

ABSOLUTE INTENSITIES OF ELECTRONIC TRANSITIONS IN DIATOMIC MOLECULES

V. N. SOSHNIKOV

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THE absolute intensities of electronic spectra of diatomic molecules have great practical and theoretical significance. The presently available experimental and theoretical data are, however, contradictory and are scattered in papers which are unrelated in either point of view or unity of purpose, and which frequently pertain to different branches of physics. The last review paper on absolute intensities, by Mulliken and Rieke,⁷ dates back to 1941. The purpose of the present article is to systematize the accumulated material on the probabilities of electronic transitions, and is closely related to the reviews of Kolesnikov and Leskov¹ and Nicholls et al.^{2,3,233} on absolute electronic intensities in atoms and on relative intensities in diatomic molecules. Papers published since 1940 inclusive have been reviewed.

1. CONNECTION BETWEEN THE QUANTITIES THAT DETERMINE THE ELECTRONIC TRANSITION INTENSITY

The intensity of absorption of monochromatic light by a gas layer of thickness *l* is characterized by an absorption coefficient *k*(ν), determined from Beer's formula^{9,10,25,31}

$$\frac{I_\nu}{I_{\nu_0}} = e^{-\Sigma k(\nu)l}, \tag{1}$$

where *I* ν and *I* ν_0 are respectively the transmitted and incident light intensities per unit wave-number interval. The factor $\Sigma = 1 - \exp(-hc\nu/kT)$, which takes into account the correction for the induced emission, can in most electronic transition be taken equal to unity. The integral $\int k(\nu) d\nu$ is taken over all the electronic bands and characterizes the intensity of the given electronic transition as a whole.

It is frequently necessary to use an absorption coefficient *k*(ν), averaged within a certain interval $\Delta\nu$ over the vibrational and rotational transitions. This coefficient can be readily obtained (see, for example, Blokhintsev,¹¹ p. 342) by averaging over all directions in space, summing over the rotational transitions, and averaging over the vibrational transitions:

$$k_{av}(\nu) = \frac{8\pi^2e^2}{3hc} n R_e^2 G' \nu \frac{1}{\Delta\nu} \sum_{\Delta\nu} q_{v',v''} w_{v''} \tag{2}$$

Singly and doubly primed symbols refer to the upper and lower state, respectively; *w* ν'' is the Boltzmann probability of finding the lower electronic state at the vibrational level ν'' ; *q* ν',ν'' is the vibrational probability (the Franck-Condon factor) for a transition between the states ν' and ν'' ,

$$q_{v',v''} = \left| \int \psi_{v'} \psi_{v''} d\tau \right|^2,$$

where $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wave functions, *n* the concentration of the absorbing molecules, *G'* the electronic degeneracy of the upper state, and *R* $_e^2$ the square of the electronic moment of the transition

$$R_e^2 = \left| \int \psi_e^* \left(\sum_i r_i \right) \psi_e d\tau_e \right|^2, \tag{3}$$

where ψ_e are the electronic wave functions, and the summation is carried out over all the electrons. In the case of degeneracy it becomes necessary to choose⁷ real ψ_e . The sum in (2) is taken over all ν' and ν'' for which the transition wave numbers lie in an averaging interval $\nu \pm \Delta\nu/2$ small compared with the spectral region occupied by the entire electron system. In the derivation of (2) it is assumed that the total probability of transition between two states is the product of the electronic, vibrational, and rotational probabilities, each of which is the square of the matrix element for wave functions that depend, respectively, only on the electronic, vibrational, and rotational coordinates.^{1,6,18,228}

One frequently employs instead of (3) the formula for the dipole velocity³⁸ a derivation of which can be found in texts on quantum mechanics.⁸⁵

$$R_e^2 = \left| \frac{h}{4\pi^2mc\nu} \int \psi_e^* \left(\sum_i \nabla_i \right) \psi_e d\tau_e \right|^2, \tag{3a}$$

where ν is the wave number of the electronic transition at a given internuclear distance and *m* is the electronic mass. In a theoretical calculation, (3) and (3a) yield different results, owing to the use of approximate wave functions.

If it is necessary to take more accurate account of the distribution of intensity over the rotational lines, additional factors, representing the rotational probabilities, must be introduced under the summation sign in (2).

Integrating over the entire electronic system, we obtain^{7,8}

$$\int k(\nu) d\nu = \int k_{av}(\nu) d\nu \equiv \frac{\pi e^2}{mc^2} n f_e^{abs}, \tag{4}$$

where *f* $_e^{abs}$ is called the electronic oscillator strength in absorption. Substituting Eq. (2) for *k* $_{av}(\nu)$, using the relation $\sum_{\nu'} q_{\nu',\nu''} = 1$,¹⁾ and dropping the super-

¹⁾In the presence of a continuous spectrum (photodissociation, photoionization) we add to the sum the integral over the continuous vibrational states.

