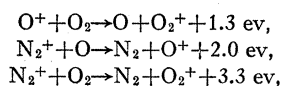## Validity of the Franck-Condon Principle in Collisions of the Second Kind

ROLAND E. MEYEROTT

Sloane Physics Laboratory, Yale University,
New Haven, Connecticut

March 17, 1947

THE application of the principle of resonance to collisions of the second kind between an atom and a molecule or between two molecules is generally uncertain, because of the lack of any rule for deciding how much energy can be absorbed as vibrational energy of the molecule or molecules. For example, the probability of the following transfer reactions in the upper atmosphere[1]

$$O^+ + O_2 \rightarrow O + O_2^+ + 1.3 \text{ ev},$$
$$N_2^+ + O \rightarrow N_2 + O^+ + 2.0 \text{ ev},$$
$$N_2^+ + O_2 \rightarrow N_2 + O_2^+ + 3.3 \text{ ev},$$

depends upon whether such a large amount of energy can be absorbed as vibrational energy. In collisions involving He_2 or He_2^+, failure to take into account the vibrational energy led to confusion as to the carrier of the excitation energy in He.[2]

In considering the latter problem, it was suggested by the present writer that the Franck-Condon (F-C) principle also applied to collisions of the second kind. Ideally, one could consider the transfer of energy as an induced emission and absorption process. In this case the F-C principle would hold for each of the colliding molecules. For very close collisions this ideal situation would need modification. However, close collisions are not likely to affect the cross sections appreciably, since to have a large cross section means a large collision radius and hence a long range transfer of excitation. In the limit, this would be essentially a radiation problem.

Experimentally, excitation of N_2 by the metastable states or ions of Xe, Kr, A, Ne, and He afford a good check of the above hypothesis. Here the metastable state or ion is atomic so that the only dependence of cross section on the F-C principle is that involving N_2. A list and a discussion of most of the states excited in N_2 is given by Bernard.[3] It is significant that all these states can also be excited by electron impact in which the F-C principle is known to hold. (The possible exception, that of the C $^2\Sigma$ state of N_2^+ excited by He^+, has now been removed, as will be shown in a paper to follow.) No new states appear (many more might be expected on theoretical grounds), and no evidence exists for excessive dissociation of N_2 although all of the metastable states involved have energies greater than the dissociation energy of N_2. Hence, it would appear that those collisions in which the transfer of energy can obey the F-C principle in the molecule are most probable.

Collisions of the second kind between two molecules are more restricted because of the fact that the F-C principle must hold for each of the colliding molecules. An examination of the molecular states excited in active nitrogen shows that in all cases (except where molecular formation takes place as the β-bands of NO), the excitation can be accounted for in detail by an application of the F-C principle

to the forbidden transitions A $^3\Sigma_u \rightarrow X$ $^1\Sigma_g$, a $^1\Pi_g \rightarrow X$ $^1\Sigma_g$, and a $^1\Pi_g \rightarrow A$ $^3\Sigma_u$ transitions in N_2.

Application of the F-C principle to the reactions listed in the first section of this letter indicates that the transfer of charge as indicated would likely be very improbable, since the potential curves of N_2^+ and O_2^+ lie directly above those of N_2 and O_2, respectively, in their ground states. Hence, no mechanism exists for converting an excess energy of the order of volts into vibrational or translational energy of the colliding molecules.

[1] D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. A187, 261 (1946).
[2] R. E. Meyerott, Phys. Rev. 70, 671 (1946).
[3] R. Bernard, Ann. de physique 13, 1 (1940).

The Elastic Constants of Sodium Chlorate

S. BHAGAVANTAM AND D. SURYANARAYAN

Department of Physics, Andhra University, Waltair, India

March 19, 1947

SODIUM chlorate ($NaClO_3$) crystallizes in the cubic tetratohedral class. It has three elastic constants and Voigt[1] reported that one of them is negative, making the crystal possess a negative value of Poisson's ratio. Recently Mason[2] remeasured these constants and found all of them to be positive in contrast to Voigt's results. A new dynamical method based on the use of a piezoelectric wedge has been developed in this laboratory[3] for measuring the elastic constants of crystals, and, in view of the importance of the above results in the case of sodium chlorate, it is considered desirable to provide independent confirmation. Fairly large sized crystals of this substance have been grown from aqueous solution and the results in Table I are obtained by working with suitable sections. The values of the c's in the last row are obtained by direct measurement and the s's are derived therefrom. The values of the s's as measured by Voigt and by Mason, and those of c's, which are deduced therefrom, are given for comparison in the first and the second rows. The symbol K in the last column stands for the bulk modulus and is equal to $(c_{11} + 2c_{12})/3$.

TABLE I. Elastic constants of sodium chlorate.

Unit Constant	(10⁻¹³ cm²/dyne)				(10¹¹ dynes/cm²)			K
	s_{11}	s_{12}	s_{44}	c_{11}	c_{12}	c_{44}		
Voigt	24.6	12.52	83.6	6.19	−2.087	1.196		0.67
Mason	23.35	−5.15	85.4	4.90	1.386	1.17		2.56
Authors	22.9	−5.35	84.7	5.09	1.55	1.18		2.73

Our results are in agreement with those of Mason and it is to be concluded that this crystal has a positive value of Poisson's ratio like most other substances. Bridgman[4] obtained 1.99×10^{11} dynes/cm² for the bulk modulus of this substance. This measured value is in qualitative agreement with that derived from the results of Mason and the authors but differs greatly from that based on Voigt's values.

[1] W. Voigt, *Lehrbuch der Kristallphysik* (Teubner, Leipzig, 1910).
[2] W. P. Mason, Phys. Rev. 70, 529 (1946).
[3] S. Bhagavantam and J. Bhimasenachar, Proc. Ind. Acad. Sci. 20 298 (1944).
[4] P. W. Bridgman, Proc. Am. Acad. 64, 51 (1929).