Note on the Selection Rules for Ions in Crystalline Surfaces

Marcel W. Nathans

Articles you may be interested in

TABLE I.

$T°K$	S^0	$-(F^0-H_0^0)/T$	C_p^0	$(H^0-H_0^0)/T$	$H^0-H_0^0$	$\Delta F_f^0(S_{rh})$
			CH₃SH			
298.16	60.86	51.16	12.12	9.70	2892	−989
300	60.94	51.23	12.15	9.71	2913	−971
400	64.67	54.10	14.11	10.57	4228	+208
500	68.08	56.60	15.96	11.48	5740	1641
600	71.13	58.76	17.62	12.37	7422	3228
700	73.96	60.73	19.08	13.23	9261	4952
800	76.59	62.55	20.38	14.04	11232	6778
900	79.06	64.25	21.53	14.81	13329	8703
1000	81.38	65.85	22.54	15.53	15530	10714
1100	83.58	67.37	23.43	16.21	17831	12800
1200	85.64	68.80	24.21	16.84	20208	14951
1300	87.60	70.17	24.89	17.43	22659	17174
1400	89.47	71.49	25.49	17.98	25172	19416
1500	91.25	72.75	26.00	18.50	27750	21783

TABLE II.

$T°K$	S^0	$-(F^0-H_0^0)/T$	C_p^0	$(H^0-H_0^0)/T$	$H^0-H_0^0$	$\Delta F_f^0(S_{rh})$
			CH₃SCH₃			
298.16	68.25	55.69	17.00	12.56	3745	+2096
300	68.36	55.77	17.15	12.59	3777	2160
400	73.75	59.64	20.25	14.11	5644	5899
500	78.55	62.92	23.27	15.63	7815	10029
600	82.99	65.90	26.07	17.09	10254	14361
700	87.19	68.66	28.56	18.53	12971	18860
800	91.15	71.23	30.76	19.92	15936	23493
900	94.91	73.69	32.68	21.22	19098	28218
1000	98.47	76.01	34.35	22.46	22460	33045
1100	101.84	78.23	35.82	23.61	25971	37941
1200	105.03	80.34	37.10	24.69	29628	42912
1300	108.02	82.33	38.22	25.69	33397	47976
1400	110.88	84.28	39.17	26.60	37240	53035
1500	113.61	86.13	40.01	27.48	41220	58213

1460 cals./mole. for CH₃SH and 1900 cals./mole. for (CH₃)₂S were obtained from the measured entropies.[1,2]

The free energies of formation of the two compounds were computed by means of the free energy functions of the reactants and products after determining ΔH_0^0 for the reactions. ΔH_0^0 was found, in each case, from Karasch's[3] heat of combustion data and Kelley's[4] data on sulfur compounds along with the functions computed here. For CH₃SH, ΔH_0^0 = −17,172 cals./mole and for (CH₃)₂S, ΔH_0^0 = −20,172 cals./mole. The data for the thermodynamic functions are accurate to 0.01 or 0.02 unit but the results for the free energies of formation may differ by as much as perhaps 10 percent from those obtained using more accurate data for the heats of formation of methyl mercaptan and dimethyl sulfide now available.

A summary of the calculations is given in Tables I and II.

[1] Russell, Osborne, and Yost, J. Am. Chem. Soc. **64**, 165 (1942).
[2] Osborne, Doescher, and Yost, J. Am. Chem. Soc. **64**, 169 (1942).
[3] J. Research Nat. Bur. Stan. **2**, 359 (1929).
[4] *Thermodynamic Properties of Sulfur and Its Inorganic Compounds,* Bureau of Mines Bulletin 406 (Washington, 1937).

Evaporation of Polar Hydrocarbon Monolayers*

J. KARLE

U. S. Naval Research Laboratory, Washington, D. C.

March 21, 1949

MONOLAYERS of cerotic acid and n-octadecylamine were produced on soda glass from the melt of the pure compounds.[1,2] The rate of evaporation of these films in vacuum was studied by means of the rate of decrease of scattered electron intensity relative to that of the substrate. It was found that throughout the course of the evaporation the structure of the films did not change. For example, analysis of the diffraction patterns[3,4] from cerotic acid on soda glass showed that the angle of tilt of the molecules remained at 25±3° throughout the course of the evaporation. The mole-cules of n-octadecylamine did not vary from a vertical position by more than 5°. This implies that the films exist as patches on the surface with evaporation occurring mainly from the edges of the patches. If evaporation occurred from within the patches an increase in the angle of tilt should be expected as the evaporation proceeds. This result is of interest since Epstein has also found evidence for a patch-work structure by means of electron microscope studies.[5]