script of f_e^{abs} , we obtain (see references 6–8):

$$f_e \simeq \frac{8\pi^2 mc}{3h} R_e^2 G \nu_{\text{max}} = 1.085 \cdot 10^{11} \nu_{\text{max}} R_e^2 G, \quad (5)$$

where R_e^2 is in cm^2 and ν_{max} is in cm^{-1} . Formula (5) in this form defines the oscillator strength not only in absorption but also in emission. Here G is the degeneracy of the final state, so chosen as to account for transitions from the initial state (either nondegenerate, or one of the components of the degenerate electronic state) to all the components of the final electronic state; ν_{max} is the wave number corresponding to the maximum of intensity of absorption or emission of the electronic band system.²⁾

The oscillator strength in emission can also be defined with the aid of (4), where $k_{\text{av}}(\nu)$ is defined by formula (2), in which the probability $w_{v''}$ is replaced by the probability of finding the upper electronic state $w_{v'}$ at the vibrational level v' and G' is replaced by G'' .

An electronic transition in an atom corresponds to a narrow spectral line, with $\nu_{\text{max}}^{\text{abs}} = \nu_{\text{max}}^{\text{em}}$. In the case of molecules, an electronic transition corresponds to a broad spectral line; $\nu_{\text{max}}^{\text{abs}}$ and $\nu_{\text{max}}^{\text{em}}$ can be determined from plots of the potential energy of the molecule, using the Franck-Condon principle²⁶ (Fig. 1).

A direct calculation of $k_{\text{av}}(\nu)$ for different molecules shows that $\nu_{\text{max}}^{\text{abs}}$ depends little on the temperature up to approximately $10,000^\circ \text{K}$.

It is known that the sum of the oscillator strengths (4) or (5), taken over all the electronic transitions from a given electronic level, is equal to the number of optically active electrons of the molecule^{215,7} (oscillator strengths corresponding to transitions to lower levels, i.e., emission, should be taken here with a minus sign).³⁾

From (2) and (5) we obtain

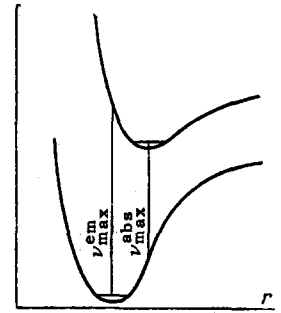
$$k_{\text{av}}(\nu) = \frac{\pi e^2}{mc^2} n f_e^{\text{abs}} \frac{\nu}{\nu_{\text{max}}^{\text{abs}}} \frac{1}{\Delta\nu} \sum_{\Delta\nu} q_{v', v''} w_{v'}. \quad (6)$$

The absorption coefficient (and through it the oscillator strength) can also be related to the intensity

²⁾The oscillator strength is sometimes defined differently, with ν_{max} replaced in (5) simply by the wave number ν in that region of the spectrum where the measurements are carried out.^{227,4,5,229,232} Such a definition is incorrect, for by it the oscillator strength is no longer a characteristic of the electronic transition as a whole. This definition caused several misunderstandings and errors, for example, in the determination of the oscillator strength of the Schumann-Runge system of the O_2 molecule.^{5,12,17} In the last of these papers it is assumed in error that $\nu_{\text{max}}^{\text{abs}} = \nu_{\text{max}}^{\text{em}}$, in which connection [compare (5) with (8)] the natural width of the rotation line²²⁴ is overvalued by approximately a factor of 10. The book by Penner²²⁷ introduces an erroneous connection between f_e^{abs} and f_e^{em} , owing to the wrong definition of the oscillator strength.

³⁾This statement is true for both atoms and molecules, if we use for the latter the definition (4) of the oscillator strength in absorption or emission. If the f_e are defined by means of the approximate expression (5), then the sum rule should be satisfied only approximately.

FIG. 1. Definition of $\nu_{\text{max}}^{\text{abs}}$ and $\nu_{\text{max}}^{\text{em}}$ according to the Franck-Condon principle. The ordinates represent $U(r)$.



of emission of an electronic system of bands. Let us consider a layer of hot gas in thermodynamic equilibrium of thickness l (Fig. 2). By Kirchhoff's law we have for emission in the direction of r

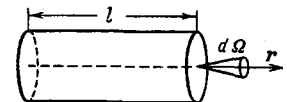
$$I_\nu = B_\nu (1 - e^{-k(\nu)l}), \quad (7)$$

where I_ν is the intensity of radiation from a unit surface of the gas into a unit solid angle per unit interval of the wave number; B_ν is the intensity of absolute black body radiation

$$B_\nu = \frac{2hc^2 \nu^3}{e^{hc\nu/RT} - 1}.$$

Let us establish also the connection between f_e^{abs} and the average lifetime of the electronic state¹¹ $\tau_{m,n}$,

FIG. 2. Radiation from a layer of hot gas of thickness l in a solid angle $d\Omega$ in the direction of r .



where m and n are the numbers of the states pertaining to the upper and lower electronic levels, respectively. Leaving out the rotational transitions, summation over which yields a factor of order unity, we obtain for the total average lifetime $\tau = 1/\sum_{v''} A_{v', v''}$, where $A_{v', v''}$ are the Einstein coefficients:¹¹

$$\sum_{v''} A_{v', v''} = \frac{64\pi^4 e^2}{3h} \sum_{v''} \nu_{v', v''}^3 q_{v', v''} R_e^2 G'' \simeq \frac{64\pi^4 e^2}{3h} R_e^2 G'' (\nu_{\text{max}}^{\text{em}})^3.$$

