

PROBABILITY OF ELECTRON-VIBRATIONAL TRANSITIONS IN DIATOMIC MOLECULES

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QUANTITATIVE studies of the distributions of intensity in spectra of diatomic molecules and radicals are attentively pursued in many laboratories here and abroad. The increased efforts in this direction are connected with the demands on spectroscopy of flames, shock waves, and electric discharges, with certain astrophysical problems, with the radiation properties of highly heated gas systems, with research on pulsed gas lasers, etc. These questions were considered earlier in reviews by Kolesnikov and Leskov^[1] and Soshnikov^[2]. The former is devoted to methods of calculating relative vibrational transition probabilities, and the latter contains results on the absolute transition probabilities in diatomic molecules.

During the years elapsed since the publication of^[1,2], essentially more rigorous methods of calculation were developed, the experimental technology has become modernized, and the limited nature of the Franck-Condon principle has become clear, and many examples have demonstrated the character of deviations from the Condon approximation. The methods and results of calculations of the Franck-Condon factors, listed in^[1], have become completely obsolete, and the dependence of the electric-transition dipole moment on the internuclear distance, which started to be studied during those years^[2], is by now already employed for technical applications. The need for systematizing the accumulated data is also brought about by the fact that the results on the intensities in the spectra of diatomic molecules are published in various papers which have little relation to one another. As a result, rough estimates and approximate measurements are still being published for molecules for which better results already exist. In the present review we attempt to fill the gaps noted above, using for the most part material published in 1958-1965.

1. MAIN PREMISES

We present here relations between the characteristics of a radiating system of diatomic molecules^[2-9]. The intensity of emission or absorption of the light by a molecule, as the latter goes over from a state *n* into a state *m*, is determined by the Einstein transition probability coefficients *A_{nm}* and *B_{mn}*. The absolute intensity, or more accurately, the power radiated from a volume of gas, is

$$I_{em}^{nm} = N_n h \nu_{nm} A_{nm}; \tag{1.1}$$

it is assumed here that self-absorption can be neglected. In turn, the absorption intensity (the radiation energy flux absorbed in a thin layer *dx* of 1 cm² cross section is

$$I_{abs}^{nm} = I_{\nu}^0 N_m B_{mn} h \nu \, dx. \tag{1.2}$$

In (1.1) and (1.2), *N_n* is the number of radiators in the volume, *N_m* the number of absorbers, and *dx* is the geometric path length. The remaining symbols are standard.

We now relate the transition probabilities with experimentally determined quantities. From Beer's law we can write

$$I_{abs}^{nm} = \int (I_{\nu}^0 - I_{\nu}) \, d\nu = I_{\nu}^0 \, dx \int K_{\nu} \, d\nu. \tag{1.3}$$

From the last two relations it follows that

$$\int K_{\nu} \, d\nu = N_m B_{mn} h \nu_{nm}. \tag{1.4}$$

On the other hand, *A_{nm}* and *B_{mn}* can be expressed in terms of the square of the modulus of the matrix element of the dipole moment *R_{nm}*:

$$A_{nm} = \frac{64\pi^4 \nu_{nm}^3}{3hc^3} |R_{nm}|^2, \tag{1.5}$$

$$B_{mn} = \frac{8\pi^3}{3h^2} |R_{nm}|^2, \tag{1.6}$$

where

$$R_{nm} = \int \Psi_m^* M \Psi_n \, d\tau. \tag{1.7}$$

Here *M* is the dipole moment, Ψ the complete wave functions, and *dτ* the element of configuration space of the electrons and the nuclei. For nondegenerate electron states, *A_{nm}* and *B_{mn}* are proportional to $|R_{nm}|^2$, and for degenerate states *A_{nm}* and *B_{mn}* are proportional respectively to

$$(1/g_n) \sum |R_{n_i m_k}|^2 \quad \text{and} \quad (1/g_m) \sum |R_{n_i m_k}|^2,$$

where *g_n* and *g_m* are the degeneracy multiplicities and the summation is carried out over all the sub-levels *n_i* and *m_k*.

It is known that in the Born-Oppenheimer approximation the square of the matrix element of the dipole moment for a given electron-vibrational-rotational transition can be written as

$$|R_{nm}|^2 = \left| \int \Psi_v \cdot R_e^{nm}(r) \Psi_{v'} \, dr \right|^2 S_{J'J''} = P_{v'v''} S_{J'J''}, \tag{1.8}$$

where

$$R_e^{nm}(r) = \int \Psi_{ne}^* M \Psi_{me} dx \quad (1.9)$$

is the dipole moment of the pure electronic transition; $\Psi_{ne}(x, r)$ and $\Psi_{me}(x, r)$ are the solutions of the wave equations of the electron motion for stationary nuclei; $\Psi_{v'}(r)$ and $\Psi_{v''}(r)$ are solutions of the wave equations for the vibrational motion of the nuclei, and $S_{J'J''}$, the so-called Henle-London factors, are the matrix elements of the rotational lines.

If we neglect the dependence of R_e^{nm} on the internuclear distance r , then the dipole moment of the electron-vibrational transition, $P_{v'v''}$, which determines the probability of the corresponding electron-vibrational transition, can be written in the form

$$P_{v'v''} = \left| \int \Psi_{v'} R_e^{nm}(r) \Psi_{v''} dr \right|^2 = |R_e^{nm}|^2 \left| \int \Psi_{v'} \Psi_{v''} dr \right|^2 = |R_e^{nm}|^2 q_{v'v''}, \quad (1.10)$$

where $q_{v'v''}$ is the square of the integral of superposition of the vibrational wave functions, called the Franck-Condon factor by Bates. Thus, in the approximation indicated, we have

$$|R_{nm}|^2 = |R_e^{nm}|^2 q_{v'v''} S_{J'J''}. \quad (1.11)$$

Using (1.4) and (1.11), and taking into account the degeneracy, whose multiplicity is equal to $2J + 1$ for rotational levels, we can write

$$B_{mnv'v''J'J''} = \frac{8\pi^3}{3h^2} \frac{\sum_{M'M''} |R_{nm}|^2}{2J'' + 1} = \frac{8\pi^3}{3h^2} |R_e^{nm}|^2 q_{v'v''} \frac{\sum_{M'M''} S_{J'J''}}{2J'' + 1}. \quad (1.12)$$

If we sum all the transition probabilities taken in accord with (1.12) over all the transitions from a given level (v'' , J''), then, taking into account the sum-rule relation

$$\sum_{J'} \sum_{M'M''} S_{J'J''} = 2J'' + 1, \quad \sum_{v''} q_{v'v''} = 1, \quad (1.13)$$

we obtain

$$B_{mn} = \sum_{v'} \sum_{J'} B_{mnv'v''J'J''} = \frac{8\pi^3}{3h^2} |R_e^{nm}|^2. \quad (1.14)$$

If we confine ourselves to summation of the transition probabilities over J' only, i.e., in one electron-vibrational band, we obtain

$$B_{mn}^{v'v''} = \sum_{J'} B_{mnv'v''J'J''} = \frac{8\pi^3}{3h^2} |R_e^{nm}|^2 q_{v'v''}, \quad (1.15)$$

where $B_{mn}^{v'v''}$ is the Einstein coefficient for one vibrational band.

As a consequence of the dependence of the electron wave functions on the internuclear distance, neither the assumption that R_e^{nm} is independent of r nor relation (1.10) is rigorous. The validity of such an approximation can be theoretically estimated by calculating the dipole moments of the electronic transitions for different internuclear distances. The number of such calculations is small [2, 9-10]; on the other hand, it is customary to calculate the moments of the electronic transitions with the aid of approximate

electronic wave functions, assuming the equilibrium configurations of the molecules to be fixed. The first work in this direction was carried out by James and Coolidge [11] in connection with a study of the intensity distribution in the continuous emission spectrum of hydrogen. They obtained rather rapid variations of R_e with variation of the internuclear distance. The subsequent calculations [12-24] revealed a distinct dependence of the dipole moments of the transition on the internuclear distance for a number of other diatomic molecules.

A summary of all the theoretical calculations of dipole moments of electronic transitions in diatomic molecules, known to us at present and carried out for different internuclear distances, is contained in Table I. Recently calculated absolute oscillator strengths f for several electronic transitions in positive [13] and negative [23] molecular ions of hydrogen and in the LiH molecule [24], as functions of the internuclear distances, are shown in Fig. 1. The oscillator strength f is connected here with the dipole moment of the transition by the relation

$$f = \frac{8\pi^2 m \nu}{3 h e^2} |R_e^{nm}|^2, \quad (1.16)$$

and the internuclear distances r are expressed for all the transitions in terms of the radius a_0 of the first Bohr orbit. It is seen from Fig. 1 that in these transitions the moment of the electronic transition also varies strongly with r , although in the important internuclear-distance region this variation is not so strong, for example at $r = (2.6-4)a_0$ for the $1\Sigma^+ - 1\Sigma^+$ transition in the LiH molecule. We note that

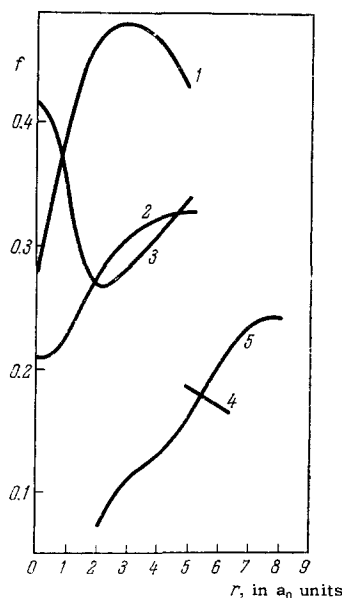


FIG. 1. Theoretical dependence of the oscillator strength on the internuclear distance for electronic transitions in diatomic molecules.

$$\begin{aligned} 1 - 3 - \text{H}_2^+ (1s\sigma - 2p\pi), (2p\sigma - 3d\pi), \\ (2p\pi - 3d\pi); \quad 4 - \text{H}_2^+ (2\Sigma_u^+ - 2\Sigma_g^+); \\ 5 - \text{LiH} (1\Sigma^+ - 1\Sigma^+). \end{aligned}$$

Table I. Summary of transition dipole moments calculated for different internuclear distances.

Molecule	Transition	Limits of r (in atomic units)	Reference
H ₂ , D ₂	$1s\sigma 2s\sigma^3\Sigma_g^- - 1s\sigma 2p\sigma^3\Sigma_u$	1.3—2.9	11
F ₂	$3,1\Pi_u - X^1\Sigma_g^+$	2.3—3	10
Cl ₂	$3,1\Pi_u - X^1\Sigma_g^+$	3.6—4.3	10
H ₂ ⁺	$2s\sigma - 2p\sigma$	0—9	12
	$1s\sigma - 2p\pi, 2p\sigma - 3d\pi,$ $2p\pi - 3d\pi$	0—5	13
	$1s\sigma - 3p\sigma, 1s\sigma - 4p\sigma$ $1s\sigma - 4f\sigma, 2p\sigma - 2s\sigma$	0—5	14
	$2p\sigma - 3s\sigma, 2p\sigma - 3d\sigma$ $2p\pi - 2s\sigma, 2p\pi - 3s\sigma$	0—5	15
	$2p\pi - 3d\sigma, 3d\pi - 3p\sigma$ $3d\pi - 4p\sigma, 3d\pi - 4f\sigma$	0—5	16
HeH ₂ ⁺	$1s\sigma - 2s\sigma, 1s\sigma - 3d\sigma$ $2s\sigma - 3d\sigma$	0—5	16
	$1s\sigma - 2p\pi, 2p\pi - 2s\sigma$ $2p\pi - 3d\sigma$	0—5	17
	$1s\sigma - 2p\sigma$ $2p\sigma - 2s\sigma, 2p\sigma - 3d\sigma$	0—10	18, 19
	$2p\sigma - 2p\pi$	0—5	18
C ₂	$3\Pi_u - 3\Pi_g$	2—3	20
Li ₂	$1\Sigma_g^+ - 1\Sigma_u^+$	4.5—5.5	21
	$1\Sigma_g^+ - 1\Pi_u$	4.5—5.5	21
Na ₂	$1\Sigma_g^+ - 1\Sigma_u^+$	4—7	22
H ₂ ⁻	$2\Sigma_u^+ - 2\Sigma_g^-$	4.9—6.3	23
LiH	$1\Sigma^+ - 1\Sigma^+$	2—9	24

these calculations are merely estimates and depend strongly on the accuracy of the employed wave functions and also owing to the approximate nature of the latter, on whether the dipole moments were calculated by means of the formula for the dipole length or for the dipole velocity. However, the results of these calculations show that the r -variations of the dipole moment of the transition cannot be disregarded.

As to the experiments, they usually agree better with the results of calculations made without the simplifying assumption that I_e is constant. Numerous recent comparisons of the Franck-Condon factors $q_{v'v''}$ with the experimentally measured transition probabilities have shown that exact satisfaction of the Franck-Condon principle is a rare exception. In most cases the dependence of the dipole moment of the transition on r results in appreciable changes in the distribution of the intensity over the bands of the systems.