The main purpose of the evaporation experiments was to study the evaporation at various temperatures in order to evaluate* the energy of activation and relate this energy to the binding energy of the molecules to each other and to the surface of attachment. It was found that when the relative amount of material evaporated was small, thereby maintaining the ratio of the number of molecules on the perimeter of a patch to those within a patch approximately constant, that the evaporation rate followed the rate equation for a first-order reaction. The specific reaction rate for a particular temperature can be found from the slope of a plot of the logarithm of the intensity of scattering *versus* the time. From the theory of reaction rates, the specific reaction rate, k, is given by

$$k = Ae^{-E/RT},$$

where E is the activation energy and A is the frequency factor which does not change very rapidly with temperature. The activation energy for the endothermic evaporation process may therefore be calculated from a determination of k at two different temperatures. The endothermic activation energy is composed of the activation energy for the exothermic process, usually a small part of the total energy, plus the energy of binding of the evaporating molecule. The energy of binding involves the energy of attachment of the polar group to the surface plus forces which may exist between the molecule and its neighbors. Application of this method to a film of cerotic acid on soda glass gave a value of 6 kcal. for the activation energy for evaporation. This value may be compared to a value of about 20 kcal., for the energy of binding of a molecule of cerotic acid within a film on Pt estimated from the work of Bigelow, Glass, and Zisman.[6] The difference is more than can be accounted for on the basis of the different energies of adsorption for a carboxyl group on glass and platinum. The value for a carboxyl group on Pt is estimated to be about 6 kcal.[6] We therefore have further evidence for evaporation taking place mainly on the perimeter of the patches since the activation energy is only a fraction of the binding energy for a molecule within the film and therefore only a fraction of the bonds has to be broken for evaporation to take place.

* Presented at the A.S.X.R.E.D. Meeting, Ste. Marguerite Station, Quebec, June 23, 1947.
[1] Bigelow, Pickett, and Zisman, J. Coll. Sci. **1**, 513 (1946).
[2] L. O. Brockway and J. Karle, J. Coll. Sci. **2**, 277 (1947).
[3] Jerome Karle, J. Chem. Phys. **14**, 297 (1946).
[4] J. Karle and L. O. Brockway, J. Chem. Phys. **15**, 213 (1947).
[5] H. T. Epstein, Bull. Am. Phys. Soc. **24**, (No. 3) 9 (1949).
[6] Bigelow, Glass, and Zisman, J. Coll. Sci. **2**, 563 (1947).

Note on the Selection Rules for Ions in Crystalline Surfaces

MARCEL W. NATHANS

Department of Chemistry, University of California, Berkeley, California

March 21, 1949

IN a theoretical investigation of the electronic energy states of ions in the interior and in the surface of a crystal it has been found that the number of distinct levels in the surface will be larger than in the interior, provided that in the interior all of the degeneracy has not already been removed. It has also been found that the absolute energies of corresponding states in the interior and in the surface are different. The entire treatment will be published shortly.

TABLE I.

$L =$	$4p$	$4p+1$	$4p+2$	$4p+3$
Γ_1	$p+1$	$p+1$	$p+1$	$p+1$
Γ_2	p	p	p	p
Γ_3	p	p	$p+1$	$p+1$
Γ_4	p	p	$p+1$	$p+1$
Γ_5	$2p$	$2p+1$	$2p+1$	$2p+2$

In general, if the z axis is chosen normal to the surface, any state whose degeneracy in the interior is due to the equivalence of the z and x (and/or y) axes, will be split in the surface. For example, in a hydrogen-like ion, the state $n=2$ is split into two states in a field of cubic symmetry, namely a $2-s$ state and a doubly degenerate $2-p$ state.[1] In the surface of a cubic crystal, where the z axis is no longer equivalent to the other axes, the p state undergoes a further splitting into a single level ($m=0$) and a degenerate level ($m=\pm1$). It will be true in general that all levels belonging to states for which $m=0$ are single. Moreover, these states have the same symmetry properties in the surface, namely they are all totally symmetric with respect to all symmetry operations for the surface field. Therefore, it is possible that all these states mix; in that case, the matrix elements of the z component of the dipole moment between two states with different principal quantum number but with (apparently) the same azimuthal quantum number will not vanish and transitions with $\Delta l=0$ become possible, in particular $s-s$ transitions.