Here $\nu_{\text{max}}^{\text{em}}$ is the wave number corresponding to the maximum probability of transition from the upper level v' to the vibrational levels v'' of the lower electronic state. G'' is the electronic degeneracy, corresponding to the number of components of the lower electronic state to which the transition takes place. Substituting f_e^{abs} from (5), we obtain

$$\tau_{f_e^{\text{abs}}} = \frac{mc}{8\pi^2 e^2} \frac{\nu_{\text{max}}^{\text{abs}}}{(\nu_{\text{max}}^{\text{em}})^3} \frac{G'}{G''} = 1.51 \frac{G'}{G''} \frac{\nu_{\text{max}}^{\text{abs}}}{(\nu_{\text{max}}^{\text{em}})^3}, \quad (8)$$

where τ is in seconds and ν_{max} is in cm^{-1} .

In addition to the relations considered above, it may be useful to employ in some cases the connection between the oscillator strength and the refractive index of the gas $n(\nu)$ (see references 11, 7, 16, 21, 132, 169, and 184) and the polarizability.^{7,11,35} Thus, for cold gas and ν lower than the long-wave absorption threshold we have

$$n^2(\nu) - 1 \approx \frac{ne^2}{\pi mc^2} \sum_i \frac{f_i^{\text{abs}}}{(\nu_{i \text{ max}}^{\text{abs}})^2 - \nu^2} + \frac{1}{\pi^2} \int \frac{k(\omega) d\omega}{\omega^2 - \nu^2}, \quad (9)$$

where the summation is over individual bands of the discrete spectrum, and integration is over the continuous spectrum. We have here for individual vibrational bands of the electronic system

$$f_i^{\text{abs}} \equiv f_e^{\text{abs}} \frac{\nu_{v', v''}}{\nu_{e \text{ max}}^{\text{abs}}} \cdot q_{v', v''},$$

where $\nu_{v', v''}$ is the wave number of the vibrational transition and $\nu_{e \text{ max}}^{\text{abs}}$ is the wave number corresponding to the maximum of absorption in the given electronic system.

The foregoing formulas are valid if the total transition probability can be represented as a product of the electronic, vibrational, and rotational probabilities. The latter, strictly speaking, is not true, since the electronic wave functions depend on the internuclear distance r , and consequently the transition probability in the electronic-vibrational band is proportional to

$$\left| \int \psi_{v'}(r) \psi_{v''}(r) R_e(r) dr \right|^2.$$

Fraser^{13,2} has shown separation is possible even in this case, but R_e^2 must be regarded as a function of ν (or of the internuclear distance $r_{v', v''}$, at which the transition takes place in accordance with the Franck-Condon principle at a wave number ν — the so-called r -centroid). At the same time, (5) becomes incorrect; f_e^{abs} as defined by (4) is no longer a constant characteristic of the electronic transition on the whole, since generally speaking $\int k(\nu) d\nu$ does not remain constant, say, when the temperature changes, etc. Sometimes formula (5) is taken as the main definition of f_e^{abs} ; then f_e^{abs} is considered a function of ν .

Since the author believes that the existence of a clear cut $R_e^2(\nu)$ relationship has not been sufficiently investigated (see the discussion of the experimental results), we shall henceforth assume everywhere $R_e^2(\nu) = \text{const}$.

2. THEORETICAL CALCULATIONS OF OSCILLATOR STRENGTHS

Except for the simplest cases, it is necessary to resort to approximate wave functions in theoretical calculations of oscillator strengths. In particular, the significant assumption is made that the total wave function of the molecule (or of the atom) can be represented as a linear combination of products of single-electron ψ functions. The state described by each such ψ function is called the electronic orbit (the orbital approximation).^{7,26-28}

Owing to the oscillating character of the wave functions, the oscillator strengths usually depend strongly on the assumptions made, so that calculations of f_e made by different methods for the same electronic

transition may deviate by several powers of ten. Therefore the data obtained by rather laborious theoretical calculations must still be regarded in most cases as tentative and as requiring experimental confirmation.

From the qualitative point of view, a very valuable classification of electronic transition was proposed by Mulliken.^{7,60,86} It is necessary to separate first transitions of the Rydberg molecular series, in which the electron goes to an excited molecular orbit close to the atomic orbit. The intensity of such transitions is usually large, and the oscillator strengths can be calculated relatively accurately. Next come transitions of external (valence) electrons between molecular orbits proper; the probability of such transitions vanishes when the nuclei are infinitely diluted. There are two methods of orbital approximations.^{7,27} In the first, the total electronic wave function is constructed with allowance for the symmetry properties and the total spin of the electron, as a linear combination of the products of wave functions of the component atoms; these functions are usually found in the orbital approximation (AO method).^{7,26,28,29,36} The second is based on single-electron ψ functions, which describe the state of the electron in the molecule and are usually linear combinations of the atomic orbital functions. The total molecular wave function is represented in the form of a linear combination of products of molecular orbital functions (LCAO MO method).^{7,26,27,19,20} Specific calculations are usually modifications of one of these methods. An idea of their use can be gained from references 7, 30, 71, 37, and 220 — 222.