Since exact electronic wave functions are unknown in most cases, the deviation from the Condon approximation is accounted for in calculations of the matrix elements R_{nm} for diatomic molecules by representing $R_e(r)$, on the basis of an analysis of theoretical and experimental results, by means of a power-law or exponential function of the interatomic distances. In this case the quantity

$$P_{v'v''} = \left| \int \Psi_{v'} R_e(r) \Psi_{v''} dr \right|^2 \quad (1.17)$$

gives, under certain assumptions concerning the

character of $R_e(r)$, the distribution of the intensity over the vibrational bands of the given system of bands when the Franck-Condon principle is fulfilled. Obviously, in the Condon approximation $R_e(r)$ is constant and the quantities $P_{v'v''}$ coincide, apart from a constant factor, with the Franck-Condon factors $q_{v'v''}$.

Schuler^[25] approximated $R_e(r)$ for the ${}^2\Sigma - {}^2\Pi$ transition of the OH radical by means of a polynomial, confining himself to the linear term

$$R_e(r) = (1 + \rho r). \quad (1.18)$$

In calculations with the aid of (1.17), he used the wave functions of the anharmonic oscillator. The coefficient ρ was determined by comparing the calculated and experimental transition probabilities. In an investigation of the distributions of the intensity in the band systems of the nitrogen molecule, Bates^[26] advanced the hypothesis that the dependence of R_e on r is weak for parallel types of transitions ($\Delta\Lambda = 0$). He calculated the relative vibrational probabilities $P_{v'v''}$ with the aid of Morse wave functions, assuming a linear dependence for $R_e(r)$. According to him, for perpendicular types of transitions ($\Delta\Lambda = \pm 1$), the character of the $R_e(r)$ dependence is indeterminable. Another variant of the calculation of the relative vibrational probabilities (assuming linear $R_e(r)$) was carried out by Poots^[27] for the second negative system of O₂⁺ bands. Manneback and Rahman^[28] obtained recurrence relations for the vibrational probabilities

in the harmonic approximation, for the case when the purely electronic transition probability depends linearly on the internuclear distance. In a subsequent paper^[29], a similar problem was solved with the aid of the wave functions of the harmonic oscillator for the case of a negative exponential $R_e(r)$ dependence.

Among the semi-empirical procedures for determining $R_e(r)$, the most widely used is an approximation having a very wide range of validity, proposed by Canadian astrophysicists^[7-9]. Its gist is that each band of the system is assigned some average internuclear distance $\bar{r}_{v'v''}$:

$$\bar{r}_{v'v''} = \frac{\int \Psi_{v',r} \Psi_{v'',r} dr}{\int \Psi_{v'} \Psi_{v''} dr}, \quad (1.18')$$

called the r -centroid, with the aid of which formula (1.17) can be rewritten in the form

$$P_{v'v''} = R_e^2(\bar{r}_{v'v''}) \left| \int \Psi_{n'} \Psi_{m''} dr \right|^2 = R_e^2(\bar{r}_{v'v''}) q_{v'v''}. \quad (1.19)$$

Equation (1.19) reflects the variations of the electronic moment of the transition for different bands of the system, and is a better approximation than the old form corresponding to the Franck-Condon principle. $P_{v'v''} = \bar{R}_e^2 q_{v'v''}$, where \bar{R}_e^2 is constant for the entire system of bands.

An analysis of the limits of applicability of the method of r -centroids has shown that relation (1.19) is a good approximation for a broad class of electronic transitions in diatomic molecules if $R_e(r)$ can be represented by means of a power-law or exponential function of the distances. In a recent paper^[262], an approximate formula was proposed for the relative transition probability $P_{v'v''}$; this formula is obtained by terminating the Taylor expansion of the moment of the electronic transition with the quadratic term. If experimentally measured probabilities $P_{v'v''}$ and calculated Franck-Condon factors $q_{v'v''}$ are available, it is possible to determine $R_e(r)$ by using (1.19). Since the results of the r -centroid method are valid only when the calculated $q_{v'v''}$ and the experimental intensities are sufficiently accurate, and also in view of the interest that attaches to these problems in themselves, let us examine in greater detail methods of calculating the factors $q_{v'v''}$ and measuring the experimental transition probabilities, before we discuss the available data on the $R_e(r)$ relations.

2. METHODS OF CALCULATING THE FRANCK-CONDON FACTORS

According to (1.10), a quantitative quantum-mechanical expression of the Franck-Condon principle is the fact that the probability of the vibrational transition is determined by a quantity $q_{v'v''}$, equal to the square of the overlap integral

$$q_{v'v''} = \left| \int \Psi_{v'} \Psi_{v''} dr \right|^2. \quad (2.1)$$

A classical treatment of this principle consists in the fact during the time of the electronic transition the nuclei do not have time to change their coordinates and momenta, and the oscillator stays for the greater part of the time at the turning points. In other words, if we consider the transitions on the potential-energy diagram, then the most intensive bands will correspond to vibrational levels whose ends on the potential curves of the upper and lower electronic states can be joined by means of a vertical line.

A detailed classical and quantum-mechanical description of the Franck-Condon principle, illustrated by numerous examples of the intensity distributions over the bands of diatomic molecules, can be found in several monographs^[3-6]. Investigations carried out during the last 30 years and devoted to the development of analytic and graphic methods of calculating the Franck-Condon factors are summarized in several review articles^[1, 7-9]. In view of the availability of the foregoing literature, we confine ourselves to the listing of the existing methods of calculating the Franck-Condon factors. We shall consider in greatest detail the domestic and foreign papers published in recent years and not included in the review^[1], where only literature prior to 1957 is covered.

To calculate the Franck-Condon factors it is necessary to substitute in (2.1) the values of the vibrational wave functions of the upper and lower states. The more accurate the analytic or numerical expressions for the wave functions in the integration interval, the more accurate will be the calculated Franck-Condon factors. The accuracy of the wave functions is determined in turn by the agreement between the employed potential curves and the true potential of the molecule, by the approximation used in the calculations, and by the reliability of the initial molecular constants. The closer the molecular oscillator model is to the true oscillations in the molecule, the more rigorously do the vibrational wave functions describe the behavior of the nuclei in the molecule, and the more accurate is $q_{v'v''}$. At the present time, the Franck-Condon factors are calculated with the aid of the following molecular potentials: harmonic, perturbed harmonic, "distorted" harmonic, Morse potential with different degrees of approximation, the Hulbert-Hirschfelder potential, and true potentials obtained on the basis of spectroscopic data. On going over from simple molecular models to more complicated ones, the accuracy of the results increases within certain range of quantum numbers, but at the same time the calculations become more cumbersome and laborious.

Among the rather crude models, even for small quantum numbers, is the harmonic approximation. In earlier work by Hutchisson^[30, 31], an analytic method was developed for estimating the overlap integral for linear-harmonic and for anharmonic oscillators of homonuclear molecules, respectively. Dunham^[32]

extended this method to include asymmetrical molecules. A large deviation of these probabilities from the experimental ones, one that increased rapidly with increasing vibrational quantum number, was observed for the second positive system of N_2 by Tawde and Patankar^[33]. In recent papers^[34,35] Tawde and his co-workers again returned to this question, reviewing the validity of Hutchisson theory as applied to asymmetrical molecules. Simple harmonic wave functions were used by Manneback^[36] to obtain recurrence relations for the Franck-Condon factors. Recently this method has been the subject of a number of Soviet and Indian investigations^[37-45]. Tawde and co-workers^[40-45] have demonstrated the equivalence of the expressions for the calculation of $q_{v'v''}$ in the theories of Hutchisson and Manneback, and obtained relations between the parameters of these two calculation methods. Since the Manneback method is the simpler and more convenient of the two, we propose to use it subsequently in the calculations of the Franck-Condon factors in the harmonic approximation.

In modifying the harmonic approximation to bring its solution closer to the solutions based on the Morse potential, Kivel, Mayer and Bethe^[46] also used integration of Hermite polynomials in calculating the factors $q_{v'v''}$ for the nitric oxide band systems. In a subsequent paper by this group^[47], the calculated $q_{v'v''}$ for the O_2 and NO bands by an approximate method, replacing the wave functions of the lower state by δ functions at the classical turning points. The same method was used by Soshnikov^[48] in a calculation of the optical absorption cross sections in the electronic bands of diatomic molecules. In the calculation of the integral absorption coefficients, French^[242] also took into account only those system bands located on the Franck-Condon parabola or near it. In^[249] the wave function for the continuous states of a bound-free transition of He_2 molecules was replaced by a δ function.

Bates^[49] published very useful two-function tables based on the use of the modified Hutchisson formula. For bands with vibrational quantum numbers $v' + v'' \leq 4$ and $v', v'' = 0$, $v' = 5$ and 6 , he gave in the harmonic approximation the values of $q_{v'v''}$ and the corrections for anharmonicity, reduced to two independent variables of the molecular constants. Related to these investigations is a new method of calculating the overlap integrals for the case of a harmonic oscillator, proposed by Ruamps^[50-52]. The simple form obtained by him by perturbation-theory methods for the wave functions of the anharmonic oscillator makes it possible to refine the Franck-Condon factor calculations. It is shown in^[53], with the BaO bands as an example, that the agreement between the theoretical and experimental data is increased by a factor of two when the anharmonicity is introduced. The eigenfunctions of the harmonic oscillator with a Gaussian per-

turbation were used to calculate $q_{v'v''}$ for the $HgCl$ band system^[250].

A graphic method of distorting the wave functions of the harmonic oscillator in order to bring them closer to the wave functions of the Morse potential was proposed by Pearse and Gaydon^[54] and used by them to calculate the intensities in the RbH band system. The gist of the method consists in plotting the values of the harmonic wave functions on the potential diagram in such a way that their principal maxima assume the same positions relative to the Morse potential curve. Further integration of the distorted vibrational wave functions is carried out graphically. In a number of papers, Pillow^[55-60] developed and improved this method, using it to calculate the Franck-Condon factors for a larger number of molecules. The disparity between the data of the latest work for CO and the results of the calculations on the basis of the Morse potential was noted in^[61]; This method was recently used to calculate $q_{v'v''}$ for the BaO bands^[62]. The method of distorted wave functions has not gained wide popularity both by virtue of its cumbersome calculations and by virtue of the intrinsic imperfection of the process of wavefunction distortion^[63]. However, the principle itself of the r_e -shift of the vibrational wave functions in modified form was used in a number of papers in which wave functions of the so-called "simplified" Morse potential were used.

In the last decade, many calculations of the Franck-Condon factors were made with the aid of the Morse potential function

$$U(r) = D_e [1 - e^{-\alpha(r-r_e)}]^2, \quad (2.2)$$

where

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}, \quad (2.3)$$

r_e is the equilibrium internuclear distance, and α is the constant. The Morse potential is a well-studied three-parameter function of the molecular constants, and describes the potential of the molecule satisfactorily. The Morse potential leads to an exact solution of the Schrödinger equation for the nuclear vibrations. The wave functions Ψ_v are expressed in terms of Laguerre polynomials, the integration of which, according to (2.1), involves basic computational difficulties, in which connection attempts were made to obtain approximate solutions. Analytic approximate methods of calculating the overlap integrals for the Morse oscillator were developed by Ta You-W^[63] and Bouigue^[64]. In^[63] the integrand was approximated by a Gaussian function and a laborious and insufficiently accurate integration procedure was used. The method of Ta You-Wu was used to calculate the overlap integrals for the $A^2\Pi_u - X^2\Pi_g$ band system of the O_2^+ ion^[65] and the Phillips bands of C_2 ^[66].

The most widely used, however, are the approximate methods of the Canadian astrophysicists. The

gist of their method of calculating the Franck-Condon factors, developed by Fraser and Jarman^[68] and called in the literature the method of "simplified" Morse potential or α -averaged Morse potential, is that the two Morse potentials are replaced by two new potentials which admit of an analytic estimate of the overlap integrals in simplified form. These new Morse potentials have the same parameters as the initial Morse potentials of the upper and lower states, with the exception of the coefficients α , which are the same for both new potentials and are equal to the arithmetic mean of α_i :

$$\alpha = \frac{\alpha_1 + \alpha_2}{2}.$$

With this simplifying assumption, it becomes possible to integrate (2.1) and to obtain simple formulas for the calculation of the Franck-Condon factors. The same authors proposed methods for improving the results with the aid of the r_e -shift^[69] and on the basis of using the first order perturbation theory^[70]. In these papers, and also in the preceding series of papers of the same school of Canadian researchers^[7-8, 71-77], these methods were used to calculate the probabilities of the vibrational transitions for 40 band systems of diatomic molecules, using first a desk calculator and then an electronic computer. The methods developed by them for calculating the Franck-Condon factors has been recently used extensively also by others^[43, 78-88].

