

## The Absorption and Reflection Spectra of the Ammonium Halides

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Citation: *The Journal of Chemical Physics* **18**, 1684 (1950); doi: 10.1063/1.1747573

View online: <http://dx.doi.org/10.1063/1.1747573>

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$^3\Sigma$ -states. Theoretical treatments of singlet-singlet interactions<sup>2,3</sup> and singlet-triplet interactions<sup>4-6</sup> have been given.

At a perturbation with known extra lines the B-value of the perturbing state can be determined. If perturbations are known, emanating from at least two consecutive vibrational levels of a perturbing state, the  $\omega_e$  and  $x_e\omega_e$ -values can be calculated. If several extra lines are found at a perturbation, it may be possible to decide whether the perturbing matrix element is J-dependent or not. The matrix element is independent of J at  $^1\Sigma^1\Sigma$ -interactions and at  $^1\Sigma^3\Pi_0$ .

This investigation<sup>1,7</sup> has shown that it sometimes may be possible to determine B-values for perturbing states with almost the same accuracy (4 figures) as for states for which full rotational information is available. It may also be possible to decide whether the perturbing matrix element is J-dependent or not.

The rotational and vibrational constants are of about the same magnitude for all the perturbing states in BaO,  $B_e \sim 0.226$ ,  $\omega_e \sim 450$ . For the analyzed states  $\Sigma$  and  $\Sigma^*$  the corresponding constants are,  $B_e$ : 0.3125 and 0.2584;  $\omega_e$ : 669.8 and 500. The matrix element for  $Y\Sigma^*$  interactions is independent of J. From this we can conclude that Y must be a  $^1\Sigma$  or a  $^3\Pi_0$  state. The matrix elements for  $X\Sigma^*$  and  $Z\Sigma^*$  interactions are with great probability J-dependent. About  $Q\Sigma^*$  perturbations nothing can be said. The following four interpretations of the perturbing states have been specially discussed:

State:	1	2	3	4
X	$^1\Pi$	$^1\Pi$	$^3\Pi$	$^1\Pi$
Y	$^1\Sigma^+$	$^1\Sigma^+$	$^3\Pi_0$	$^3\Pi_0$
Z	$^1\Pi$	$^3\Sigma^-_{J+1}$	$^3\Sigma^-_{J+1}$	$^3\Pi_1$
Q	Singlet	$^3\Sigma^-_{J-1}$	$^3\Sigma^-_{J-1}$	Singlet

After a thorough investigation of these four possibilities we consider the third interpretation as the most likely.

A detailed discussion is published in *Arkiv för Fysik*.<sup>7</sup>

<sup>1</sup> Barrow, Lagerqvist, and Lind, *Proc. Phys. Soc.* (to be published) (1950).

<sup>2</sup> I. Kovács, *Zeits. f. Physik* 93, 669 (1937).

<sup>3</sup> I. Kovács, *Hung. Phys. Acta.* (to be published).

<sup>4</sup> A. Budó and I. Kovács, *Zeits. f. Physik* 109, 393 (1938).

<sup>5</sup> A. Budó and I. Kovács, *Zeits. f. Physik* 111, 633 (1939).

<sup>6</sup> A. Budó and I. Kovács, *Hung. Phys. Acta.* (to be published).

<sup>7</sup> I. Kovács and A. Lagerqvist, *Arkiv. f. fysik.* (to be published).

## The Absorption and Reflection Spectra of the Ammonium Halides

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October 16, 1950

IN a previous letter,<sup>1</sup> the definite result was given that there was no direct spectroscopic evidence which could justify the postulation of free rotation in the ammonium halides. This investigation of the infra-red spectra at various temperatures has now been completed on all the four ammonium salts and this conclusion fully supported. During the course of the investigation, it was noticed that consistent spectra were not obtained and this experimental result could neither be entirely attributed to the difficulties of working in regions of strong water vapor absorption nor to variation in the orientation of the crystallites forming the sample. Further work with crystals and sublimed layers of measured thickness showed that these differences could be largely attributed to the effect of selective reflection from the solid layer and this phenomenon has now been investigated. Table I summarizes the frequencies of strong absorption lines (corrected for any reflection effect) and reflection peaks at  $-150^\circ\text{C}$  and  $-120^\circ\text{C}$  respectively. These data are presented since the lines are more narrow at low temperatures, and the experimental errors are less.