Among the orbital transitions of the valence type, Mulliken distinguishes between transitions from the ground state (N) into the excited one (V), which are close to Rydberg transitions (sometimes being simply the lower terms of the Rydberg molecular series), and usually have a high intensity (NV transitions). From the point of view of the AO method, the V state corresponds to an ionic structure of the initial atomic wave functions with the nuclei highly diluted. This type usually includes a parallel Σ - Σ transitions. The following estimates have been derived⁷ for NV transitions: for those similar to NV transitions in H_2 ,

$$R_e \approx \frac{r}{\sqrt{2(1-S^2)}} \text{ (LCAO MO)}, \quad (10)$$

and

$$R_e \approx \frac{Sr}{\sqrt{1-S^4}} \text{ (AO)}, \quad (11)$$

and for transitions similar to NV transitions in H_2^+ ,

$$R_e \approx \frac{r}{2\sqrt{1-S^2}} \text{ (AO and LCAO MO)}, \quad (12)$$

where r is the distance between nuclei A and B, and S is the integral of the overlap of the two initial atomic

single-electron wave functions

$$S(r) = \left| \int \Psi_A(V) \Psi_B(V) dV \right|.$$

Equation (11) should be used for large r and (10) for small r . Tables of molecular integrals,^{33,34} are useful in the calculation of S and of other molecular quantities.

Finally, we can single out the so-called NQ transitions, much less intense than the NV and due to transitions of electrons between a non-binding π -orbital and a binding or repelling σ orbital.^{7,26} These usually include the perpendicular Σ - Π transitions. Their low intensity is explained by the fact that the transition $np\sigma$ - $np\pi$ is forbidden in the combined atom (i.e., the atom whose nuclear charge is equal to the sum of the charges of the component nuclei). From the point of view of the AO method, the Q state corresponds to the initial wave functions of the neutral atoms. Not all the transitions of the valence electrons are of the NV or NQ type; thus, one cannot assign to these states transitions that are strong in the combined atom, if the molecular orbits of the outer electrons of the V and Q states are close to the atomic orbits of the latter. The NV and NQ transitions are of greatest practical interest, since they fall in the visible and ultraviolet regions of the spectrum.

In connection with the estimate of the oscillator strengths, we mention a theoretical paper by ter Haar,³² who established the following "sum rule" for single-electron transitions. If λ is the orbital quantum number, $\lambda = 0, 1, 2, \dots$, corresponding to $\sigma, \pi, \delta \dots$ states, and if by the selection rules $\Delta\lambda = 0, \pm 1$, then

$$\sum_{\Delta\lambda=\pm 1} f_e = \frac{1 \pm \lambda}{3}, \quad \sum_{\Delta\lambda=0} f_e = \frac{1}{3}, \quad (13)$$

where the summation is over all the transitions of the electron from the given molecular orbit to all the others. Individual oscillator strengths can be either positive (in absorption) or negative (in emission).

Table I lists the theoretically calculated oscillator strengths with an indication of the method employed and the corresponding literature reference.

3. EXPERIMENTAL DETERMINATION OF OSCILLATOR STRENGTHS

The experimental values of the oscillator strengths are frequently quite indeterminate, owing to the following principal difficulties. If $k(\nu)$ is experimentally determined with the aid of formula (1), the resolving power of the instrument and the presence of a rotational band structure are of appreciable significance.¹⁰ If the values of l are not too small, total absorption takes place in the maxima of the rotational lines. Consequently, if the resolving power is low, the change in the intensity in the transmitted radiation is determined, depending on the pressure p and on l , by the regions with minimal $k(\nu)$, and

$$-\frac{1}{l} \ln \left[\frac{I_\nu}{I_{\nu_0}} \right]_{\text{av}}$$

may prove to be less than $(1/l)k_{\text{av}}(\nu)$ by a factor of several times ten. We can assume that

$$(e^{-\xi k(\nu)l})_{\text{cp}} \approx e^{-\xi k_{\text{av}}(\nu)l} \quad (1a)$$

only when the rotational lines overlap, when the resultant spectrum is continuous, or when l is small, so that even at the maxima of the rotational lines we have

$$\xi k_{\text{max}}^{\text{rot}}(\nu)l \ll 1, \quad (14)$$

and

$$\left(\frac{I_\nu}{I_{\nu_0}} \right)_{\text{av}} \approx \xi k_{\text{av}}(\nu)l. \quad (1b)$$