Comparison of the results of the calculation by this approximate method with data of more accurate calculations, carried out in a number of previously listed papers, has shown that, in the best case, $q_{v'v''}$ accurate to 5-10% are attained for low quantum numbers v' , $v'' \leq 3$, and for values

$$\left| \frac{\alpha_1 - \alpha_2}{\alpha_1 + \alpha_2} \right| |r_{e1} - r_{e2}| \cdot 100\% \text{ \AA} \leq 0.1\% \text{ \AA}.$$

At larger values of these quantities, the distortion introduced in the potential curves by averaging the coefficients α becomes more noticeable, and the results of the α -averaging method differ little in accuracy from the methods using harmonic wave functions. The application of the r_e -shift to the data of the "simplified" Morse potential method improves the results very slightly, if at all.

Simultaneously with development of approximate methods on the basis of the Morse function, numerical integration of the wave functions of the Morse oscillator was carried out^[46, 61, 66, 84-80, 89-114, 243, 244, 253-260], starting with the paper by D. R. Bates^[26]. The fundamental difficulties arising when the Morse wave functions are integrated are due to the fact that the obtained solutions reduce to integrals that cannot be evaluated and are expressed in terms of alternating-sign series. Owing to progress in computational techniques and to the extensive use of high-speed electronic computers, these difficulties could be overcome.

The results of numerical integration of the Morse wave functions for several NO bands, carried out for comparison with the data obtained by integrating the harmonic wave functions, are given in^[46]. The first large table of Morse-type Franck-Condon factors for the Schumann-Runge band system of O₂ was obtained by Losev^[89] with the "Strela" electronic computer. The overlap integrals of the Morse wave functions for the Phillips bands of C₂ were calculated graphically in^[66]. Nicholls^[90-99, 255-260] used an electronic computer to tabulate, in steps of 0.01 Å, the vibrational wave functions of the electronic states of a number of molecules, assuming that the potentials of these states are given by Morse functions. He carried out with the aid of these wave functions a large series (approximately 85 electronic transitions) of calculations of $q_{v'v''}$, greatly extending thereby the range of the vibrational quantum numbers v' and v'' , which reach ~ 20 for some individual transitions. The Franck-Condon factors obtained by numerical integration of the Morse vibrational wave functions for bands with small quantum numbers v' and v'' in transitions of certain metal oxides were obtained by Indian scientists^[84-85, 103-106, 143-144] and in^[100, 101, 253] for ionization transitions.

Ortenberg^[80, 107-108] calculated the Morse factors $q_{v'v''}$ for more than 25 transitions in different molecules, using a single program suitable for an arbitrary electronic transition in a diatomic molecule, first using the high speed "Strela" computer^[80] and then using the M-20^[107-108]. In the latter case the calculation was carried out with the maximal number of 18 digits in all the operations, thus overcoming the difficulties connected with the alternating signs of the obtained solutions, and ensuring reliable summation for $v' + v'' \leq 15$. Comparison of these results with the data of the above-described calculation methods for $q_{v'v''}$ has shown that the use of approximate methods for calculating Franck-Condon factors is limited. Childs^[109] obtained for the polynomials, with the aid of a generating function, recurrence relations that made it possible to calculate the overlap integrals for the Morse wave functions, and calculated $q_{v'v''}$ for four systems of N₂, NO, and CH bands. The Franck-Condon factors of the molecules OH, OD, and CS, obtained by numerical integration with an electronic computer using the Morse potential curves, were published by Felenbok^[110-111, 252].

In recent papers, Ory et. al.^[112-114] calculated the Morse factors $q_{v'v''}$ with an electronic computer, using an integration interval of 0.01 Å for O₂^[112] and NO^[113, 114], for a wide variation of v' and v'' , reaching a maximum value $v' = 31$. The calculations were simplified by using recurrence relations for the hypergeometric functions in terms of which the Laguerre polynomials are expressed. In the case of the Schumann-Runge O₂ bands, for large v' , they observed deviations from the classical expression of

the Franck-Condon principle, connected with the complicated structure of the upper state and the large difference Δr_e . In addition, owing to the use of the Morse potential coinciding with the true potential curve better than the Morse curve used by Nicholls, the values of $q_{v'v''}$ for the upper vibrational levels differed from the data of Nicholls^[90] by one order of magnitude. A noticeable isotopic effect was observed in the Morse Franck-Condon factors obtained^[67,254] for a large number of electronic transitions of neutral and ionized molecules of stable isotopes of H_2 , N_2 , NO , O_2 , CO , and HCl , wherein an appreciable difference was observed in the reduced mass of the molecules of the isotopes and the values of the equilibrium states.

To attain in the calculation of $q_{v'v''}$ a larger accuracy than afforded by the Morse potential in the case of large quantum numbers, Wyller^[115-116] used, in computer calculations, the potential function in the form given by Hulbert and Hirschfelder:

$$U(r) = D_e \{ [1 - e^{-\alpha(r-r_e)}]^2 + (\alpha^3 (r-r_e)^3 e^{-2\alpha(r-r_e)} \times [1 + b\alpha(r-r_e)]) \}, \quad (2.4)$$

where the parameters entering in the formula are expressed in terms of the spectroscopic constants ω_e , $\omega_e x_e$, B_e , α_e , and D_e . To construct the vibrational wave functions, he used the WKB method, which Ta You-Wo^[63] previously proposed to apply to this problem. The same method was used by Biberman and Yakubov^[117], who developed a very convenient approximate procedure for calculating the Franck-Condon factors, applicable for large vibrational quantum numbers, provided the true potential functions for these quantum numbers are well described by Morse potentials. Near the turning points, where the quasi-classical solutions experience discontinuities, they approximate the exact Morse wave functions by suitable sections of Hermite functions. Subsequently this method was used to carry out several concrete calculations^[118-120]. Different variants of the WKB method as applied to calculations of $q_{v'v''}$ for diatomic molecules are considered in^[121].

With the aid of the Petrashen'-Fock generalized quasi-classical method, Zhirnov^[122] obtained approximate solutions of the Schrödinger equation with a Morse potential; these solutions were continuous over the entire interval of variation of the internuclear calculations (including also the turning points), and can be relatively simply expressed in terms of Hermite functions and are more suitable for calculations^[151] of the factors $q_{v'v''}$ for arbitrary values of the vibrational quantum numbers. In his subsequent paper^[123] he constructed by the same method the vibrational wave functions corresponding to the true potential-energy curves of diatomic molecules for both the discrete and the continuous spectrum. The factors $q_{v'v''}$ were calculated in^[124] with an electronic computer, by the WKB method, for two transi-

tions in the H_2 molecule, assuming that the potential functions have the form given by Hulbert and Hirschfelder.

The three-parameter Morse curve (2.2) and the five-parameter Hulbert-Hirschfelder curve (2.4) are the most accurate analytic representations of the molecular potentials. Even they, however, differ from the true potentials of the molecules, especially at large vibrational quantum numbers. Recently, true potential curves were recently constructed for the electronic states of many molecules on the basis of spectroscopic data by the method of Klein-Dunham and by the method of Rydberg-Klein-Rees (RKR), improved by Vanderslice (see, for example^[139]). It was shown that the turning points of the true molecular oscillators are shifted relative to the turning points of the Morse and Hulbert-Hirschfelder oscillators, and the shift increases rapidly with increasing vibrational quantum number.

Sometimes the agreement between the analytic and the true potentials is improved by using in (2.2), not the dissociation energy given by (2.3), but by its experimental value. In this case one speaks of a quasi-Morse potential function. By way of an example, Fig. 2 shows for the ground state $X^2\Pi_{3/2}$ of the NO molecule the true potential curve, the Hulbert-Hirschfelder curves, the Morse curve, and the quasi-Morse potential curve, for which the dissociation energy was taken from the thermochemical tables. It is seen that the right-side branches of the curves differ appreciably, especially for the Morse potential. Since this deviation, as already indicated, can lead to serious errors in the calculation of $q_{v'v''}$ the efforts of the researchers were aimed at obtaining vibrational wave functions for the true potential curves.

An attempt was made in^[125-128] to refine the calculations of the Franck-Condon factors for several molecules in this way. The method proposed in^[126]

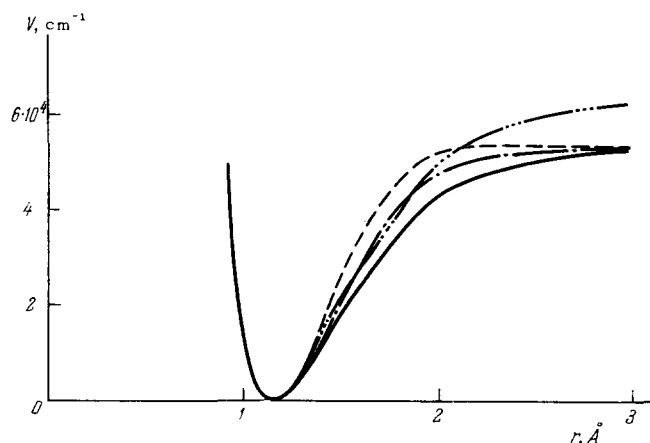


FIG. 2. Curves of the potential energy of the state $X^2\Pi_{3/2}$ of the NO molecule, obtained by different methods. - . . . - Morse curve; - - - Hulbert-Hirschfelder curve; - . - Rydberg-Klein-Rees curve; — quasi-Morse curve.

consists in dividing the true potential curve, obtained by the RKR method, into a number of segments described by quadratic trinomials, and use these segments to calculate the quasi-classical wave functions. It is noted that the difference between the quasi-classical wave function, corresponding to the true potential, and the Morse wave function for several vibrational levels of C_2 is that expected from the forms of the true and Morse potentials. In^[127], the Morse wave functions of the ground state and the quasi-classical vibrational wave functions of the excited state, obtained on the basis of true RKR potentials analytically and by numerical means, were used to calculate the Franck-Condon factors of the RbH system. The factors $q_{v'v''}$ were similarly calculated for the band systems of C_2 in^[128].

The results of the calculation of the vibrational wave functions for the molecular ion N_2^+ were reported by French workers in^[129-131]. We call attention to^[131], in which the true potential curve was constructed on the basis of experimental terms by successive approximations. This potential curve was used to find the approximate wave function when solving the corresponding Schrödinger equation with an analog computer. In^[132] it is noted that the solutions of the Schrödinger equation obtained with the analog computer agree with the quasi-classical wave functions.

Jarmain^[133-135] developed a method for calculating the Franck-Condon factors for the Klein-Dunham potential-energy curves, and employ this method for electronic computation of a series of Schumann-Runge bands of O_2 . Individual deviations of the results from the Morse factors $q_{v'v''}$ were observed, amounting for example to 30% for the (8,4) band.

Using a numerical method, described in^[137], for solving the radial Schrödinger equation, the authors of^[138-140,245,251] used an electronic computer to calculate the Franck-Condon factors on the basis of true potentials with account taken of the vibrational-rotational interaction for the band systems of I_2 , Na_2 , RbH , and N_2 . They, too, observed noticeable deviations from the Morse factors $q_{v'v''}$. It was noted that, owing to the rapid oscillations of the vibrational wave functions for large v' and v'' , a shift in potential by only 0.002 \AA alters appreciably the calculated values of $q_{v'v''}$. It is shown that neglect of the vibrational-rotational interactions results in an error of $\pm 10\%$ for the rotational number $J = 34$ and $\pm 20\%$ for $J = 113$. The influence of the vibrational-rotational interaction on the transition probabilities for the radical OH was considered in^[141,267]. The same method^[137], of directly solving with an electronic computer the radial Schrödinger equation for an arbitrary potential function, was used by Spindler^[142] in calculations of $q_{v'v''}$ for the CN and C_2 bands. In estimating the sensitivity of the calculations to small changes in the values of the turning points of the potential functions

(i.e., to the accuracy of the calculation of the RKR curves), it was found that an error of 0.1% for the turning point of the zeroth vibrational level of the potential curve of the upper state $A^2\Pi$ leads to a 1% error in the values of $q_{v'v''}$ of the (0, 0) band of the red system of CN.

In a recent paper, Flynn et al.^[143] present extensive tables of the Franck-Condon factors for the γ ($v'' \leq 36$, $v' \leq 12$) and β ($v'' \leq 33$, $v' \leq 12$) bands of NO, obtained on the basis of potential functions constructed by the RKR method. Owing to the use of continuous solutions of the Schrödinger equation, obtained with an analog computer, the difficulties of numerical integration, connected with the oscillator nature of the wave functions, especially at large quantum numbers, are eliminated. It is interesting that for the (0, 0) band of the γ system, the factor q_{00} differs from the Morse factor by 40%, in spite of the agreement between the true and the Morse potential curves for the zero levels. The authors attribute this to the fact that sections of the wave functions, located beyond the classical turning points for the given level, are altered by the difference in the potential functions that lie above this level. Because of this, the agreement between the approximate and true potentials for the given vibrational level cannot serve as an indicator of the accuracy with which the wave functions and the factors $q_{v'v''}$ have been calculated. The extent to which the results of the calculations of $q_{v'v''}$ are sensitive to the form of the potential curve can be seen in Fig. 3, where a comparison is presented, for the progression $v' = 7$, of the factors $q_{v'v''}$ from the discussed paper^[143] and the Morse Franck-Condon factors^[112] for the transition $A^2\Sigma - X^2\Pi_{3/2}$. The different potential functions of lower state for this transition of NO were compared in Fig. 2.