This can be generalized for the case of atoms and ions with any number of electrons by applying the group theoretical method developed by Bethe[1] to the energy levels of an ion in the surface. In the surface the highest possible symmetry is C_{nv}, where $n=2, 3, 4,$ or 6. For all values of L and all integral values of J one can show that the totally symmetric representation is contained at least once in the $2L+1$-, $2J+1$-dimensional representation of the three-dimensional rotation-reflection group. The procedure is exactly the same as Bethe's. Because Bethe does not give the characters for the classes consisting of reflections, they will be given here. Since all planes of reflection pass through the z axis, which is considered normal to the surface, the effect of a reflection in one of these planes is merely the replacement of a right-handed coordinate system by a left-handed system. Therefore, $P_1^m(\cos\vartheta)e^{im\varphi}$ will go over into $P_1^m(\cos\vartheta)e^{-im\varphi}$, but $P_1^0(\cos\vartheta)$ will go over into itself. Therefore, the characters of the symmetry classes which consist of these reflections are all $+1$. Once these characters have been obtained it is simple to reduce the $2L+1$-, the $2J+1$-dimensional representations of the rotation-reflection group. If, for example, the symmetry of the crystal is cubic, the 100-plane has C_{4v}-symmetry. This group has five symmetry classes and eight elements. Therefore, there are four one-dimensional representations and one two-dimensional representation. Following Bethe[1] these shall be called Γ_1, Γ_2, Γ_3, Γ_4, and Γ_5. Γ_1 is the totally symmetric representation. In Table I the frequency of occurrence of these irreducible representations has been given. In this table, p may be any positive integer.

This result is remarkable in one respect. Although the C_{4v} and D_4 groups are isomorphic, the $2L+1$-dimensional representations reduce differently in the two groups.

Physically it is clear that all states which have axial symmetry about the z axis, i.e., states for which M_L or M_J are zero, and which do not depend on φ, are symmetric with respect to all operations of the groups C_{nv}. It follows that the matrix elements connecting these states will in general not vanish. Mixing of states with different L (or J) values will, therefore, be more pronounced for the surface than for the inside of a crystal. In this case, the matrix elements of the z components of the dipole moments between these states will in general not vanish. Consequently, a breakdown of the

selection rules for L or J in the surface will take place to a considerably higher extent than in the inside of a crystal. In particular the transition $J=0\rightarrow0$ may become allowed. A quantitative investigation of the change in the absolute transition probabilities has not yet been made.

The application of this to the absorption spectra of rare earth ions in crystals is evident. It reopens the question of the cause of the additional lines observed in reflection over that found in absorption, which was originally reported by Freed and Spedding.[2] The explanation proposed by Spedding and Baer[3] that the additional lines were due to a "filter effect" has been generally accepted. Unquestionably both effects play a role. At present, it is not possible to evaluate the relative importance of each.

[1] H. Bethe, Ann. d. Physik 3, 133 (1929).
[2] S. Freed and F. H. Spedding, Phys. Rev. 39, 212 (1930).
[3] F. H. Spedding and R. S. Baer, Phys. Rev. 39, 948 (1932).

The Infra-Red and Raman Spectra of Chlorine Trifluoride*

E. A. Jones, T. F. Parkinson, and R. B. Murray**
K-25 Research Laboratories, Carbide and Carbon Chemicals Corporation,
Oak Ridge, Tennessee
February 28, 1949

THE Raman spectrum of liquid chlorine trifluoride and the infra-red absorption spectrum of the gas in the 2 to 25 μ-region have been investigated. Material from two commercial sources was used. Purification by fractional distillation may not have been entirely successful, and it is possible that some of the infra-red bands currently listed may be due to impurities.

The infra-red data from 2 to 15 μ were obtained with a Perkin-Elmer Model 12B automatic recording spectrometer with NaCl optics. The 15 to 25 μ-region was mapped with a KBr prism in a similar spectrometer. Fluorothene[1] absorption cells with NaCl or KBr windows as described in another letter[2] were used in the infra-red investigation. A fluorothene Raman tube suitable for handling highly corrosive materials was developed for this work. Technical details on the use of fluorothene in infra-red and Raman spectroscopy are scheduled for publication in the near future.

The Raman spectrum of the liquid was obtained with a Lane Wells Spectrograph, Type 40-A, and Excitation Unit Type 60-A. Because of absorption of ClF_3 in the 4047A and 4358A regions, it was necessary to use Hg 5461A as the exciting line. Exposure times were of the order of several hours. Raman tubes were supported vertically in an unsilvered Dewar flask and were cooled by a stream of nitrogen which had passed through a coil immersed in liquid nitrogen. The sample was maintained at approximately -60°C. The filter used was an aqueous solution of neodymium nitrate contained in an outer jacket of the Dewar flask.

TABLE I. Infra-red and Raman frequencies in the ClF_3 spectrum.

Infra-red bands (gas) cm^{-1}	Raman lines (liquid) cm^{-1}
	321 v.w.
485 m.s.	424 v.w.
540 m.s.	
630 m.w.	502 v.s.
710 v.s.	514 v.s.
741 m.s.	
759 m.s.	753 m.s.
848 v.w.	
888 v.w.	
952 v.w.	
1028 v.w.	
1110 m.s.	
1235 m.s.	
1265 m.s.	