In the latter case (absence of self absorption), Eq. (7) is also simplified and becomes

$$I_\nu \approx B_\nu \xi k(\nu)l. \quad (7a)$$

If emission in a certain interval $\Delta\nu$ is considered, the quantity $k(\nu)$ in (7) and (7a) can be replaced by its value (6)^{4,5,12} only if the rotational lines overlap or if the values of l satisfy (14). It is also easy to verify^{11,2} that if (14) is satisfied the intensity of the light absorbed or emitted in the vibrational band is respectively

$$I_{\nu', \nu''}^{\text{abs}} = D'' n'' R_e^2 q_{\nu', \nu''}^{\nu \nu'} G', \quad (1c)$$

$$I_{\nu', \nu''}^{\text{em}} = D' n' R_e^2 q_{\nu', \nu''}^{\nu \nu''} G', \quad (7b)$$

where D' and D'' are constants that depend on the choice of the system of units and on the geometrical characteristics of the experimental setup; n'' and n' are the concentrations of the absorbing and emitting molecules, respectively.

The electronic oscillator strength can be determined by measuring the coefficient of absorption in an individual rotational line, provided the vibrational and rotational transition probabilities are known. Since the resolving power is usually insufficient to separate the individual portions of the rotational lines, appreciable corrections must be introduced in such measurement.¹⁰ Examples of such calculations can be found in references 160, 177, and 17 (in the last work we repeated the numerical calculations, which take account of the insufficient resolving power, and obtained the same result).

In some cases f_e^{abs} can be obtained from low-resolution measurements if the exact relative intensities and contours of the rotational lines are known.^{88, 226} But in this case it is necessary to know the impact half-width of the line and the arrangement of the rotational lines. Attempts to make the rotational lines overlap by adding broadening gas at high pressure may be unsuccessful. Thus, Weber and Penner⁸⁹ added helium at a pressure of several atmospheres in a determination of f_e^{abs} of the NO γ system; strangely enough, Beer's law, i.e., linearity of the function

Table I. Theoretical oscillator strengths of diatomic molecules^a

Molecules	Transition	Assumed value of f_e (A)	As-summed value of f_{abs}^{max}	Calculated f_{abs}^{max}	Method	f_e (abs)	Bibliography	Remarks	
H ₂	$B^1\Sigma_u^+ - X^1\Sigma_g^+$	0.74	99	98	MO	0.24	7	d	
	Lyman bands	0.74	99		MO	0.48	39	c	
	$C^1\Pi_u - X^1\Sigma_g^+$	b	0.74	99		AO	0.21	7	d
		c	0.74	99		AO	0.58	7	c
	Werner bands	b	0.74	104	106	MO	0.38	7	d
		c	0.74	104		MO	0.42	30	c
	$3\Sigma_g^+ - 3\Sigma_u^+$ continuum		0.74	104		AO	0.37	7	Transition to lower repulsion state; $R_2^+(r)$ and emissivity
						g		7, 40-43, 223	
	H ₂	$2p\sigma_u - 1s\sigma_g$	1.06	100		f	0.3	6	Upper state repulsive
								44, 50, 80, 65, 66	
$2p\sigma_u - 1s\sigma_g$		1.59	45.5		g, i, k, e	0.29		Coefficient of continuous absorption and emissivity at different T and ν	
$2p\pi_u - 1s\sigma_g$		1.59	114			0.48		Small energy minimum in the upper state	
$3p\sigma_u - 1s\sigma_g$			1.59	143			4.1-10 ³		Upper state repulsive
$3d\pi_g - 1s\sigma_g$		1.59	148			7.6-10 ⁻⁷		Small energy minimum in the upper state	
						1.55-10 ⁻³			
						4.4-10 ⁻⁴			
						0.10			
$3d\sigma_g - 2p\sigma_u$		1.59	93.4			0.29	44, 87, 45-49, 35, 50-53, 56, 58	Both states repulsive	
$3d\pi_g - 2p\sigma_u$		1.59	102			0.28		Small energy minimum in the upper state	
						0.016			
						0.15			
$3d\sigma_g - 2p\pi_u$		1.59	28.0			0.10		Both states repulsive	

Molecules	Transition	Assumed value of f_e (A)	As-summed value of f_{abs}^{max}	Calculated f_{abs}^{max}	Method	f_e (abs)	Bibliography	Remarks		
H ₂	$3d\pi_g - 2p\pi_u$	1.59	34.0			0.31		Upper state repulsive		
						~3.8-10 ⁻⁴				
	$3s\sigma_g - 2p\pi_u$		1.59	48.7			~0.15		Both states repulsive	
							~0.016			
	Photoionization	$1s\sigma_g, 2s\sigma_g, 3s\sigma_g$	1.59	21.9			~0.15	46, 35	Reference 35 contains also a calculation of the polarizability	
	HeH ⁺	$2p\sigma - 1s\sigma^n$	1.59	251		g, i, k, n	0.053		Small energy minimum in the upper state	
		$2p\pi - 1s\sigma$		1.59	332			0.30		Both states repulsive
								0.051		
$3d\sigma - 1s\sigma$			1.59	364			0.074		Upper state repulsive	
							0.13	87, 61-64, 67		
$2s\sigma - 2p\sigma$			1.59	99			0.013	54, 55, 57, 288	Lower state with small minimum of potential energy	
							0.31			
HI		$1\Sigma^+ - X^1\Sigma^+$	1.60	78		MO	0.96	7	b	
		$3,1\Pi - X^1\Sigma^+$	1.604		48	MO	0.10	6, 7		
		1.604			AO	0.057	7			
HBr	$3,1\Pi - X^1\Sigma^+$	1.414		55	MO	0.113	6, 7			
		1.414			AO	0.057	7			
HCl	$3,1\Pi - X^1\Sigma^+$	1.275		62 (?)	MO	0.12	6, 7			
		1.275			AO	0.059	7			
HF	$3,1\Pi - X^1\Sigma^+$	0.917		70 (?)	MO	0.059	7			
		0.917			AO	0.015	7			
I ₂	$1\Sigma_u^+ - X^1\Sigma_g^+$	2.66	56		MO	1.21	7	e		
	$3,1\Pi_u - X^1\Sigma_g^+$	2.667		18.5	MO	1.9-10 ⁻²	7			
		2.667		(cf. ref. 84)	AO	4.8-10 ⁻³	7			