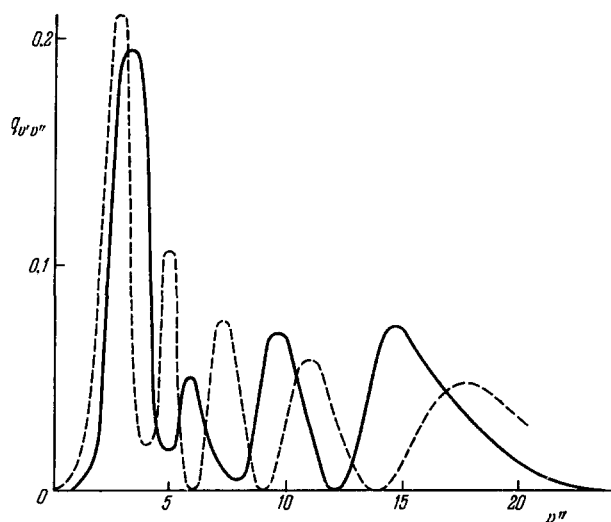


FIG. 3. Dependence of the factors $q_{v'v''}$ on the vibrational number v'' for the progression $v' = 7$ of the γ system of NO. Solid — true potentials; dashed — Morse potentials.

Table II. Electronic transitions in diatomic molecules, for which the Franck-Condon factors were calculated.

Molecule	System	Electronic transition	Reference	Calculation method
AlO		$A^2\Sigma^+ - X^2\Sigma^+$	92 103, 246	g) g)
B ₂		$A^3\Sigma_u^- - X^3\Sigma_g^-$	8	f)
BH		$B^1\Sigma^+ - A^1\Pi$	8	f)
BN		$A^3\Pi - X^3\Pi$	8	f)
BO	α -system	$A^2\Pi_i - X^2\Sigma^+$	8, 75	f)
	β -system	$B^2\Sigma^+ - X^2\Sigma^+$	8	f)
	Intercombination	$B^2\Sigma^+ - A^2\Pi_i$	8	f)
BaO		$A^1\Sigma - X^1\Sigma$	62 80 80	l) b, f)
BeO	Blue-yellow	$B^1\Sigma^+ - X^1\Sigma^+$	108 80 80 75 87	g) b) f) f) f)
C ₂	Swann	$A^3\Pi_g - X^3\Pi_u$	42 42 42 8 107 128 142 260	c, d) l) g) f) g) f, h, k) l) g)
	Mulliken	$d^1\Sigma_u^+ - a^1\Sigma_g^+$	8 260	f) g)
	Delandre-Asambuch	$c^1\Pi_g - b^1\Pi_u$	8 260	f) g)
	Phillips	$b^1\Pi_u - a^1\Sigma_g^+$	8 107 66 142 260	f) g) g) l) g)
	Fox-Herzberg	$B^3\Pi_g - X^3\Pi_u$	8 128 260	f) f, h, k) g)
	Ballik-Ramsay Freimark	$A^3\Sigma - X^3\Pi$ $e^1\Sigma_u^+ - b^1\Pi_u$	260 260	g) g)
CH	$\lambda = 3900 \text{ \AA}$	$B^2\Sigma^g - X^2\Pi$	109	g)
	$\lambda = 4300 \text{ \AA}$	$A^2\Delta - X^2\Pi$	109	g)
CH ⁺		$A^1\Pi - X^1\Sigma^+$	8, 75	f)
CN	Violet	$B^2\Sigma^+ - X^2\Sigma^+$	37 98 142	c) g) l)
	Red	$A^2\Pi_i - X^2\Sigma^+$	98 116 142	g) h, j) l)
CO	Fourth positive	$A^1\Pi - X^1\Sigma$	37 76 107 96 120	c) f) g) g) g, h)
	Third positive	$b^3\Sigma^+ - a^3\Pi_r$	75 107	f) g)
	Angstrom	$B^1\Sigma^+ - A^1\Pi$	75 107	f) g)
	Cameron Hopfield-Birge b Hopfield-Birge a Triplet	$a^3\Pi - X^1\Sigma^+$ $b^3\Sigma^+ - X^1\Sigma^+$ $a'^3\Sigma^+ - X^1\Sigma^+$ $a^3\Pi - a^3\Pi$	96 96 96 60 125 61	g) g) g) l) g, k) g)
		(CO) $X^1\Sigma - (\text{CO}^+) X, A, B$	100, 101 67	g) g, r)
CO ⁺	Tails of comets First negative	$A^1\Pi_i - X^2\Sigma^+$ $B^2\Sigma - X^2\Sigma$	93 37 93 96	g) c) g) g)
CS	Balde-Johnson	$B^2\Sigma^+ - A^1\Pi_i$ $A^1\Pi - X^1\Sigma$	93 98	g) c)
CaH		$A^2\Pi - X^2\Sigma$	252 80 80	g) b) f)
CaO	Second infrared	$1\Sigma^+ - 1\Sigma$	108 151	g) h)
CrO		$A - X$	105	g)
H ₂	Lyman	$1\Sigma_u^+ - 1\Sigma_g^+$ $1\Pi_u - 1\Sigma_g^+$	124 257 124	h, j) g) h, j)

Table II. (Cont'd)

Molecule	System	Electronic transition	Reference	Calculation method	
He ₂	Werner	$D^1\Pi_u - X^1\Sigma_g^+$	67	g, r)	
		$(H_2) X^1\Sigma_g^+ - (H_2^+) X^2\Sigma_g^+$	253	g)	
			67	g, r)	
		$(HD) X^1\Sigma_g^+ - (HD^+) X^2\Sigma_g^+$	253	g)	
		$(D_2) X^1\Sigma_g^+ - (D_2^+) X^2\Sigma_g^+$	253	g)	
			67	g, r)	
		$(HCl) X^1\Sigma^+ - (HCl^+) X^2\Pi_z$	67	g, r)	
		$(HCl) X^1\Sigma^+ - (HCl^+) A^2\Sigma^+$	67	g, r)	
		$A^1\Sigma_u^+ - X^1\Sigma_g^+$	249	g, n)	
			250	b)	
			97	g)	
			138-140, 251	l)	
		LaO	Yellow-green	$B^2\Sigma - X^2\Sigma$	44
	108			g)	
Red	$A^2\Pi_{1/2, 3/2} - X^2\Sigma$		108	g)	
Li ₂	Red	$A^1\Sigma_u^+ - X^1\Sigma_g^+$	119	g, h, b)	
	Green	$B^1\Pi_u - X^1\Sigma_g^+$	119	g, h, f)	
MgH		$A^2\Pi - X^2\Sigma$	80	b)	
			80	f)	
MgO	Mulliken	$B^1\Sigma - X^1\Sigma$	39	c)	
			82	f)	
			80	b)	
MgO	Mulliken	$B^1\Sigma - A^1\Pi$	80	f)	
			243	g)	
			108	g)	
N ₂	Second positive	$C^3\Pi_u - B^3\Pi_g$	92	g)	
			91	g)	
			245	l)	
	First positive	$B^3\Pi_g - A^3\Sigma_u^+$	254	g, r)	
			91	g)	
			254	g, r)	
			109	g)	
			245	l)	
	Vegard-Kaplan		$A^3\Sigma_u^+ - X^1\Sigma_g^+$	91	g)
				254	g, r)
				96	g)
				245	l)
		Lyman-Birge-Hopfield	$a^1\Pi_g - X^1\Sigma_g^+$	96	g)
			245	l)	
Birge-Hopfield	$b^1\Pi_u - X^1\Sigma_g^+$	254	g, r)		
		96	g)		
	$X^1\Sigma_g^+ - C^3\Pi_u$	96	g)		
Gaydon-Green	$^3\Sigma - ^3\Pi$		245	l)	
			99	g)	
			96	g)	
	$(N_2) X^1\Sigma_g^+ - (N_2^+) X^2\Sigma_g^+$	91, 96	g)		
		67	g, r)		
	$(N_2) X^1\Sigma_g^+ - (N_2^+) A^2\Pi$	91, 96	g)		
		67	g, r)		
	$(N_2) X^1\Sigma_g^+ - (N_2^+) B^2\Sigma$	91, 96	g)		
		67	g, r)		
	$(N_2) X^1\Sigma_g^+ - (N_2^+) B^3\Pi_g$	96	g)		
	$(N_2) X^1\Sigma_g^+ - (N_2^+) ^2\Pi_g$	96	g)		
	$(N_2) X^1\Sigma_g^+ - (N_2^+) C^3\Sigma^+$	96	g)		
	N ₂ ⁺	Meinel	$A^3\Pi_u - X^2\Sigma_g^+$	91	g)
			254	g, r)	
First negative		$B^2\Sigma_u^+ - X^2\Sigma_g^+$	91	g)	
			131	o)	
			254	g, r)	
Second negative Genin-d'Incan		$C^2\Sigma^+ - X^2\Sigma^+$	96	g)	
		$^2\Pi_g - A^2\Pi_u$	94, 96	g)	
	$D^2\Pi_g - A^2\Pi_u$	129			
NO	β -system	$B^2\Pi - X^2\Pi$	254	g, r)	
			75	f)	
			46	a)	
			107	g)	
			92, 256	g)	
			112	g)	
			254	g, r)	
	γ -system	$A^2\Sigma - X^2\Pi$	143	l)	
			75	f)	
			46	a)	
			107	g)	
			92, 256	g)	
			112	g)	
	254	g, r)			
	143	l)			
	75	f)			
	46	a)			
	107	g)			
	92, 256	g)			
	112	g)			
	254	g, r)			
	143	l)			

Mole- cule	System	Electronic transition	Reference	Calcula- tion method	
	δ -system	$C^2\Pi - X^2\Pi$	114 256 254	g) g) g, n)	
	ϵ -system	$D^2\Sigma^+ - X^2\Pi$	114 256 254	g) g) g, r)	
	Ogawa 1	$B', ^2\Delta - B^2\Pi$	256	g)	
	Ogawa 2	$b^4\Sigma - a^4\Pi$	109 256	g) g)	
	β' -system	$B', ^2\Delta - X^2\Pi$	256	g)	
	γ' -system	$E^2\Sigma^+ - X^2\Pi$	256	g)	
	Fest 1	$D^2\Sigma^+ - A^2\Sigma^+$	256	g)	
	NO	Fest 2	$E^2\Sigma^+ - A^2\Sigma^+$	256	g)
		'M' bands	$a^4\Pi - X^2\Pi$	256 254	g) g, r)
	Na ₂		(NO) $X^2\Pi - (NO^+) X, A$	100, 101	g)
	O ₂	Schumann-Runge	$B^3\Sigma_u^- - X^3\Sigma_g^+$	67	g, r)
139				k)	
47				n)	
8				f)	
89				g)	
90				g)	
96				g)	
113				g)	
136				g, l)	
118				g, h)	
133-135				k)	
254	g, r)				
Herzberg I	$A^3\Sigma_u^+ - X^3\Sigma_g^-$	259 254	g) g, r)		
Herzberg II	$C^1\Sigma_u^- - X^3\Sigma_g^-$	259	g)		
Herzberg III	$D^3\Delta_u - X^3\Sigma_g^-$	259	g)		
Chamberlain	$D^3\Delta_u - a^1\Delta_g$	259	g)		
Broida-Gaydon	$A^3\Sigma_u^+ - b^1\Sigma_g^+$	259	g)		
Noxon	$b^1\Sigma_g^+ - a^1\Delta_g$	259	g)		
Atmospheric	$b^1\Sigma_g^+ - X^3\Sigma_g^-$	259 254	g) g, r)		
Infrared atmos- pheric	$a^1\Delta_g - X^3\Sigma_g^-$	259 254	g) g, r)		
		$(O_2) X^3\Sigma_g - (O_2^+) X, a, A, b$	100, 101	g)	
			67	g, r)	
O ₂ ⁺	First negative	$b^4\Sigma_g^- - a^4\Pi_u$	258	g)	
	Second negative	$A^2\Pi_u - X^2\Pi_g$	65 75 258 254	m) f) g) g, r)	
OD	Violet	$A^2\Sigma^+ - X^2\Pi$	111	g)	
OH			40	c, d)	
			8	f)	
			111, 255	g)	
			141	p)	
			110	g)	
PbO			$B^2\Sigma^+ - A^2\Sigma^+$	8	f)
			$D - X^1\Sigma^+$	8	f)
			$A - X^1\Sigma^+$	8	f)
PN			$A^1\Pi - X^1\Sigma^+$	88	f)
RbII			$1\Sigma - 1\Sigma^-$	27	g, h, l)
ScO	$A^2\Pi - X^4\Sigma$	139	k)		
	$B^2\Sigma - X^4\Sigma$	138	g)		
SH	$A^2\Sigma^+ - X^2\Pi_j$	118	g)		
SD	$A^2\Sigma^+ - X^2\Pi_j$	75	f)		
SiN	$B^2\Sigma^+ - X^2\Sigma^+$	75	f)		
SiO	$B^2\Sigma^+ - X^2\Sigma^+$	102	g)		
	$A^1\Pi - X^1\Sigma^+$	77	f)		
SrO	$A^1\Sigma - X^1\Sigma$	92	g)		
		92	g)		
TiO	α -system	$C^3\Pi - X^3\Pi$	80 80 104 106	f) g) g) g)	
VO	γ -system	$A^3\Delta - X^3\Pi$ $A^2\Delta - X^2\Delta$	80 83 80 92	g) f) g) g)	
			106, 244	g)	

