The Raman Spectra of Nitric Acid and Aqueous Solutions of Certain Nitrates

By

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Since the discovery of the so-called Raman effect announced by Prof. Raman and Mr. Krishnan,[1] a number of interesting papers on this subject have been published by various investigators.

The Raman spectra of HNO_3 and aqueous solutions of $NaNO_3$ and NH_4NO_3 have already been investigated by A. Carrelli, P. Pringsheim and B. Rosen.[2] In these substances, they observed that certain Raman lines have a wave-number smaller by about 1040 cm^{-1}. than the corresponding exciting lines, and showed that these Raman lines are due to the inactive vibration of NO_3 ions.

The present experiment was undertaken in order to study whether lines having a difference of about 1040 $cm.^{-1}$ in the wave-number can also be found in the other nitrates, not examined by them, and to find the other Raman lines, if any, common to them, and to compare them with their infra-red absorption lines.

Method of the Experiment

The glass bulb containing the liquid under examination was placed close to the wall of the quartz mercury lamp used as the source of exciting radiation. The lights scattered by the liquid were focussed, by means of a condensing glass lens of short focus, on the slit of a spectrograph provided with two glass prisms and a camera of 50 cm. focus, suitable apertures being used to eliminate stray light.

1 C. V. Raman and K. S. Krishnan: Indian J. Phys., 2 (1928) 387.

2 A. Carrelli, P. Pringsheim and B. Rosen: Zeits. f. Phys., 51 (1928) 511.

With this arrangement, the Raman spectra of lights scattered from pure nitric acid and saturated water solutions of certain nitrates at 80°C. were photographed, 48 hours' exposure being given and very rapid plates used.

The spectrograms obtained with this arrangement show only the visible region of the spectrum.

Results of the Experiment

The spectrograms obtained in this experiment are reproduced in the accompanying Plate. Certain Raman lines and Raman bands due to water can be seen distinctly on the Plate, while other lines get very faint in the reproduction.

The spectrograms were measured with a comparator and the wave-lengths of the Raman lines were calculated from the comparator measurement, Hartmann's simplified interpolation formula

$$\lambda = \lambda_0 + \frac{c}{n - n_0}$$

being applied and the mercury lines at 4916, 4358 and 4047 Å. taken as the standards.

The wave-lengths of the exciting mercury lines and the corresponding Raman lines, wave-number differences between the exciting and the excited Raman lines, the calculated wave-length in the infra-red and the wave-lengths of infra-red radiation directly obtained by Coblentz are given in Table I. Table II gives the mean wave-number differences, the corresponding wave-lengths in the infra-red and the values directly observed by Coblentz.

Table I

Substances	Exciting Hg-lines		Accompanying Raman lines			Wave-number differences in cm.$^{-1}$	Corresponding wave lengths in Infra-red in μ.	Coblentz's values in μ.
	Wave-length in A.U.	Wave-number in cm.$^{-1}$	Wave-length in A.U.	Wave-number in cm.$^{-1}$	Intensity			
HNO_3	4358	22937	4621	21636	4	1301	7.68	
			4566	21896	4	1041	9.60	
			4548	21978	3	959	10.4	
			4496	22246	2	691	14.4	
			4482	22306	2	631	15.8	
	4047	24704	4272	23403	4	1041	7.68	
	4078	24515	4259	23474	1	1301	9.60	
			4225	23663	3	1041	9.60	
	4047	24704	4209	23747	2	957	10.4	
			4166	24000	2	704	14.2	
			4155	24062	1	642	15.5	

