	0	8	
1495	1524	21	7	5	0	42	4	0	9	23	
480	501	10	1	34	7	9	26	6	13	7	
396	386	3	0	6	1	12	24	18	30	12	
243	240	1	0	0	1	0	0	34	49	16	
575	580	0	8	24	0	2	29	13	1	10	

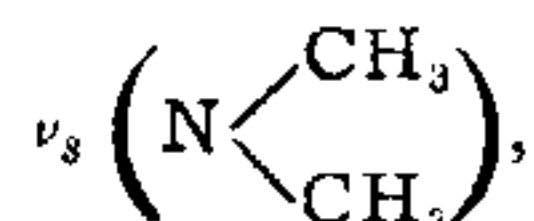
The bands at  $1280\text{ cm.}^{-1}$  and  $760\text{ cm.}^{-1}$  are due to the asymmetric and symmetric stretching vibrations of



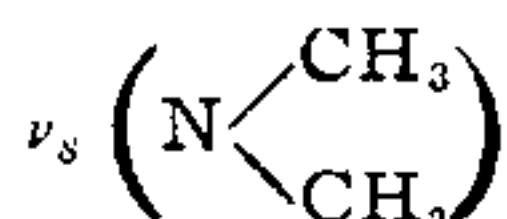
group. It can be seen from Table III that to the



mode of vibration,



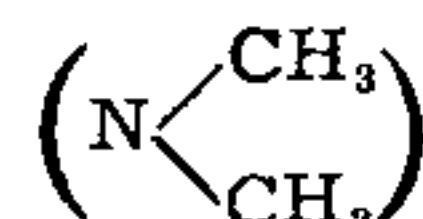
$\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{N})$  modes of vibrations contribute considerably. But for



only  $\nu(\text{C}-\text{C}_2\text{H}_5)$  makes substantial contribution. The band at  $1014\text{ cm.}^{-1}$  is assigned to the  $\nu(\text{C}-\text{C}_2\text{H}_5)$  and the potential energy distribution shows that the contribution from  $(\text{N}-\text{CH}_3)$  stretching and  $\delta(\text{O}=\text{C}-\text{N})$  bending vibrations to this mode are considerable. The bands at  $1668\text{ cm.}^{-1}$  and  $1495\text{ cm.}^{-1}$  are assigned to  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{N})$  vibrations respectively

and there is considerable couplings between these two modes of vibrations. Similar results were obtained by Suzuki<sup>2-4</sup> in case of acetamide and by the authors<sup>5</sup> in case of N,N-dimethylformamide and N,N-dimethylacetamide.

The bands at  $480\text{ cm.}^{-1}$ ,  $243\text{ cm.}^{-1}$  are assigned to the bending and rocking vibrations of



group and those at  $395\text{ cm.}^{-1}$  and  $571\text{ cm.}^{-1}$  to the rocking vibrations of  $(\text{C}-\text{C}_2\text{H}_5)$  group and  $(\text{O}=\text{C}-\text{N})$  bending vibrations respectively.

One of the authors (V. V. C.) is grateful to C.S.I.R., for the award of a Senior Research Fellowship.

1. Tatsuo Miyazawa, Takehiko Shimanouchi and Mizushima, S. I., *J. Chem. Phys.*, 1958, **24**, 408.
2. Isao Suzuki, *Bull. Chem. Soc. Japan*, 1960, **33**, 1360.
3. —, *Ibid.*, 1962, **35**, 540.
4. —, *Ibid.*, 1962, **35**, 1280.
5. Venkata Chalapathi, V. and Venkata Ramiah, K., *Proc. Ind. Acad. Sci.* (Under publication).
6. Venkata Ramiah, K., Venkata Chalapathi, V. and Indira Chai, C. A., *Curr. Sci.*, 1966, **35**, 350.

## MICRODETERMINATION OF CERIUM IN MARINE ENVIRONMENT \*

T. M. KRISHNAMOORTHY, V. N. SASTRY AND T. P. SARMA

Health Physics Division, Bhabha Atomic Research Centre, Bombay

**T**HE distribution of trace elements between sea-water, sediments and biological species will aid in the understanding of the geochemical processes taking place in the sea. Since rare-earths belong to the group of elements dispersed in sea, the R.E. distributions together with other data is useful in the study of distribution of water masses in the oceans and in the solution of many geobiological problems. Due to the recent contamination of water masses by long-lived radioisotopes such as caesium-137, strontium-90 and cerium-144, etc., from bomb-explosions and discharges from nuclear installations, the study of rare-earths, especially cerium-144 distribution, is particularly important. Very little data are available of the distribution of R.E. in marine environment. The first measurements are that of Goldsmid<sup>1</sup>

and Balshov and Khitrov<sup>2</sup> on Indian Ocean waters. The procedure adopted by Balshov and Khitrov is for total rare-earth in sea-water samples only and there is a loss of about 5-25% of R.E. on activated charcoal. Goldberg<sup>3</sup> determined the concentrations of the rare-earths in the Pacific Ocean Waters, Manganese nodules and Phosphorite samples by activation analysis. It is the objective of this investigation to develop a uniform colorimetric method for the estimation of cerium in all the three matrices of the marine environment, viz., sea-water, sediments and biological samples and to use this method for determining the cerium content in the marine environment off West Coast of India.

The sea-water and sediment samples are collected from Tarapur region (Latitude  $19^{\circ} 45' \text{ N}$ , Longitude  $72^{\circ} 36' \text{ E}$ ) about 2-3 km. offshore. Most of the biological samples are collected from nearby regions.

\* This work is carried out under IAEA/BARC research Agreement No. 155/R3/CF.