Table II (Cont'd)

Mole- cule	System	Electronic transition	Reference	Calcula- tion method
YO	Blue-yellow	$B^2\Sigma - X^2\Sigma$	80	g)
ZrO	Orange	$A^2\Pi - X^2\Sigma$	108	g)
	α -system	$C^3\Delta - X^3\Delta$	80	f)
	γ -system	$A^3\Phi - X^3\Delta$	80	g)
			80	f)
			80	g)

a) Harmonic approximations; b) method of perturbation of harmonic wave function; c) calculation by Manneback formula; d) calculations by Hutchisson's formulas; e) method of distorted wave functions; f) method of simplified Morse potential; g) integration of wave functions of the Morse potential; h) quasi-classical wave function; j) Hulbert-Hirschfelder potential function; k) Klein-Dunham potential curves; l) Rydberg-Klein-Rees potential curve; m) approximate method based on Morse potential; n) δ -like wave functions of lower state; o) Morse potential curve deformed in accord with spectroscopic data to bring it close to the true curve; p) allowance for vibrational-rotational interaction with Morse-Pekeris potential; r) calculation carried out for isotopic molecules.

The evolution of the methods of calculating the Franck-Condon factors, described in this section, illustrates how computers make it possible to carry the solution of the problem through to conclusion. At the present time the problem is to include as many transitions of diatomic molecules in the calculations of the values of $q_{v'v''}$ on the basis of the true potentials, and also to refine and improve the available methods of constructing the true potential curves.

When studying the character of the dependence of the series of the Franck-Condon factors on the molecular parameters, it is useful to have three-dimensional representations of $q_{v'v''}$, in which the vibrational quantum numbers v' and v'' are given as independent variables. Such three-dimensional $q_{v'v''}$ surfaces are given in [80, 97, 144]. The geometric loci of the most intense bands in the Franck-Condon factor tables, or the so-called Condon parabolas, were investigated again in two recent papers by Nicholls [145, 146]. He obtained equations for the connection between v' and v'' for the main and secondary Condon parabolas. Interpolation curves for the calculation of the factors $q_{v'v''}$ are the subject of his papers [147, 148]. He obtained with the aid of the interpolation methods the Franck-Condon factors for a large number of systems of bands of air molecules and for a carbon-air mixture [150]. A table in the review [1] presents the electron-vibrational systems of the bands of diatomic molecules, for which the relative vibrational transition probabilities were theoretically calculated. We present a supplement to this table based on material published since [1], bringing the review on the calculations of the Franck-Condon factors to date up to 1965. It is characteristic that our table II, which reflects work done on the calculation of $q_{v'v''}$ during the last seven years, is larger than the table of the review [1], in which the results are summarized for a much larger time interval. (Osc No. 1) records the signals from photomultipliers 2 and 3, and is used to measure the velocity of

the incident shock wave; the second oscilloscope (Osc No. 2) records a signal proportional to the emission of the gas in the wavelength interval from $\lambda_1 = 5090 \text{ \AA}$ to $\lambda_2 = 5170 \text{ \AA}$ (bands (0, 0), (1, 1), (2, 2) of the Swann system). This signal is produced by a photoelectric attachment of the spectrograph (ISP-51, No. 1), which receives radiation through the end window of the LPC. The spectrograph ISP-51 No. 2 serves to obtain the glow spectrograms. The drum-type photographic camera PC records the picture of the gas flow when the shock wave is reflected from the end. In particular, the photographic records make it possible, knowing the sweep rate (ω), to set a definite depth of the radiating layer of gas behind the reflected wave in correspondence with each point on the gas-glow oscillogram. It is useful to note that when the emitting layer has a small optical thickness, the growth of the intensity with time, recorded by the oscillograph, is linear [160]. This property of such an arrangement of the apparatus is very valuable and favorably distinguishes this procedure from an arrangement in which the radiation to be measured by photometry is viewed not through an end window but through a side window in the LPC. In the latter case, the question of presence or absence of reabsorption in the source remains open and calls for additional research. After the experiment was performed, the sensitivity of the photoelectric installation (ISP-51 No. 2 plus a photomultiplier) was calibrated against emission from a standard comparison source—band lamp BL, modulator M, and rotating mirror Mir.

Such are the typical operating conditions when a shock tube is used as a spectroscopic radiation source. Similar investigations are described in [161-163, 271-273]. The use of the emission procedure is especially advantageous in the study of transitions that do not include the ground-state level of the molecule, for example the first and second positive systems of N_2 . In the study of transitions that include the ground level, it is more advantageous to use in most

cases an absorption procedure.

The absorption procedure is free, to a considerable degree, from the shortcomings of the procedure considered above. In particular, there is no need for such high temperatures as in the emission method. Let a flux $I_0(\nu) d\nu$ be incident on a layer of absorbing gas and let it pass a distance l in the absorbing substance. Then in the case of weak absorption ($K_\nu l \ll 1$) we have

$$A \equiv \int \left(1 - \frac{I_l(\nu)}{I_0(\nu)}\right) d\nu = \frac{\pi e^2}{m_0 c} l f_{mn} N_n. \quad (3.1)$$

An experimental determination of the total absorption A makes it possible to calculate $f_{mn} N_n$ from (3.1). A shortcoming of this method is, first, the need for verifying the fulfillment of the condition $K_\nu l \ll 1$ and, second, the low accuracy of the absorption experiment if $K_\nu l \ll 1$.

The extension of the latter method to include the case of large optical thicknesses yields f_{mn} by a method completely free of the foregoing shortcomings and makes it possible to operate with large optical thicknesses of gases. This method turns out to be especially convenient in the case of molecular spectra corresponding to transitions that include the ground state of a molecule.

From (1.4) and (1.12) we obtain

$$\int K_\nu d\nu = \frac{8\pi^3}{3hc} N_{mv'j''} v_{mnv''} v' j'' |R_e^{nm}|^2 q_{v'v''} \frac{S_{j'j''}}{2j'+1}. \quad (3.2)$$

Thus, to determine $|R_e|^2$ from (3.2) it is necessary to measure experimentally $\int K_\nu d\nu$ for at least one rotational line in the absorption spectrum of the gas, and to know $N_{mv''j''}$, which in the case of thermal equilibrium is determined from the Boltzmann formula. Using (3.2), we can obtain in principle $|R_e^{nm}|^2$ by measuring $\int K_\nu d\nu$ for only one rotational line. However, if the bands corresponding to different vibrational transitions (v' , v'') can be separated in the spectrum and measured individually, then one can use simpler relations and obtain higher accuracy. Using (1.4) and (1.14), and replacing $N_{Mv''j''}$ by means of Boltzmann's formula, we obtain for the entire band

$$\int_{v'v''} K_\nu d\nu = \frac{8\pi^3 \nu}{3hc} \frac{N_0}{Z_{el} Z_{vib}} e^{-\frac{E_{el} + E_{vib}}{kT}} |R_e^{nm}|^2 q_{v'v''}. \quad (3.3)$$

With the aid of (3.3) we can calculate $|R_e^{nm}|^2$ by measuring $\int K_\nu d\nu$ for the entire electron-vibrational band.

The advantage of this method is that in this case it is not necessary to have such high temperatures as in the emission method, especially if m (the lower electronic state of the transition) is the ground state of the molecule. Another important methodological simplification (compared with emission) is that it is no longer necessary that the geometrical factors in the registration of the radiation from the investigated and standard sources be equal, thus, eliminating the

danger of serious methodological errors. A shortcoming of this method is the need for an additional (transilluminating) continuous-spectrum source, and also the need for taking into account the influence of the apparatus function of the instrument on the measured values of $\int K_\nu d\nu$. The numerical value of this quantity, obtained with a real spectral instrument, depends on the apparatus function^[164-165] and turns out to be underestimated. Failure to take this factor into account in the older measurements has frequently led to serious errors^[166].

In the post-war years Wilson and Wells developed a so-called "extrapolation procedure" for eliminating the influence of the apparatus function^[167], the gist of which consists in the following. One considers an integral absorption factor

$$\left\{ \int K_\nu d\nu \right\}_{v'v''} \equiv \alpha_{v'v''} \equiv \frac{1}{pl} \int \ln \frac{I_0 \nu}{I_\nu} d\nu. \quad (3.4)$$

The experiment yields not the true value of $\alpha_{v'v''}$, but the observed value $\alpha''_{v'v''} < \alpha_{v'v''}$. Wilson and Wells^[167] have shown that

$$\lim_{pl \rightarrow 0} \alpha''_{v'v''} = \alpha \quad (3.5)$$

under the condition that the dependence of K_ν on ν can be neglected within the limits of $\varphi(\nu)$ (i.e., $K_\nu = \text{const}$ over the width of the apparatus function). In the practical realization of the procedure it is necessary to calculate

$$B \equiv \int \ln \left(\frac{J_{0\nu}^{\text{obs}}}{J_{\nu}^{\text{obs}}} \right) d\nu = \alpha' pl \quad (3.6)$$

and to plot the dependence of B on pl . As the values of pl decrease, the obtained values of α' continuously increase (α' represents in this case the slope of the extrapolation curve), until $\alpha' = \text{const} \equiv \alpha$, i.e., the true value not distorted by the influence of the apparatus function, is obtained at low values of pl .

3. EXPERIMENTAL METHODS OF MEASURING TRANSITION PROBABILITIES

For decades, the classical sources used for the measurement of atomic transition probabilities were the electric arc and the so-called King oven. The electric arc between filled carbon electrodes (containing the investigated element) was used to measure the transition probabilities of many atomic lines. The thermodynamic equilibrium called for by the conditions of the method was observed many times in an arc discharge at atmospheric pressure, and is regarded now as self-evident. This consideration, however, is not absolute in character: thus, for example, it has been observed in^[153] that an arc burning in He and in Ar is not in equilibrium if the discharge current is sufficiently large.

Among the shortcomings of such a source are the following: 1) Spatial inhomogeneity. If this inhomogeneity has an axially-symmetrical character (this is

far from always the case), then the true distribution of the emitters in the discharge can be revealed by using the transverse-spectrum procedure with subsequent processing by the method of Abel integrals^[153]. 2) Temporal and spatial instability—"running" of the arc. 3) Contamination of the discharge plasma by the electrode material. 4) Finally, the high temperature of the arc discharge ($> 6,000^\circ\text{K}$), which prevents a study of many diatomic molecules having a low dissociation energy. In^[154] a somewhat modified arc discharge was proposed, in which the shortcomings mentioned in items 2 and 3 are eliminated, and which is axially stabilized by a current of the investigated gas. The investigated gas is drawn out through annular channels surrounding water-cooled bulky metallic electrodes. Such an arc discharge in pure nitrogen was used in^[155] to measure the transition probabilities for the first positive system of N_2 .

The already mentioned King oven was successfully used in various modifications for the investigation of emission and absorption of light by either atoms (see, for example^[156]) or molecules, but has been rarely used of late in view of the large complexity and many specific difficulties (not the least among which is the condensation of the investigated substances on the observation windows).

Recently a new radiation source was developed, which is sufficiently flexible and universal, namely a shock tube. As is well known^[157-158], a shock-tube can be used for adiabatic heating of gas samples under thermal conditions. The samples are sufficiently homogeneous in this case, and the parameters of the gas in the sample can be set and maintained with sufficient accuracy. The nonstationary nature of the processes in the tube and their short duration make it necessary to use relative complicated recording apparatus. However, the same short duration of the

adiabatic heating of the sample makes the method much more fruitful, permitting an investigation of not only the stability of the molecules, but also the intermediate reaction products, the radicals.