Substances	Exciting Hg-lines		Accompanying Raman Lines			Wave-number differences in cm.$^{-1}$	Corresponding wave lengths in Infra-red in μ.	Coblentz's values in μ.
	Wave-length in A.U.	Wave-number in cm.$^{-1}$	Wave-length in A.U.	Wave-number in cm.$^{-1}$	Intensity			
$NaNO_3$	4358	22937	4567	21899	4	1046	9.56	9.6
			4496	22237	1	700	14.3	14.4
	4078	24515	4260	23469	2	1046	9.56	
	4047	24704	4226	23658	4	1046	9.56	
			4166	24000	1	704	14.2	
KNO_3	4358	22937	4566	21896	5	1041	9.60	9.6
			4496	22237	2	700	14.3	14.3
	4078	24515	4259	23474	3	1041	9.60	
	4047	24704	4225	23663	5	1041	9.60	
			4165	24004	2	700	14.3	
NH_4NO_3	4358	22937	4566	21896	4	1041	9.60	
			4495	22242	1	695	14.4	
	4078	24515	4259	23474	2	1041	9.60	
	4047	24704	4225	23663	4	1041	9.60	
			4165	24004	1	700	14.3	
$Cd(NO_3)_2$	4358	22937	4566	21896	3	1041	9.60	
			4496	22237	1	700	14.3	
	4078	24515	4260	23469	1	1046	9.56	
	4047	24704	4225	23663	3	1041	9.60	
$Pb(NO_3)_2$	4358	22937	4566	21896	3	1041	9.60	
			4496	22237	1	700	14.3	
	4078	24515	4260	23469	1	1046	9.56	
	4047	24704	4225	23663	3	1041	9.60	
$Ba(NO_3)_2$	4358	22937	4566	21896	3	1041	9.60	
	4078	24515	4260	23469	1	1046	9.56	
	4047	24704	4225	23663	3	1041	9.60	
$Hg(NO_3)_2$	4358	22937	4565	21901	3	1036	9.65	
	4078	24515	4260	23469	1	1046	9.56	
	4047	24704	4224	23666	3	1038	9.63	
$Ca(NO_3)_2$	4358	22937	4565	21896	2	1036	9.65	
	4078	24515	4260	23469	1	1046	9.56	
	4047	24704	4225	23663	2	1041	9.60	
$Sr(NO_3)_2$	4358	22937	4566	21896	3	1041	9.60	
	4078	24515	4260	23469	1	1046	9.56	
	4047	24704	4225	23663	3	1041	9.60	

Table II

Substances	Mean wave-number differences between exciting lines and accompanying Raman lines in cm.$^{-1}$	Corresponding wave-lengths in Infra-red in μ.	Coblentz's value in μ.
HNO_3	1301 1041 958 698 637	7.68 9.60 10.4 14.3 15.7	
$NaNO_3$	1046 702	9.56 14.2	9.6 14.4
KNO_3	1041 700	9.60 14.3	9.6 14.3
NH_4NO_3	1041 698	9.60 14.3	
$Cd(NO_3)_2$	1043 700	9.59 14.3	
$Pb(NO_3)_2$	1041 700	9.60 14.3	
$Ba(NO_3)_2$	1043	9.59	
$Hg(NO_3)_2$	1041	9.60	
$Ca(NO_3)_2$	1041	9.60	
$Sr(NO_3)_2$	1043	9.59	
Mean	1301 1042 958 700 637	7.68 9.59 10.4 14.3 15.7	