Table I. (cont'd)

Molecules	Transition	Assumed value of r_e (Å)	Assumed ν_{abs} max	Calculated ν_{abs} max	Method	f_e^{abs}	Bibliography	Remarks
Br ₂	$1\Sigma_u^+ - X^1\Sigma_g^+$	2.28	(64)		MO	1.00	7	e
	$3,1\Pi_u - X^1\Sigma_g^+$	2.284		23 (cf. ref. 84)	MO	$2.1 \cdot 10^{-2}$	6, 7	
		2.284			AO	$6.0 \cdot 10^{-3}$	7	
Cl ₂	$1\Sigma_u^+ - X^1\Sigma_g^+$	1.98	(72)		MO	0.83	7	e
	$3,1\Pi_u - X^1\Sigma_g^+$	1.983		31 (cf. ref. 84)	MO	$2.1 \cdot 10^{-2}$	7	i
		1.983			AO	$4.7 \cdot 10^{-3}$	7	
F ₂	$1\Sigma_u^+ - X^1\Sigma_g^+$	1.435	(80)?		MO	0.45	7	e
	$3,1\Pi_u - X^1\Sigma_g^+$	1.435		34.5 (cf. ref. 84)	MO	$2.2 \cdot 10^{-3}$	6, 7	i
		1.435			AO	$2.2 \cdot 10^{-4}$	7	
BH	$A^1\Pi - X^1\Sigma^+$	1.232		22	MO and AO ^m	0.07—0.12	220	
CH	$A^2\Delta - X^2\Pi$	1.12		23	AO, MO	0.0018	72	In accordance with the experimental f_e^{abs} (OH) = $1.2 \cdot 10^{-3}$ See also discussion in ref. 76 See also ref. 176
	$B^2\Sigma^- - X^2\Pi$	1.118	23.2	MO and AO ^m ₃	0.010—0.014	220	73	
					0.008—0.002	74		
	$C^2\Sigma^+ - X^2\Pi$	1.12		27.2	MO and AO ^m	0.008—0.018	220	
	1.12		30.4	MO and AO ^m	0.007—0.010	220		
NH	$A^3\Pi - X^3\Sigma^-$	1.04		30	AO, MO	0.0029	72	In accordance with the experimental f_e^{abs} (OH) = $1.2 \cdot 10^{-3}$
		1.04		MO, AO ^m	0.009—0.019	220		
OH	$A^2\Sigma^+ - X^2\Pi$	0.971		33	MO	$4.3 \cdot 10^{-3}$	7	c
		0.971			AO	$6.1 \cdot 10^{-4}$	7	
		0.971			MO, AO ^m	$2 \cdot 10^{-3}$ — $4 \cdot 10^{-3}$	220	
		0.971			MO, AO ^m	~ 0.1	220	
B ₂	$A^3\Sigma_u^- - X^3\Sigma_g^-$	1.59	30.6	30	h	0.077	68	Without allowance for hybridization

Molecules	Transition	Assumed value of r_e (Å)	Assumed ν_{abs} max	Calculated ν_{abs} max	Method	f_e^{abs}	Bibliography	Remarks
C ₂	$A^3\Pi_g - X^3\Pi_{u,g}$ Swan bands	1.29	19	20	h	0.029	77	Without hybridization and orthogonalization In different approximations $f_e^{abs} = 0.02-0.03$; k c In accordance with the experimental f_e^{abs} (CN) = 0.081 i Orthogonalization and hybridization Without hybridization and orthogonalization In different approximations $f_e^{abs} = 0.03-0.4$; k c
		1.31	19.4		MO	0.13	78	
		1.31	19.4		MO, AO, MO	0.18, 0.075	79, 80, 72	
	$c^1\Pi_g - b^1\Pi_u$, Deland-D'Asambuch system	1.29	26	26	h	0.039	77	
		1.32	26		MO	0.17	78	
		1.32	26		MO	0.23	79, 80	
Li ₂	$A^1\Sigma_u^+ - X^1\Sigma_g^+$	2.65		15	MO	~0.51	71	i, k, c i, k, c
		2.65		MO	~0.49	71		
	$B^1\Pi_u - X^1\Sigma_g^+$	2.65		21	MO	~1.00	71	
		2.65		MO	~0.66	71		
N ₂	$C^3\Pi_u - B^3\Pi_g$, Positive system II	1.18	30	32	h	0.033	77	
N ₂ ⁺	$B^2\Sigma_u^+ - X^2\Sigma_g^+$, Negative system I	1.117	26	26	MO, f	0.04	82	See also ref. 176 In different approximations $f_e^{abs} = 0.025-0.3$; k c
		1.117	25.5		MO	0.12	78	
		1.117	25.5		MO	0.18	79, 80	
Na ₂	$A^1\Sigma_u^+ - X^1\Sigma_g^+$	3.08	14.7	16	h	0.039	68	Without allowance for hybridization
		1.78	14.7		h	0.26	69	
		~3.08	14.7		MO	~0.2	70	Within the limits $f_e^{abs} = 0.03-0.6$; c, i, k