Let us consider a typical experiment of this kind. Figure 4 shows the diagram of the experimental apparatus used to measure the transition probabilities of the Swann bands of the C_2 molecule^[159]. The shock tube consists of a steel high-pressure chamber (HPC) and a glass low-pressure chamber (LPC) (diameter 30 mm, length 1500 mm). After breaking the diaphragm D, a shock wave will propagate to the right through the LPC, and will heat the gas mixture to incandescence. Photomultipliers 1 and 4 provide starting signals for pulse oscilloscopes, one of which

It must be noted that in general the condition $p\bar{l} \rightarrow 0$ can be satisfied by two methodologically non-equivalent methods: 1) $p = \text{const}$, $\bar{l} \rightarrow 0$ and 2) $\bar{l} = \text{const}$, $p \rightarrow 0$. The first method is somewhat cumbersome, since it calls for the use of interchangeable cuvettes and an accurate maintenance of other conditions (concentration). The second method is likewise not too convenient, for when small additions of the absorbed gas are manipulated working concentration becomes more dependent on the adsorption and desorption of molecules on the walls of the cuvette^[168]. Therefore certain investigators, especially Penner and Weber^[168-169] developed a procedure connected with broadening of the rotational lines by Lorentz collisions with molecules of an extraneous gas introduced into the cuvette at relatively high pressures. It can be shown^[168] that the result of such an operation is equivalent to the Wilson and Wells extrapolation, i.e., $\alpha' \rightarrow \alpha$ with increasing pressure of the extraneous gas. It follows from the foregoing considerations that at sufficiently large extraneous-gas pressure, as well as for sufficiently small $p\bar{l}$, it is possible to

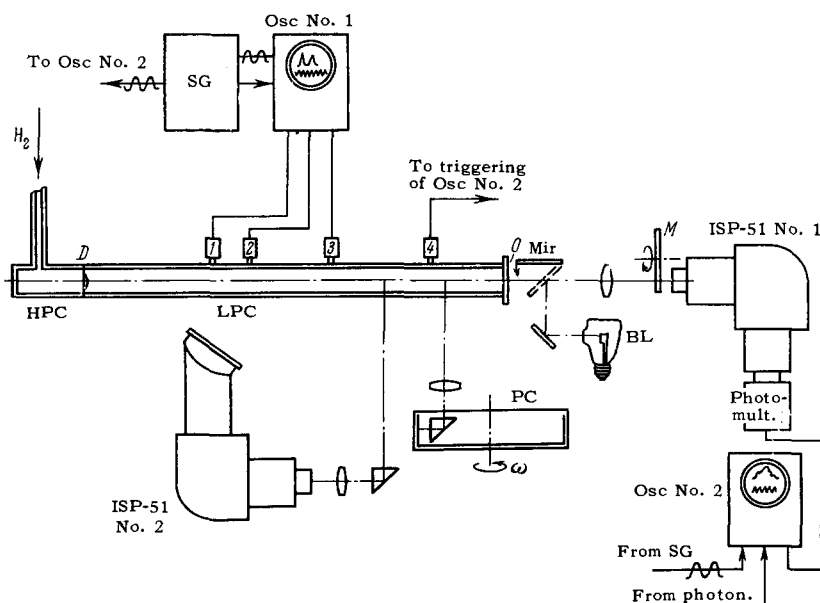


FIG. 4. Arrangement of the apparatus when working with a shock tube by the radiation method.

measure the ratio (3.3) directly, and the influence of the apparatus function can be neglected. In order to become assured in practice that the apparatus function can be neglected, it is meaningful to carry out measurements at different values of the apparatus function, for example, by varying the width of entrance slit of the spectral apparatus. If constant values of $\int K_\nu d\nu$ are obtained in this case (other conditions being equal), then the apparatus function can be regarded as eliminated.

It is quite simple to carry out the experiment with absorption of light in a gas at room temperature. Experiments of this type are described in^[4]. Usually the apparatus includes a continuous-spectrum source, the emission from which passes through a cuvette containing the investigated gas mixture, and enters the spectral instrument that registers the absorption spectrum. The continuous spectrum source can be tungsten ribbon lamp and, in the ultraviolet region, either a hydrogen lamp or a high-pressure gas-discharge lamp (GSVD-120, or DKSSh-1000). In the latter case a difficulty arises, connected with the specific influence of the strong scattered radiation due to the character of the spectral distribution of such a source. For this reason it is necessary to avoid in such measurements the use of spectral instruments built on the autocollimation principle.

If it is desired to study transitions with $v'' > 0$, measurements with hot gas are necessary. The absorbing cuvette is placed in this case in an oven of some type^[170-171]. However, the use of heating is quite frequently limited by the faster thermal decomposition of the investigated components^[171]. One way out of the difficulty is to use a shock tube in which the heating of the investigated gas sample is sufficiently rapid, and to obtain the absorption spectrum within a time of several dozen microseconds by using a pulsed high-intensity source of light.

By way of an example let us consider the experimental conditions for obtaining the absorption spectra of NO at temperatures up to 2500°K^[172]. The arrange-

ment of the apparatus is shown in Fig. 5. The experiment proceeds in the following manner. After the diaphragm is ruptured, compression waves begin to travel along the channel and form a shock wave. At the same time, the acoustic pulse due to the diaphragm vanes striking the tube wall propagates along the tube and, overtaking the shock wave, strikes the piezoelectric pickup P_5 . The resultant electric pulse is fed to the synchronization block (SB), which delays the received signal and triggers at the appropriate instants of time the sweep of pulsed oscilloscopes and the pulsed gas-discharge source EV-45^[173]. The radiation from the EV-45 source is guided by a system of mirrors and quartz lenses to the shock tube, crosses it in a vertical direction at a distance of 20 mm from the reflecting end, and is then focused on the slit of a spectrograph (DFS-13) which records the absorption spectrum. The temperature is measured by the generalized method of spectral-line inversion^[174-175]. One of the oscilloscopes (OK-17M I) registers the signals from a two-channel photoelectric attachment (marked "From photomult." on Fig. 5) of the ISP-51 spectrograph that is used to register the temperature, and another oscilloscope (OK-17M II) is used to register the signals from the piezoelectric pickups P_{1-4} of the shock-wave velocity measuring system.

When the shock wave is reflected from the end of the shock tube, the investigated gas, heated first by the incident and then by the reflected shock wave, stops and is at rest for some interval of time ("stands still") relative to the shock-tube walls. The standing time of the gas, determined by the instants of arrival of the reflected wave at the given point and of the contact surface^[157], was measured from oscillograms of the gas emission and amounted to $\approx 400 \mu\text{sec}$. It was necessary to obtain within this time the absorption spectrum and the oscillogram for the temperature measurement.^[172]

It is useful to note a characteristic feature of this investigation, namely, the absorption spectrum is measured in nitric oxide, which is not in equilibrium

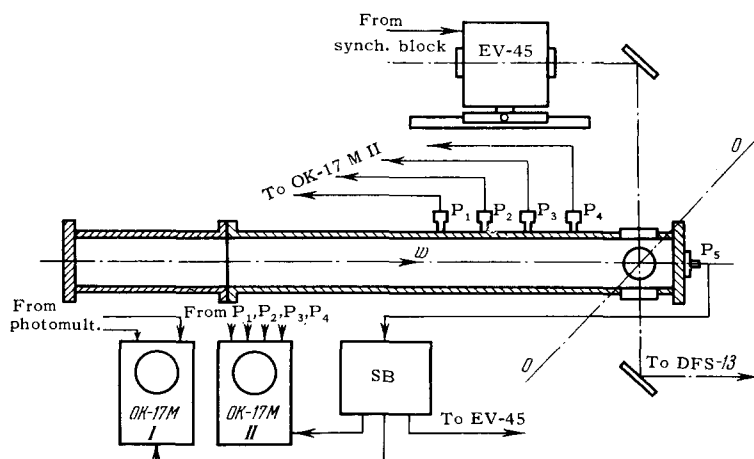


FIG. 5. Arrangement of apparatus when working with a shock tube by absorption method.

at the operating temperatures 2500°K for about 1300 μ sec (method of "frozen-in concentrations"). In principle it is possible to operate also with equilibrium concentrations of the absorbing molecules, as was done in the investigation of the molecules O_2 [176-178], CN [179-180], and C_2 [159]. At 6000°K, the equilibrium concentrations of NO are sufficiently high [182], but under the conditions of equilibrium the gas mixture must contain molecular oxygen, which produces in the investigated region strong Schumann-Runge bands that overlap the investigated γ bands.

The possibility of working with "frozen-in concentrations" is a unique feature of the shock-wave tube, greatly extending the possible applicability of this technique. It goes without saying that in planning experiments it is necessary to analyze from all angles all the available data on the relaxation times, and to choose an exposure time in accordance with this analysis. Thus, in the investigation discussed above [172], the instant of triggering the EV-45 source was chosen such as to already establish by that instant in the vibrational levels v'' of the lower electronic state a population corresponding to the external kinetic temperature ($\sim 2500^\circ K$), but still before the start of the dissociation of the NO molecule.

Let us examine the question of accuracy. It is obvious that

$$\frac{\Delta |R_e|^2}{|R_e|^2} = \frac{\Delta \int I_\nu d\nu}{\int I_\nu d\nu} + \frac{\Delta N_0}{N_0} + \frac{E}{kT} \frac{\Delta T}{T}. \quad (3.7)$$

Assume that the photometric measurements are carried out with accuracy to 10% (good accuracy), and the emitter concentration N_0 is specified with 5% error, the temperature is estimated with 10% accuracy, $E = 20,000 \text{ cm}^{-1}$, and $T^0 = 700^\circ K$ (Swann bands—conditions of [159]). In this case (3.7) yields $\Delta |R|^2 / |R|^2 = 60\%$. In such an idealized scheme we can calculate only the expected random experimental error, and the systematic experimental errors are not taken into account. One of the essential errors when working with a large vessel (absorption cuvette, shock tube) may be due to insufficiently good mixing of the gases in the working mixture (local variations of the absorber concentration), and also to adsorption and desorption on the walls of the vessel [168]. The experimental errors in absorption estimated in approximately the same way, using relation (3.2); an example of such an estimate is given in [172], where the error for R_e of the NO molecule amounts to 30–60%.

Summarizing, we can conclude that in ordinary measurements, using the foregoing technique in either emission or absorption, we can obtain an accuracy of 40–50% without any special measures. This figure should be regarded as more "correct" for absorption measurements than for emission, where absolute measurements of the energy fluxes are needed and involve the difficulties described at the beginning of this section.

We now consider the capabilities of the method of measuring the lifetime of the excited state. If the number of excited atoms N_n decreases with time only because of spontaneous transitions, then

$$N_{n,t} = N_{n0} e^{-t/\tau_n}, \quad (3.8)$$

where

$$\tau_n = \frac{1}{\sum_{m=0}^{n-1} A_{nm}}. \quad (3.9)$$

The summation is over all the energy states lying below the n -th. In the case of a resonant transition

$$\tau_1 = \frac{1}{A_{10}}. \quad (3.10)$$

Thus, the probability of such a transition can be obtained by measuring the lifetime τ_1 of the excited state. This method has in many cases undisputed advantages which favorably distinguish it from emission and absorption procedures, since the result of the measurement of τ_n is directly connected with the transition probability, without the use of any additional parameters, and no knowledge of the concentration of the atoms participating in the de-excitation is necessary. Yet the lifetime procedure is not free of certain specific limitations, limiting the possible regions of its application or necessitating a special analysis of the conditions in each individual case. Special notice must be taken of: 1) the possibility of cascade transitions from a level higher than the investigated one; 2) the possibility of influence of shock quenching and dragging of radiation in the source on the observed time τ_n . The pressure dependence can be taken into account by extrapolating the experimental data to zero pressure.

The possibility of measuring the lifetime of excited states was used long ago. However, it was in only the last decade that the method began to find extensive use for the investigation of molecules. This is apparently connected in part with the improvements in high speed oscillography techniques, which made it possible to observe attenuation of the radiation from an excited volume of gas directly. Data were obtained for N_2 [183], CN [184], NH [185,248], CO , CO^+ [186,269,270], N_2^+ , PH [248], NO , NO^+ [269], and other molecules. The pulsed sources of molecule excitation are electron beams [183-186], and pulsed high frequency discharges [187]. In two of these investigations [186,187], systematic measurements of the lifetime of the excited states were carried out in order to determine the dependence of R_e on r . Optical excitation with an intense light flash has many major advantages, but is limited by the lack of powerful radiation sources with sufficiently short duration; in this respect, apparently the prospects of using laser beams offer some promise.

In a somewhat different variant, the laser beam was used for the same purpose in [188]. By focusing a laser beam on a graphite block, the authors obtained

an intense pulsed radiation source, with the aid of which they measured the lifetime of $A^3\Pi_g$ of the C_2 molecule. When the conditions are thoroughly analyzed and all the influencing factors are taken into account, experiments on the de-excitation time can ensure an accuracy of $\pm 10-20\%$.

Using (1.1), (1.5), and (1.19) it can be shown that the intensity of the electron-vibrational band in the emission spectrum is determined by the relation^[3]

$$I_{v'v''} = \frac{64}{3} D \pi^4 c \nu_{v'v''}^4 N_{v'} R_e^2(\bar{r}_{v'v''}) q_{v'v''} \quad (3.11)$$

Here D is a geometrical factor, and the remaining symbols were defined above. Measuring the relative intensity of the bands with $v' = \text{const}$ (and hence $N_{v'} = \text{const}$) in a number of bands (v', v'') we can obtain an idea of the relative variation of R_e with ($r_{v'v''}$).

