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DURATION OF MOLECULES IN UPPER QUANTUM STATES

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In an article which has been presented to the *Physical Review* for publication the author has shown the possibility of calculating from data on the intensity of absorption lines the mean life τ of atoms and molecules in excited quantum states, and the specific rate A_{21} at which they spontaneously leave the excited state 2 to return to the lower state 1. The calculations are based on Fñchtbauer's¹ method of determining the probability that molecules will be activated by the absorption of a quantum of light, combined with Einstein's² views as to the mechanism of light absorption and emission. The following equation is derived connecting A_{21} with experimentally determinable quantities

$$A_{21} = \frac{8\pi\nu^2}{c^2N_1} \frac{p_1}{p_2} \int_0^\infty \alpha d\nu$$

A_{21} is the chance per unit time that a molecule in quantum state 2 will spontaneously jump to quantum state 1 in the absence of exciting radiation, ν is the frequency of the light emitted in such a jump, and p_1 and p_2 are the *a priori* probabilities of states 1 and 2, while N_1 and α are data obtained in some particular absorption experiment made on the line accompanying the change from state 1 to state 2, N_1 being the number of molecules per unit volume in the lower quantum state and α the absorption coefficient for light which is producing the quantum jump under consideration. The integral $\int \alpha d\nu$ is to be taken across the whole effective width of the absorption line.

Using the above equation and data which could be obtained either directly or indirectly from the literature, values of A_{21} and τ were calculated which are repeated in table I.

The first column of table I gives the substance experimented on, the second column gives the quantum numbers designating the quantum jump

TABLE I

SUBSTANCE	LINE $n, j, k \rightarrow n', j', k'$	λ	p_1/p_2	A_{21}	τ
Mercury	6,1,1 \rightarrow 2,2,2	2537Å	1/3	9.68×10^6	1.03×10^{-7}
Sodium	3,1 $\frac{1}{2}$,1 \rightarrow				
	3,2 $\frac{1}{2}$,2	5890Å	1/3	3.25×10^6	3.08×10^{-7}
	3,1 $\frac{1}{2}$,2	5896Å	1/3	6.21×10^6	1.61×10^{-7}
Caesium	6,2 $\frac{1}{2}$,1 \rightarrow				
	7,2 $\frac{1}{2}$,2	4555Å	1/3	3.56×10^5	2.80×10^{-6}
	7,2 $\frac{1}{2}$,2	4593Å	1/3	1.16×10^5	8.64×10^{-7}
	8,2 $\frac{1}{2}$,2	3877Å	1/3	2.37×10^5	4.21×10^{-6}
	9,2 $\frac{1}{2}$,2	3612Å	1/3	1.58×10^4	6.33×10^{-5}
	9,1 $\frac{1}{2}$,2	3617Å	1/3	7.98×10^4	1.26×10^{-5}
Iodine	—	5461Å	—	3.90×10^{12}	2.94×10^{-3}
	$m, n \rightarrow m', n'$				
HCl	12,0 \rightarrow 13,1	3.239 μ	12/13	57.7	0.0174
	8,0 \rightarrow 9,1	3.299 μ	8/9	5.69	0.176
	3,0 \rightarrow 4,1	3.394 μ	3/4	1.75	0.571
	2,0 \rightarrow 3,1	3.415 μ	2/3	1.21	0.829
	1,0 \rightarrow 2,1	3.439 μ	1/2	1.94	0.515
	1,0 \rightarrow 0,1	3.489 μ	$\left\{ \begin{array}{l} \infty \\ 1 \\ 0 \end{array} \right.$	$\left\{ \begin{array}{l} \infty \\ 4.48 \\ 0 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 0.223 \\ \infty \end{array} \right.$
	2,0 \rightarrow 1,1	3.516 μ	2	5.93	0.169
	3,0 \rightarrow 2,1	3.544 μ	3/2	3.41	0.293
	8,0 \rightarrow 7,1	3.699 μ	8/7	6.38	0.157
	12,0 \rightarrow 11,1	3.846 μ	12/11	33.1	0.0303
HCl	23/2,0 \rightarrow 25/2,1	3.239 μ	12/13	31.3	0.0320
	15/2,0 \rightarrow 17/2,1	3.299 μ	8/9	3.80	0.263
	5/2,0 \rightarrow 7/2,1	3.394 μ	3/4	1.52	0.660
	3/2,0 \rightarrow 5/2,1	3.415 μ	2/3	1.10	0.910
	1/2,0 \rightarrow 3/2,1	3.439 μ	1/2	1.87	0.535
	3/2,0 \rightarrow 1/2,1	3.489 μ	2	4.77	0.210
	5/2,0 \rightarrow 3/2,1	3.516 μ	3/2	3.34	0.299
	7/2,0 \rightarrow 5/2,1	3.544 μ	4/3	2.71	0.369
	17/2,0 \rightarrow 15/2,1	3.699 μ	9/8	8.58	0.117
	25/2,0 \rightarrow 23/2,1	3.846 μ	13/12	57.5	0.0174
HF	6,0 \rightarrow 7,1	2.395 μ	6/7	$20.5 \times 1/p_{HF}$	$0.0488 \times p_{HF}^3$
	2,0 \rightarrow 3,1	2.475 μ	2/3	8.19	0.122
	1,0 \rightarrow 2,1	2.499 μ	1/2	4.81	0.208
	2,0 \rightarrow 1,1	2.578 μ	2	13.6	0.0738
	5,0 \rightarrow 4,1	2.671 μ	5/4	13.1	0.0764
HF	11/2,0 \rightarrow 13/2,1	2.395 μ	6/7	11.37	0.0880
	3/2,0 \rightarrow 5/2,1	2.475 μ	2/3	6.88	0.145
	1/2,0 \rightarrow 3/2,1	2.499 μ	1/2	4.46	0.224
	5/2,0 \rightarrow 3/2,1	2.578 μ	3/2	8.52	0.117
	11/2,0 \rightarrow 9/2,1	2.671 μ	6/5	17.94	0.0557