Table I. (cont'd)

Molecules	Transition	Assumed value of r_e (Å)	Assumed ν_{\max}^{abs}	Calculated ν_{\max}^{abs}	Method	f_e^{abs}	Bibliography	Remarks
O ₂	$B^3\Sigma_u^- - X^3\Sigma_g^-$	1.20	69	69	MO	0.27	7	^e See also ref. 176
	Schumann-Runge system	1.24	69		MO	0.01-0.9	83	Different MO approximations

Remarks. a) At small relative shift of potential curves, ν_{\max}^{abs} has been obtained with the aid of reference 6, assuming a harmonic oscillator and using the Franck-Condon principle; at large shifts, the calculated values of the Franck-Condon factors¹⁻³ were used. The parentheses contain the values of ν_{\max}^{abs} of the unobserved spectra. ν_{\max}^{abs} is given everywhere in units of 10³ cm⁻¹. b) By the formula $R_e = (R_e^{\text{AO}} + R_e^{\text{MO}})/2$, where R_e^{MO} and R_e^{AO} are taken from (10) and (11). c) From the dipole velocity (3a). d) In reference 7 - comparison with the experimental data on dispersion and polarizability. e) From the formula $R_e = R_e^{\text{MO}}/2$, where R_e^{MO} is taken from (10). f) By formula (12). g) Exact two-center wave functions. h) Single-electron approximation of the type H₂⁺. i) Calculation for various r . k) Comparison with f_e^{abs} (LCAO MO), calculated in various approximations. l) For perpendicular transitions - strong dependence of $R_e^2(r)$. m) AO with further account of the "interatomic correlation interaction" as proposed by Holley. n) In reference 64 is given the electron probability of the transition $2p\sigma - 1s\sigma$, $\text{He}^{++} + \text{H} \rightarrow \text{He}^+ + \text{H}^+ + h\nu$ as a function of ν .

$$\varphi(pl) = - \int \log \left[\frac{I_\nu}{I_{\nu_0}} \right]_{\text{av}} d\nu,$$

where the integral was taken over the vibrational band, was satisfied. Nonetheless, the $\psi(x)$ lines did not pass through the origin, meaning that no overlap of the rotational bands was achieved and that the actual oscillator strength could be many times greater than the resultant value, $f_e^{\text{abs}} = 0.0025$ (cf. references 88, 226). It is also difficult to employ Beer's law at low values of pl , at which (14) is satisfied, owing to the very weak absorption.

In references 100, 114, 115, 125, 134, and 150 and others, a light source with a line spectrum was used to measure the coefficient of absorption of the continuous spectrum (photoionization, photodissociation). However, the measurements were again carried out in regions where discrete bands were superimposed on the continuous spectrum. In these regions, naturally, a considerable spread in the measurement results was observed, and the true coefficient of absorption could not be determined from these results.

It is obvious that a direct measurement of the intensity of emission of gases in a discharge can hardly be used to determine f_e , since the concentrations of the excited molecules are not known, and all the more since the system may not be in thermodynamic equilibrium.

In the analysis of measurements of absorption and emission of gases heated to high temperatures in shock tubes^{5,81,37} it is usually assumed that the rotational lines completely overlap, owing to impact and Doppler

broadenings or owing to fulfillment of (14). This, however, does not always take place. The main difficulty is that the quantity measured is usually the emission from a mixture of components, and that the same overall intensity can be produced by a rather wide choice of individual oscillator strengths. In addition, the temperatures of the radiating gases, measured in reflected shock waves, are always subject to error because it is difficult to account for the energy losses in inelastic reflection. This may cause the values of f_e to be in error by a factor of several times, owing to the sharp temperature dependences of the component concentrations and of the absorption cross sections. A special study is also needed to ascertain whether thermodynamic equilibrium obtains.

Nor is the value of f_e determined from the lifetime τ of the upper electronic state sufficiently reliable. The transition to the lower state may be in the form of a cascade, depending on the excitation conditions. The quantity measured in this case is only one value of the time, pertaining to transitions between different electronic states, if the time corresponding to one of the electronic states can be singled out at all.