The relative intensities of the bands are measured by the method of heterochromic photometry^[152], using a comparison source with a known energy distribution over the spectrum. When working in the ultraviolet region, such a source may be a hydrogen lamp, the spectrum of which has been thoroughly studied^[189]. Measurements of this kind were carried out at the Physics Institute of the Academy of Sciences (see Fig. 7) for the γ system of NO, and the sources used were a high-frequency discharge and a high-voltage Hunter-Pearse discharge^[191]. A photoelectric method was used in the well known studies of Nicholls and Robinson^[74] aimed at determining $R_e(r)$ for O_2 , N_2 , CO, and NO. In choosing a source for measurements by this method it is necessary to bear in mind besides operating convenience, also the temperature of the gas in the discharge and the possible influence of the absorption. The temperature of the gas is important because, as a rule, it determines the rotational temperature of the molecule^[192], and the latter governs the size of the individual bands in the band system and the overlaps of the tails and edges of the neighboring bands. Thus, it is possible to choose a low-temperature source (for example, a high-frequency discharge), in which the bands are sufficiently well separated from one another. The effect of reabsorption in the source on the intensity is universally known and, as a rule, should be verified by one of the existing methods, for example by control measurements with a back mirror that doubles the optical thickness of the source. Attention should be called to the great potential of this method when used in conjunction with a procedure for measuring the lifetime of the excited state. Such a combination can be realized relatively easily, since the methods of excitation and registration are similar in both procedures. Such measurements would provide essentially independent estimates of $R_e(r)$ for the same system of bands, investigated under the same excitation conditions.

4. DEPENDENCE OF THE MOMENTS OF THE ELECTRON K TRANSITION ON r

Let us examine in greater detail the dependence of the moments of the electronic transition, obtained with the aid of the r -centroid procedure, on the internuclear distances. In those cases when this method is applicable we can, using the experimental intensities of the bands and the calculated Franck-Condon factors, determine in accordance with (1.19) the dependence of R_e on the average intermolecular distance $\bar{r}_{v'v''}$ or on the frequency $\nu_{v'v''}$ of the band (see^[261] concerning the relations between $\bar{r}_{v'v''}$ and $\nu_{v'v''}$). The use of information on the electron-vibrational spectral energy distribution for diatomic molecules makes it possible, knowing the factors $q_{v'v''}$, to determine the relative character of the variation of R_e over the bands of the system^[7-9]. From absolute measurements, say emission and absorption experiments with shock tubes^[193-194], one determines the absolute values of the dipole moment of the transition for a number of bands or for an individual band of the system.

In the latter case, in knowing the relative $R_e(r)$, dependence, we can normalize this dependence to the absolute value of R_e , provided the value of $\bar{r}_{v'v''}$ of this band lies in the range of internuclear distances in which the relative dependence $R_e(r)$ is specified^[195]. When using the $R_e(r)$ dependences, it should be noted that the obtained functions cannot be extrapolated beyond the limits of $\bar{r}_{v'v''}$ within which these dependences are defined. Neglect of this precaution may lead to serious misunderstandings (see, for example,^[196]).

The practice of allowing for deviations from the Condon approximation came into use only in the last decade, and the progress attained is connected with the use of the r -centroid procedure. The questions that arise here, concerning the form of the $R_e(r)$ dependence for different electronic transitions, concerning the degree of deviation from the Condon approximation and the need for taking $R_e(r)$ into account in calculations of the intensities, concerning the presence of a strong $R_e(r)$ dependence, etc., can be solved for the time being only on the basis of an analysis of the results of the obtained semi-empirical $R_e(r)$ dependences for different molecular transitions.

In this connection, particular importance attaches to the reliability of the obtained $R_e(r)$ dependences, which is determined by the accuracy of the experimental measurements and of the calculated $q_{v'v''}$ factors. As follows from the data of Sec. 2, different molecular-oscillator models lead to greatly different $q_{v'v''}$ factors. Therefore it is important in the calculations of the employed Franck-Condon factors that the anharmonicity be taken into account consistently, preferably on the basis of true molecular potentials.

In the opposite case, the use of rough $q_{v'v''}$ factors to determine $R_e(r)$ leads to false results. Great uncertainty in the $R_e(r)$ dependence is introduced by the relatively low accuracy of the experimental measurements (see Sec. 3). However, the presently obtained results show that the changes in the moment of the electronic transition on going from band to band greatly exceed the experimental error.

There is no unambiguous interpretation of the discrepancies between the calculations and experiment in the sense of the $R_e(r)$ dependences, and the deduction that the $R_e(r)$ dependence influences the observed intensity distribution should be preceded by an analysis of the concrete band system. Thus, for example, a likely explanation of the sharp redistribution of the intensity in the β system of the bands of NO was presented by Ory^[197], who assumed that this redistribution is connected with the perturbation of the upper state $B^2\Pi$ of this system when the curve of the $B^2\Pi$ state crosses the potential curves of the $C^2\Pi$ and $D^2\Sigma$ states. Another example is the dependence of the moment of the electronic transition on the conditions in the discharge, observed for the second positive system of N_2 ^[198, 263] and contradicting the theory.

In the majority of the investigations, however, the $R_e(r)$ dependences were reliably determined for the electron-vibrational band systems. These dependences are satisfactorily described by power-law and exponential functions of the internuclear distances. For some band systems the $R_e(r)$ dependences can be neglected, and the distribution of the intensity over the bands is governed by the Franck-Condon principle; for others the contribution of $R_e(r)$ to the intensity distribution is quite appreciable. In the latter case, the oscillator strength (1.16) is no longer a constant characteristic of the entire electronic transition, and it is necessary to operate directly with the dipole moment of the transition, which depends on the inter-

nuclear distance $\bar{r}_{v'v''}$. We note that the assumption made by Bates^[26], that the $R_e(r)$ dependence is weak for parallel electronic transitions ($\Delta\Lambda = 0$), is apparently completely incorrect, and the $R_e(r)$ dependences of identical electronic transitions of different molecules have possibly some features in common.^[199] Nicholls^[96] proposed, supplementing to the Bates criterion, that $R_e(r)$ depends also on the total change in the r -centroid. It is proposed in^[245] that the dipole moment of the electronic transition changes. With changing the internuclear distance by not more than a factor of 2 for strong transitions ($\tau \sim 10^{-6} - 10^{-9}$ sec), and experiences appreciable changes for weak transitions ($\tau > 10^{-6}$ sec). This hypothesis, that $R_e(r)$ is constant for strong band systems and experiences strong variations for forbidden transitions, is confirmed by many early data, and also by a number of new results^[265-266].

We present results known to us on the $R_e(r)$ dependences. For the molecules of air, O_2 , NO, and N_2 , which are of special interest and have therefore been studied, the results will be considered in greater detail; for all other molecules the dependence of the moments of the electronic transitions and in internuclear distances are gathered in Table III. We indicate here the following for each transition: name of the system, changes in the internuclear distances within the limits of which the data reduction gives the obtained formulas for $R_e(r)$, and the method of experimentally measuring the probabilities. If a system has been investigated by several authors, all the obtained $R_e(r)$ dependences are given.

O_2 molecule. The Schumann-Runge system of bands (transition $B^3\Sigma_u^- - X^3\Sigma_g^-$) of O_2 has singularities which determine its major role in the radiation of hot air^[200]. This is connected, first, with the presence of a large difference between the equilibrium internuclear distances of the upper and lower states, which causes the Schumann-Runge system to spread greatly over the spectrum. In addition, the intensity of the Schumann-Runge bands is quite large in absolute magnitude (large oscillator strengths^[176-178]). The intensity of the Schumann-Runge bands was determined by a number of investigators. Measurements of the absorption in the bands $v'' = 0$ were carried out by Ditchburn and Heddle^[201] and by Bethke^[202]. Measurements of the absorption in the photodissociation continuum were carried out in^[203-205]. Absorption^[206, 176-178] and emission^[147] measurements were also made in a shock tube, as well as relative measurements of the band intensity in discharge emission^[207]. These measurements are represented in Fig. 6. It can be seen that the measurements of Bethke and of Ditchburn and Heddle, which are similar in type, differ greatly in their results. An analysis of the conditions of these experiments and a comparison with the measurements of the continuum^[204, 205] offer evidence, however, in

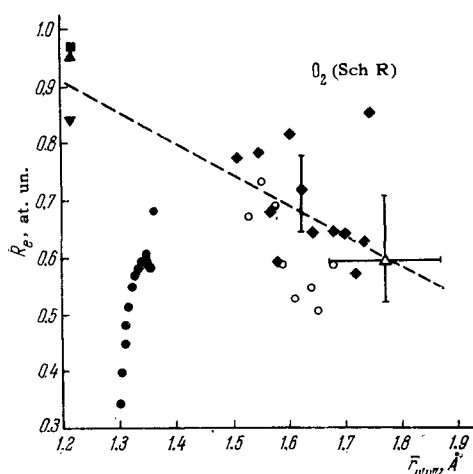


FIG. 6. Moment of electronic transition as a function of the r -centroids for the Schumann-Runge bands of O_2 . \blacktriangle - [203]; \triangle - [47]; \bullet - [202]; \circ - [177]; ∇ - [205]; \blacklozenge - [206]; \blacksquare - [201].

Table III. $R_e(r)$ dependences obtained by the r -centroid method

Molecule	System	Transition	$R_e(r)$	Limits of r , Å	Reference	Remarks
AlO	Blue-azure	$A^2\Sigma^+ - X^2\Sigma^+$	$c(1 - 1.093r)$		103, 261	Arc discharge with aluminum electrode.
			$c(1 - 0.46r)$	1.50—1.85	230	Arc discharge with aluminum electrode.
			$c(1 - 0.46r)$	1.50—1.85	231	Excitation of aluminum powder in shock tube, explosion of aluminum foil.
BO	α -system	$A^2\Pi - X^2\Sigma$	$c(-1 + 1.66r)$	1.25—1.36	232	Source with active nitrogen
	β -system	$B^2\Sigma - X^2\Sigma$	$c(-1 + 1.434r)$	1.30—1.50	232	and BCl_3 vapor with oxygen.
BaO		$A^1\Sigma - X^1\Sigma$	$ce^{-6.07r}$	1.98—2.13	80	Measurements in discharge.
			$c(1 - 0.536r)$		53	Measurements in discharge.
BeO	Blue-green	$B^1\Sigma^+ - X^1\Sigma^+$	$c(1 + 0.59r)$	1.20—1.54	80	Measurements in discharge.
			$c(-1 + 0.99r)$	1.222—1.708	42	Arc discharge between carbon electrodes with Be filling.
C ₂	Swann	$A^3\Pi_g - X^3\Pi_u$	$c(1 + 0.056r)$	1.17—1.62	209	Measurements in King's oven.
			$c(1 + 0.428r)$	1.1663—1.5029	128	Measurements in King's oven.
			$R_e(r_{00}) [1 - 0.8(r - r_{90})]$	1.1—1.7	188	Measurement with excitation by laser beam.
			$-0.15(1 - 5.07r)$	1.10—1.50	247	Measurements in King's oven.
CN	Violet	$B^2\Sigma^+ - X^2\Sigma^+$	$c(-1 + 2.579r)$	0.95—1.32	209	Arc discharge between carbon electrode.
			$c(1 + 0.03r)$	0.95—1.32	233	Measurements in King's oven. See also [179-181, 184].
			$c(1 + 0.166r)$	1.04—1.27	234	Source with active nitrogen and CCl_4 vapor; see also [235].
CO	Fourth positive	$A^1\Pi - X^1\Sigma$	const	Bands of $v' = 0-4$ progressions	226	Measurements in discharge.
			const		236, 268	Excitation with electron beam.
	Angstrom	$B^1\Sigma^+ - A^1\Pi$	$c(-1 - 1.745r + 0.768r^2)$	1.12—1.19	74	Measurements in discharge.
	Third positive	$b^3\Sigma - a^3\Pi$	$c(-1 + 0.943r)$	1.08—1.16	74	Measurements in discharge.
CO ⁺	Comet tails	$A^2\Pi - X^2\Sigma^+$	$c(1 + 0.643r)$	1.048—1.156	237	Measurements in discharge.
			$c(-1 + 1.73r - 0.74r^2)$	1.10—1.21	232	Excitation with electron beam.
			$43(-1 + 1.73r - 0.74r^2)$	1.100—1.277	93	Lifetimes and relative measurements in discharge.
CaO	Second infrared	$1\Sigma - 1\Sigma$	const	Bands of $v' = 0-2$ progressions	238, 266	Excitation with electron beam.
			$ce^{-1.79r}$	1.1—1.4	80	Measurements in discharge.