Reflection spectra from sublimed layers are similar to those from crystals and in the examination of solids, consideration

TABLE I.

NH <sub>4</sub> F		NH <sub>4</sub> Cl		NH <sub>4</sub> Br		NH <sub>4</sub> I	
Absorption*	Re-flec-tion	Absorption*	Re-flec-tion	Absorption*	Re-flec-tion	Absorption*	Re-flec-tion
cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>
1484 (30)	1494	1397 (30)	1410	1407 (35)	1413	1397 (30)	1403
1503				1430 (25)	1434	1424 (6)	
		1796 (20)		1729 (15)		1685 (5)	
		2022		1958 (10)		1916 (5)	
		2068 (10)					
		2175					
2005 (110)							
2080	2015						
2135 (10)							
2260 (60)							
2508				2805 (20)		2795 (12)	
2575 (10)				2850			
2594							
2830 (85)	2860	2824 (40)					
3024 (15)		3041 (140)	3052	3025 (80)		3017 (100)	
3100 (100)		3132 (110)	3155	3122 (85)	3060	3070 (100)	3030
3212 (70)		3210 (10)		3192 (20)	3150	3170 (15)	
						3210 (15)	

\* Figures in brackets give relative intensities for lines in one compound.

should be given to the possible influence of reflection on absorption measurements, particularly when the intensities of components of a doublet are compared. In the absence of suitable techniques for cutting thin layers of ionic solids, the reflection spectra from single crystals may again become important in the elucidation of crystal structure, since the orientation of the axes of the crystal may be definitely known.

The data at low and room temperatures can be more satisfactorily interpreted if the ammonium ion has a higher symmetry (Wagner and Hornig)<sup>2</sup> than  $C_{3v}$  or  $C_3$  (Couture and Mathieu),<sup>3</sup> except in the case of ammonium fluoride where the lower symmetry is also supported from crystallographic data.<sup>4</sup> It should be added that this investigation has also provided spectroscopic evidence for hydrogen bonding in NH<sub>4</sub>F.

The spectra taken at temperatures between  $20^\circ\text{C}$  and  $-150^\circ\text{C}$  showed that in the chloride and bromide, changes in the bands occurred in the vicinity of the  $\lambda$ -point temperatures and continued over a range of some  $50^\circ\text{C}$  below, with a decrease in the rate of change below  $-100^\circ\text{C}$ . The ammonium fluoride when cooled, gave essentially only a sharpening of the characteristic room temperature spectrum. No variation corresponding to that in the chloride and bromide was noticed in ammonium iodide and the spectrum showed no definite alteration from that at room temperature until approximately  $-120^\circ\text{C}$ , when large changes occurred. The variation of the spectra with temperature support an order-disorder theory for the chloride and bromide but the absence of any corresponding effect in the iodide is surprising since dilatometric measurements<sup>5</sup> gave a transition over the range  $-40^\circ\text{C}$  to  $-58^\circ\text{C}$ ; this difference may be in part influenced by the crystallographic change from the NaCl to CsCl type of structure which occurs at  $-17^\circ\text{C}$ . Work at Brown University has independently confirmed the results on ammonium iodide.<sup>6</sup>

This investigation has been carried out during the tenure of a Ministry of Education Further Education and Training Scheme Grant.

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<sup>1</sup> L. F. H. Bovey and G. B. B. M. Sutherland, *J. Chem. Phys.* 17, 843 (1949).

<sup>2</sup> E. L. Wagner and D. F. Hornig, *J. Chem. Phys.* 18, 296 and 305 (1950).

<sup>3</sup> L. Couture and J. P. Mathieu, *Proc. Ind. Acad. Sci.* 28, 401 (1948).

<sup>4</sup> W. Zachariasen, *Zeits. f. physik. Chemie* 127, 218 (1927).

<sup>5</sup> A. Smits and D. Tollenaar, *Zeits. f. physik. Chemie* B52, 222 (1942).

<sup>6</sup> The author is indebted to Dr. D. F. Hornig for showing him these results prior to publication.