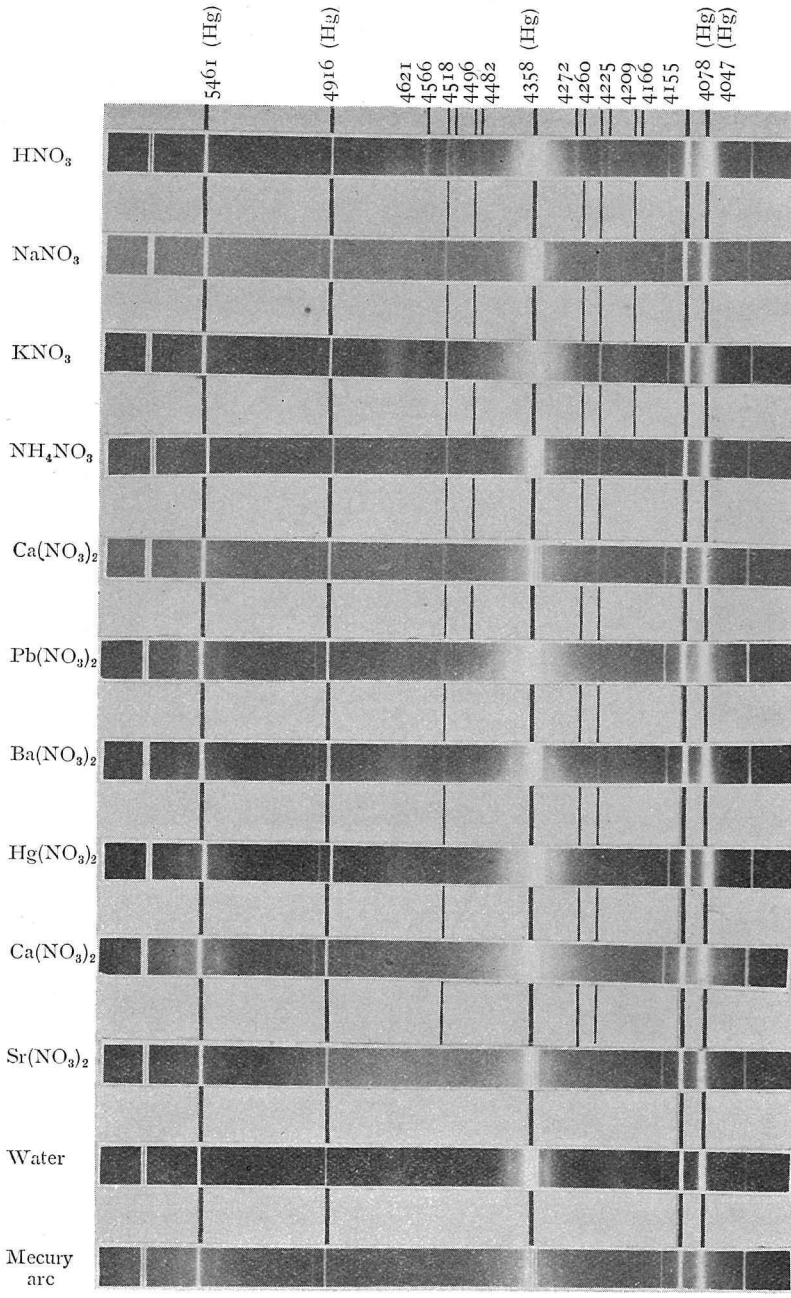
As is seen from the tables, the present writer found, in addition to the lines already observed by Carrelli, Pringsheim and Rosen, one Raman line at λ 4259 Å. with HNO_3 and two lines at $\lambda\lambda$ 4496 and 4166 Å. with $NaNO_3$. These lines are faint of course. The present writer also observed in the case of NH_4NO_3 five new lines at $\lambda\lambda$ 4566, 4495, 4259, 4225 and 4165 Å.

The present experiment showed that Raman lines having a difference of 1042 cm^{-1}. in the wave-number are excited in all the substances used in the present experiment. Besides the above lines the writer observed other Raman lines having the wave-number difference

of about 700 cm^{-1}. in the case of HNO_3, $NaNO_3$, KNO_3, NH_4N_3O, $Cd(NO_3)_2$ and $Pb(NO_3)_2$, while no such Raman lines could be observed in the case of $Ba(NO_3)_2$, $Hg(NO_3)_2$, $Ca(NO_3)_2$ and $Sr(NO_3)_2$. This is perhaps due to a lower concentration of NO_3 ions in the solutions, as the solubility of these substances is generally small,

Comparing the present experimental results with those obtained by Coblentz in his infra-red investigation, most of the observed Raman lines of these substances correspond to his infra-red lines as is shown in the above tables.

In conclusion, the author wishes to express his sincere thanks to Prof. M. Kimura for his kind guidance.



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