under consideration, (n, j, k being respectively total, inner and azimuthal quantum number, and m, n being respectively rotational and oscillational quantum number), the third column gives the ratio of *a priori* probabilities, the fourth column the values of A_{21} and the fifth column the mean life τ . This latter quantity is merely the reciprocal of A_{21} and is the mean life of molecules in quantum state 2 provided the molecules are leaving that state only by the one process of jumping to state 1. The values for the halides are calculated for the same lines both on the theory of whole and on the theory of half azimuthal quantum numbers.

The following conclusions are drawn as to the values obtained. They agree with the meagre data on mean life obtained by other experimental methods and hence lend support to Einstein's 1917 position as to the emission and absorption of radiant energy. Values of mean life may vary for different quantum states at least over the range 1 to 10^{-8} seconds. The rate of decay is not a simple function of the frequency of the emitted light. The rate corresponding to the emission of a line of high frequency may be greater or less than for a line of lower frequency. The data now available for the alkali doublets $1s - mp_1$ and $1s - mp_2$ indicate a higher rate of decay the smaller the change in total quantum number for the line under consideration. The rate of decay from a given mp_1 state is m times as great as from the corresponding mp_2 state, (already stated in another form by Füchtbauer and Hofmann). In the case of the rotation-oscillation spectra of the hydrogen halides, the rate of decay is greater for quantum states with one unit of oscillation and many of rotation than for those with one unit of oscillation and only a few of rotation; and in the case of different molecules but the same quantum numbers the rate of decay is greater for the molecule with the greater frequency of oscillation.

In the article mentioned the importance of determining further accurate values of $\int \alpha d\nu$ and developing other methods of determining rate of decay is emphasized. The possibility and method of calculating absolute values of A_{21} from the Bohr correspondence principle is also indicated. It is hoped to make such considerations the subject of a later paper.

¹ Füchtbauer, *Physik. Zs.*, **21**, 322 (1920).

² Einstein, *Ibid.*, **18**, 121 (1917).

³ p_{HF} is the unknown partial pressure of undissociated hydrogen fluoride HF present in the absorption tube. The results, given in the table, have relative significance and since p_{HF} was almost certainly less than one, some absolute significance.