Table III. (Cont'd)

Molecule	System	Transition	$R_e(r)$	Limits of r , Å	Reference	Remarks
MgO	Violet	$B^1\Sigma - X^1\Sigma$	$ce^{-0.35r}$	1.2—2.1	80	Measurements in discharge.
OH	Green	$A^2\Sigma^+ - X^2\Pi$	$c(1 - 0.756r)$	0.8—1.3	209	Measurements in discharge.
			ce^{-3r}		141	Assumed in calculations of vibrational rotational interaction; see also [240,241].
			$ce^{-2.5r}$		239	
PN		$A^1\Pi - X^1\Sigma^+$	$ce^{0.1784r}$	1.426—1.630	88	Measurements in discharge.
SiN		$B^2\Sigma^+ - X^2\Sigma^+$	$c(1 - 1.27r + 0.412r^2)$ const	1.38—1.71 $r > 1.71$	102	Source with active nitrogen and SiCl_4 vapor.
TiO	α -system	$C^3\Pi - X^3\Pi$	$ce^{-2.57r}$	1.58—1.72	80	Measurements in King's oven.
VO	Yellow-green	$2\Delta - 2\Delta$	$c(1 - 0.18r)$	1.53—1.68	80	Measurements in King's oven.

favor of the data of Bethke^[208], which were obtained with great care and are guaranteed against the influence of the apparatus function, owing to the use of large extraneous-gas pressures. The use of new q_v'' factors^[134], calculated by using potential curves in the Klein-Dunham form, for the reduction of Bethke's data, makes these data agree better with those of^[201].

Analytic $R_e(r)$ dependences for the Schumann-Runge bands were proposed on the basis of these data at various times in^[2,209,210,138,195]. The dashed curve in Fig. 6, drawn without inclusion of the results of^[177,202], can be described by the equation^[195]

$$R_e(r) = 0.68 \exp[-0.72(r - 1.60)], \quad 1.2 < r < 1.9 \text{ \AA}. \quad (4.1)$$

For the second negative system (transition $A^2\Pi - X^2\Sigma$) of the ionized oxygen molecule O_2^+ , measurements were made of the relative intensities of the bands in a discharge. On the basis of these measurements, a linear and a quadratic relative dependences of $R_e(r)$ were obtained in^[7] and^[74]:

$$R_e(r) = C(1 - 0.614r), \quad 1.27 < r < 1.37, \quad (4.2)$$

$$R_e(r) = C(-1 + 1.539r - 0.587r^2), \quad 1.27 < r < 1.37. \quad (4.3)$$

NO molecule. The bands of the γ system of NO correspond to the transition $A^2\Sigma - X^2$. The importance of these bands in radiative heat exchange in hot air is due to two factors:

1. The equilibrium concentrations of NO are quite large in air at the temperatures (6000–8000°K) and pressures of practical importance.

2. The upper state of the γ system of NO reveals a bond of the type b as defined by Hund, while the lower state $X^2\Pi$ has a bond of a type intermediate between a and b as defined by Hund. This causes the selection rules both with respect to J and with re-

spect to K not to be strictly satisfied, so that when the doublet and Λ splittings are taken into account, 12 branches of different intensity appear in each band. The spectrum of this system is consequently quite broad and has an almost continuous character at high pressure.

Investigations of the γ system were made many times. Measurements of the absorption in cold gas^[211,169] yielded the oscillator strengths for the bands with $v'' = 0$. Later measurements with shock tubes^[172,212] and with an electric oven^[171] yielded data for the bands with $v'' > 0$; recent measurements of the lifetimes of the excited state^[213] also made it possible to estimate R_e for several bands with $v'' = 0$. In addition, there are several rather obsolete measurements of emission of the γ bands in a gas discharge^[74]. These measurements were recently repeated to correct the data of^[74].

An analysis of the experimental data available for the establishment of the $R_e(r)$ dependence was made many times^[195,214]. The latest and apparently most reliable information on the $R_e(r)$ dependence is shown in Fig. 7, where the data were reduced by

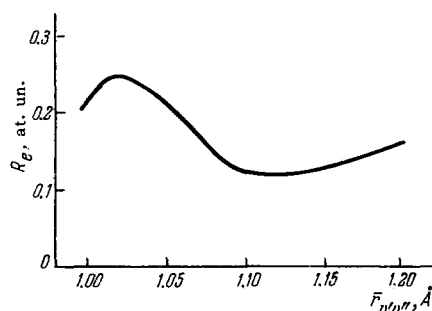


FIG. 7. Moment of electronic transition as a function of the r -centroid of the γ system of the bands of NO.

means of the $q_V'v''$ factors calculated by Flynn^[143] from exact potential curves.

For the bands of the β system of NO, there are two known absolute measurements of absorption^[211,172] and one emission measurement^[47]; measurements were also made of the relative intensities of the bands of the β system in a gas discharge^[74]. In the opinion of Allen^[195], the measurements of^[47] on the β system are quite reliable and can be used to normalize the dependence obtained in^[74]. The results of such a normalization, shown in Fig. 8, can be expressed by

$$R_e(r) = 0.32(r - 0.62), \quad 1.33 < r < 1.54 \text{ \AA}. \quad (4.4)$$

It must be noted that by taking into consideration the fact that the Morse $q_V'v''$ factors used by Bethke^[211] were in error, and by recalculating these data for the Flynn's $q_V'v''$ factors of Flynn^[143], we find that when the dependence given above is extrapolated to the region $r < 1.33 \text{ \AA}$ it fits the data of Bethke. The result for the band β (2, 4), obtained later with shock-tube experiments^[215], agrees within the limits of measurement accuracy with the discussed dependence.

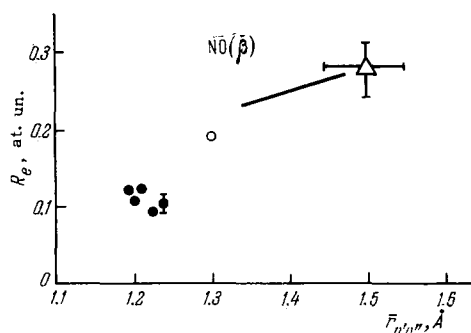


FIG. 8. Moment of electronic transition as a function of the r -centroid for the β system of the NO bands. ● - [211]; Δ - [47]; ⊙ - [215].

N₂ molecule. The first positive system of N₂ ($B^2\Pi_g - A^3\Sigma_u^+$) makes an appreciable contribution to the red and near-infrared regions of the spectrum. The oscillator strengths for the system were obtained in^[216-217] from measurements of radiation from hot N₂. The normalization of the available relative measurements^[219] to these data was carried out in^[195]. The results of this procedure, shown in Fig. 9, can be written in absolute form:

$$R_e(r) = 0.46 \exp [3.02(r - 1.23)], \quad 1.17 < r < 1.59 \text{ \AA}. \quad (4.5)$$

Subsequent measurements of the intensity of radiation of hot air in the red and near-infrared regions^[220,273] have shown that the radiation in this region is much greater (by one order of magnitude) than for the case of pure N₂. It had been assumed^[222] that this radiation could be due to CN and NO. To take into account the contribution of these components,

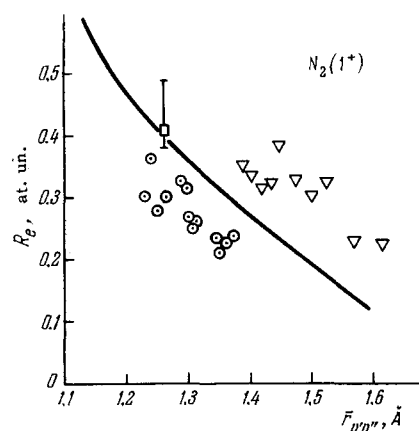


FIG. 9. Moment of electronic transition as a function of the r -centroid for the first positive system of N₂. ▽ - [216]; ⊙ - [217]; □ - [195].

Allen et al.^[195] propose to ascribe this entire radiation, in practical calculations of air radiation, to the first positive system of N₂, assuming for this system

$$R_e(r) = 0.9 \exp [-3.02(r - 1.23)], \quad 1.17 < r < 1.59 \text{ \AA}. \quad (4.6)$$

It is shown in a recent paper^[265] that the Franck-Condon factors calculated on the basis of the true RKR curves^[245] agree well with the experimental data^[219], thus casting doubts on Eq. (4.6).

The second positive system of the N₂ bands (transition $C^3\Pi_u - B^3\Pi_g$) makes a contribution to the near-ultraviolet and blue regions of the spectrum. However, this contribution is apparently not very large (owing to the low population of the high levels C and B of nitrogen^[221]). This is confirmed by experience with shock tubes, where it was impossible to observe the bands of the second positive system of nitrogen in the equilibrium radiation of air in a shock tube up to the highest operating modes of the apparatus ($\sim 7500^\circ\text{K}$). There are many known measurements of the lifetime of the level $C^3\Pi$ ^[213,133], which can be used to estimate the absolute value of R_e for several bands of this system. The discrepancy between the results of^[213] and^[183] is relatively small (approximately by a factor of 1.5), but the presence of cascade transitions in the upper levels^[213] makes these data unreliable. The known relative measurements^[223] of the band intensity were normalized^[195,234] to the absolute data of^[47] and^[183]. An example of such a normalization is shown in Fig. 10, and is expressed by

$$R_e(r) = 0.84 [1 - 4.9(r - 1.06)^2], \quad 1.02 < r < 1.35 \text{ \AA}. \quad (4.7)$$

The above-described Kolesnikov arc source was used^[155] to obtain a pure spectrum of N₂ under thermal conditions at a temperature $8,000^\circ\text{K}$. The quantitative data obtained in the preliminary experiment are in approximate agreement with^[213] and^[183].

The relative change in the moment of the electronic transition for the Vegard-Kaplan bands (transition

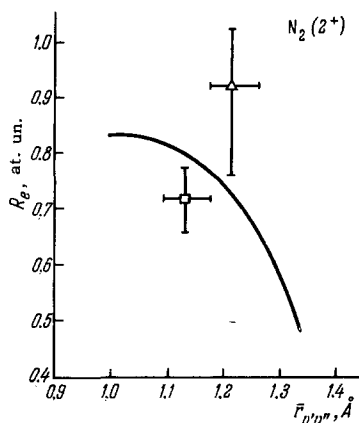


FIG. 10. Moment of electronic transition as a function of the r -centroid for the second positive system of bands of N_2 : Δ - [47]; Δ - [47].

$A^3\Sigma_e^+ - X^1\Sigma_g^+$ was investigated in a discharge tube with pure N_2 [225]. An increase of R_e with increasing internuclear distance was observed at $r = 1.24 - 1.32 \text{ \AA}$, and a constant value for R_e at $r = 1.32 - 1.38 \text{ \AA}$. A second forbidden transition $a^1\Pi_g - X^1\Sigma_g^+$ in N_2 , corresponding to the Lyman-Birge-Hopfield bands, was investigated in [226-228]. On the basis of measurements of the initial intensities [226-227] of a large number of bands (up to 50) it was shown that the moment of the electronic transition remains practically unchanged within the limits of the investigated bands. According to [228], the observed correspondence between the distributions of the intensity in electron impact and in ultraviolet absorption and the calculations with the aid of the Franck-Condon factors is proof that the electronic and nuclear motions can be separated and that R_e varies slowly with r for this transition.

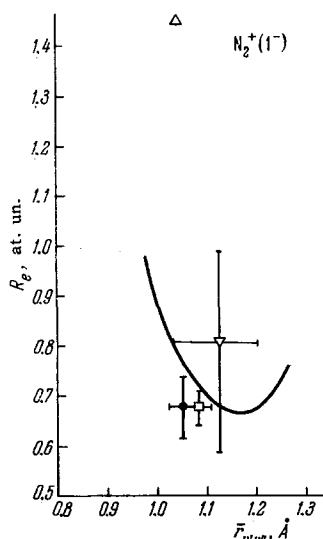


FIG. 11. Moment of electronic transition as a function of the r -centroid for the first negative system of bands of N_2^+ . Δ - [47]; ∇ - [216]; \square - [183]; \bullet - [271].

The first negative system, corresponding to transition $B^2\Sigma_u^+ - X^2\Sigma_g^+$, belongs to the ion N_2^+ and cannot be observed in absorption. Absolute measurements of the emission in shock tubes, carried out in [47, 216, 271], gave strongly diverging results (Fig. 11). More accurate measurements of the lifetime were made by Bennett and Dalby [183], although according to their communication these measurements were affected by upper cascade transitions to the investigated level. The normalization proposed in [195] for the relative measurements of [223] according to the data of [216, 183], which yields the dependence plotted in Fig. 11,

$$R_e(r) = 0.67 [1 + 12.3(r - 1.16)^2], \quad 0.97 < r < 1.26 \text{ \AA}, \quad (4.8)$$

is somewhat arbitrary in character. A similar normalization [223] against the data of [183] was made by Nicholls [224]. In another of his papers, the relative dependence $R_e(r)$ was obtained from measurements of the intensity in the spectrum of the northern aurora for the Meinel band system ($A^2\Pi - X^2\Sigma$) of the molecular ion N_2^+ , was obtained in the form

$$R_e(r) = C(-1 + 0.987r), \quad 1.067 < r < 1.104 \text{ \AA}. \quad (4.9)$$

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