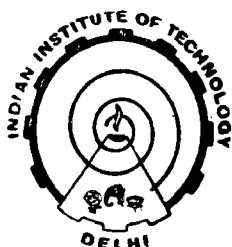


**SPECTROSCOPIC AND THEORETICAL  
INVESTIGATIONS ON ION-MOLECULE  
INTERACTIONS**

**ANAND P. BHARDWAJ**

A thesis submitted to the  
Indian Institute of Technology, Delhi  
for the Degree of  
**DOCTOR OF PHILOSOPHY**



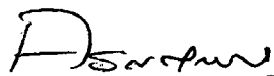
**DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY, DELHI  
1983**

*Dedicated*  
*to*  
*My Parents*

CERTIFICATE

This is to certify that the thesis entitled,  
"Spectroscopic and Theoretical Investigations on  
Ion-molecule Interactions" being submitted by  
Anand P. Bhardwaj to the Indian Institute of Technology,  
Delhi, for the award of the degree of 'Doctor of Philosophy'  
in Chemistry, is a record of bonafide research work  
carried out by him. Mr. Anand P. Bhardwaj has worked  
under my guidance and supervision and has fulfilled the  
requirements for the submission of the thesis, which to  
my knowledge has reached the requisite standard.

The results contained in this dissertation have  
not been submitted, in part or in full to any University  
or Institute for the award of any degree or diploma



A.S.N. MURTHY  
Thesis Supervisor

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(ANAND P. BHARDWAJ)

## ABSTRACT

The interaction of a series of polyatomic positively charged ions with neutral donors have been examined by electronic absorption spectroscopy. The ions include cationic dyes such as thionine, methylene blue and toluidine blue, and N-methylquinolinium ion, N,N-dimethyl-4,4'-bipyridylium ion and N-methyl 4-cyanopyridinium ions. The donors include primary, secondary and tertiary amines. Phenols and anilines have been used in some cases. New electronic transitions and isosbestic points have been observed. This evidence and a satisfactory correlation of transition energies with ionization potentials of donors indicate that the interaction is predominantly charge transfer in nature. The thermodynamic data for the interaction of ions with electron donors ( $K$  and  $\Delta H$ ) have been calculated. Spectroscopic and thermodynamic data have been employed to calculate empirical energy parameters based on the Mulliken's charge transfer model.

The charge transfer interaction of ferrocyanide ion with a few positive ions has been investigated by electronic absorption spectroscopy and thermodynamic data determined.

(iv)

$^{13}\text{C}$  NMR spectra of a few carbonyl donors in the presence of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{++}$  ions have been recorded. The changes in the carbonyl and alkyl group carbon chemical shifts have been evaluated. The ionic potential of the cation seems to determine the magnitude of the shifts and hence the interaction. Similarly changes in  $^{23}\text{Na}$  NMR spectra of  $\text{NaClO}_4$  and  $\text{NaBPh}_4$  have been determined in presence of a few carbonyl donors. An attempt has been made to determine the solvation numbers in a limited systems.

A combination of the semi-empirical CNDO/Force and compliance constant methods have been employed to calculate the vibrational frequencies, particularly in the low frequency region, for 1:1  $\text{Li}^+-\text{OH}_2$ ,  $\text{Na}^+-\text{OH}_2$  and  $\text{Mg}^{++}-\text{OH}_2$  ion- molecule interacting systems and <sup>the</sup> trends discussed. The energetics for the interaction of  $\text{Na}^+$  and  $\text{Mg}^{++}$  ions with electron donors, water, formamide, formaldehyde, ammonia, hydrogen cyanide and benzene have been calculated by CNDO/2 method and compared with those for the  $\text{Li}^+$  ion.

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