The Vibrations of Polyatomic Molecules in Excited Electronic States

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The vibration frequencies found in the excited states of the molecules CO_2, CS_2, H_2O, ClO_2, SO_2, O_3, NH_3, PCl_3, C_2H_2, C_2H_4, C_6H_6 and $(CH_3)_2CO$ are considered. The frequencies appearing most strongly in *all* cases, and in most cases the only frequencies occurring, are totally symmetrical. This is in accord with the extension of the Franck-Condon principle to such molecules by Herzberg and Teller.

THE normal modes of vibration of a number of molecules are now well known. The numerical values of the frequencies, given by Raman and infrared spectra, have been assigned correctly to the proper modes of vibration in many cases. The frequencies which are present in the excited electronic states have not received so much attention, and the experimental data have been few until very recently.

The selection rules for vibration-electronic transitions have been given in some detail by Herzberg and Teller.[1] It appears from their discussion that in absorption from the non-vibrating level of the ground state, only totally symmetrical vibrations (those whose coordinates do not change sign under any operations of the symmetry group) are strongly excited in the upper electronic state. The rules governing weaker transitions from this ground state as well as other lower states are also discussed. Herzberg and Teller considered the spectra of four molecules in relation to their rules and predictions. The spectrum of CH_3I was found to be in complete accord with theory. The fluorescence spectrum of benzene was also in accord. The spectrum of ClO_2 was in partial agreement with the theory also.[2] The analysis of the SO_2 spectrum was not in accord with theory.[3]

Since the publication of this important paper more data on other molecules have been published. The purpose of the present note is to show that totally symmetrical vibrations are indeed the ones occurring in excited states in all

cases where spectra have been adequately studied and analyzed. The other vibrations are either rather weak or entirely absent. For the sake of brevity the results are summarized in Table I, which is largely self-explanatory. References to the *normal* state vibrations are omitted, if they can be found in Stuart's *Molekülstruktur*.[4] The designation of these vibrations by subscripts is that used by Stuart rather than the original investigators, in order to avoid confusions. The totally symmetrical vibrations are starred.

DISCUSSION

In the examples given above the normal vibrations are known with some certainty. Three cases, however, call for comment. In benzene there are only two totally symmetrical frequencies, and there is little doubt that one of them has the value 991. The only observed frequency in the excited state, 920, is closer to this value than any other, totally symmetrical or otherwise. In ethylene the situation is less certain because there are a number of normal frequencies not differing greatly in value. It is difficult to decide to which normal frequencies those in the excited states correspond. The assignment of Price, however, is as reasonable as any.

In acetone there seems little doubt that the excited state frequency 745 corresponds to 788, and 210 and 325 correspond to 376. 1190 was considered by Noyes, Duncan and Manning to be a modification of 1220, or some other $C-H$ bending frequency in this region. One of which must be totally symmetrical. The possibility that this is the $C-O$ frequency v_2 (π) (1710 in normal state) must also be considered.[21]

[1] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

[2] H. C. Urey and H. Johnston, Phys. Rev. **38**, 2131 (1931). The more recent analysis of Ku removes all disagreement with the theory.

[3] A recent analysis of the spectrum of SO_2 by J. H. Clements is in complete accord with the ideas of Herzberg and Teller.

[4] H. A. Stuart, *Molekülstruktur*, Julius Springer, Berlin, 1934.

TABLE I.

Molecule	Normal vibrations	Excited state vibrations	Molecule	Normal vibrations	Excited state vibrations
CO_2	v_1* 1322 v_3 2363 v_2 667.9	v_1 1330–1110[5]	PCl_3[11]	v_1* 257 v_2 190 v_3* 510 v_4 480	v_1 230–265[12] v_2 ——— v_3 ——— v_4 ———
CS_2	v_1* 655 v_3 1523 v_2 396.8	v_1 600±50[6]	C_2H_2	$v_1(s)$* 1975 $v_2(s)$* 3370 $v(a)$ 3277 (3288) $\delta(a)$ 729 $\delta(s)$ 600	$v_1(s)$ 1810, 1760[13] $v_2(s)$ ——— $v(a)$ ——— $\delta(a)$ ——— $\delta(s)$ 300–0
H_2O	v_1* (3600) v_2* 1595.4 v_3 3756	v_2 1300, 1600, (800)[5]			
ClO_2[7]	v_1* 1105 v_2* 529 v_3 954	v_1 721.7[2, 7] v_2 ——— v_3 ———	C_2H_4[14]	$v_1(\pi s)$* 3019 $v_2(\pi s)$* 1623 $\delta(\pi s)$* 1342 (9 others not totally symmetrical)	$v_1(\pi s)$ ——— $v_2(\pi s)$ 1340, 800, 300,[13] 230, 200 $\delta(\pi s)$ 480, 150
SO_2	v_1* 1146 v_2* 560 v_3 1340	v_1 ——— v_2 230[8] v_3 ———	C_6H_6[15, 16]	v_1* 991 v_2* 3063 (only totally symmetrical vibrations)	v_1 990 (fluorescence)[17] 920 (absorption)[18]
O_3	v_1* 1046 v_2* 700 v_3 1357	v_1 1099[9] v_2 566.7 v_3 ———			
NH_3	v_1* 964.3, 933.8 v_2 1630 v_3* 3336 v_4 (3300)	v_1 878, 936, 902, 954[10] v_2 ——— v_3 ——— v_4 ———	$(CH_3)_2CO$[11, 19]	$v_1(\pi)$* 788 $v_2(\pi)$* 1712 $\delta(\pi)$* 376	$v_1( )$ 715[20] $v_2( )$ ——— $v_3( )$ 210, 325 ? 1190

Thus it appears that the symmetrical frequencies are most strongly excited by absorption from a nonvibrating ground state even in relatively complicated molecules. The same must be expected in more complicated molecules which give discrete spectra. So it may be concluded that a search for these frequencies should form a logical starting point in the analysis of complicated spectra.

Information on absorption from higher levels of the ground state is available in so few cases that it does not seem profitable to apply the rules of Herzberg and Teller which cover these cases.

[5] G. Rathenau, Zeits. f. Physik 87, 32 (1933).
[6] G. Rodloff, Zeits. f. Physik 91, 511 (1934).
[7] Z. W. Ku, Phys. Rev. 44, 376 (1933).
[8] J. H. Clements, Phys. Rev. 47, 224 (1935).
[9] O. R. Wulf, Proc. Nat. Acad. Sci. 16, 508 (1930).
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[11] K. W. F. Kohlrausch, Der Smekal-Raman-Effekt, Julius Springer, Berlin, 1931.
[12] A. B. F. Duncan, unpublished observations of far ultraviolet spectrum.
[13] W. C. Price, Phys. Rev. 47, 444 (1935).
[14] Reference 4, p. 337.
[15] E. B. Wilson, Jr., Phys. Rev. 45, 706 (1934).

[16] D. E. Teets and D. H. Andrews, J. Chem. Phys. 3, 175 (1935).
[17] G. B. Kistiakowsky and M. Nelles, Phys. Rev. 41, 595 (1932).
[18] C. V. Shapiro, R. C. Gibbs and J. R. Johnson, Phys. Rev. 38, 1170 (1931). References to earlier work here.
[19] The C−C and C−O frequencies are those of H_2CO (reference 4, p. 327). The nontotally symmetrical frequencies are probably 490, 526 and 1066.
[20] W. A. Noyes, Jr., A. B. F. Duncan and W. M. Manning, J. Chem. Phys. 2, 717 (1934).
[21] This was pointed out to the writer by Dr. W. C. Price. See also V. Henri, Comptes rendus 199, 849 (1934).