Neglect of the rotational structure of the vibrational bands can lead to serious errors in the measurement of either the absolute or the relative intensities, in particular in an experimental determination of the function $R_e^2(\nu)$ with the aid of formulas (1c) and (7b). We note that the data of Nicholls²² concerning a sharp dependence of R_e^2 on ν for the Schumann-Runge bands of the O₂ molecule are based on the erroneous meas-

urements of Ditchburn and Heddle.^{17,23,12} The influence of the rotational structure of the bands in other cases, such as the γ system of NO^{14} , positive system I of N_2 (reference 24) and others, is not known. In particular, we mention a paper unavailable to us,¹⁵ in which doubts are raised concerning the correctness of the theoretical and experimental data for positive system I of N_2 (see also reference 136).

Obviously, therefore, in spite of the decisive significance of an experimental measurement of f_e , a thorough analysis of the experimental conditions with use of the theoretical data is necessary in each case. Let us consider briefly the principal experimental results for individual molecules.

Oxygen, O_2 . The absorbing system in the visible and ultraviolet portions of the spectrum is the Schumann-Runge system, the principal part of which is situated at low temperatures in the continuous photodissociation spectrum. It is therefore relatively easy to obtain the total value of $\int k(\nu) d\nu$, which gives $f_e^{\text{abs}} = 0.16$ for the oscillator strength.¹⁰³ Using the data of Ditchburn and Heddle,¹⁷ who measured the oscillator strengths of the vibrational bands of the Schumann-Runge system, Nicholls²² derived a dependence of R_e^2 on ν . However, the data of Ditchburn and Heddle^{17,120} for the discrete portion of the spectrum were in error both in absolute and in relative magnitude^{12,23} (see also footnote 2). Bethke²³ measured the oscillator strength of the Schumann-Runge bands in absorption, adding argon with total pressure up to 125 atm, and found from the oscillator strength of the (0, 0) band ($\nu \sim 49,400 \text{ cm}^{-1}$), in accordance with (5), a value $f_e^{\text{abs}} = 0.16$. The calculated values of f_e^{abs} decrease, with increasing ν , i.e., on going to larger v' , up to $v' = 15$, for which f_e^{abs} decreases by a factor of four.

This change in f_e^{abs} is apparently due to the use of incorrect Franck-Condon factors,* since $f_e^{\text{abs}} \approx 0.16$ at still larger values of ν , corresponding to the photodissociation region. Adding to this the measurements of absorption¹²¹ and emission^{5,12,234} in a shock tube, we obtain as the most probable plot of $R_e^2(\nu)$ the curve shown in Fig. 3.[†] References 90–130 list the works devoted to absolute measurements of the intensity in O_2 .[‡] Ladenburg and co-workers^{16,24} measured the refractive index directly in the region $\lambda = 5900 - 1920 \text{ \AA}$, and found an empirical formula similar to (9), with $f_1 = 4.0 \times 10^{-5}$ and $(\nu)_{\text{max}}^{(1)} \sim 52,600 \text{ cm}^{-1}$ (transition $v'' = 0 \rightarrow v' = 5$ of the Schumann-

*This may be due to the unsuitability of the Morse model for the potential curve of the upper state (see also table of Franck-Condon factors^{117,234}).

†More recent data on the absolute values of $R_e^2(\nu)$ are contained in reference 232.

‡Noteworthy among these are the investigations of Meyer,⁹⁶ Heilpern,⁹⁷ Herman,⁹⁹ Robin^{110,240} and the series of researches by Dianov-Klovov⁹⁸ who consider the change of the coefficient of absorption in forbidden electronic transitions with increasing pressure and on going to the liquid state of O_2 .

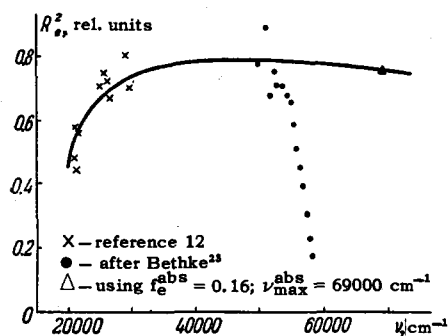


FIG. 3. Dependence of the square of the electronic moment of the transition of the O_2 molecule in the Schumann-Runge system (in atomic units) on the wave number.

Runge system); $f_2 = 0.202$ and $\nu_{\text{max}}^{(2)} \sim 68,200 \text{ cm}^{-1}$ (the Schumann-Runge continuum); $f_3 = 5.93$, $\nu_{\text{max}}^{(3)} \sim 184,000 \text{ cm}^{-1}$ (ionization continuum). Stueckelberg⁹⁰ gives a theoretical calculation of the coefficient of absorption of the Schumann-Runge continuum, and the remaining papers report measurements of the coefficient of absorption in the ultraviolet and extreme ultraviolet (see Table II).

Nitrogen, N_2 . The best known nitrogen systems are positive I (for which, however, there are neither theoretical nor reliable experimental data on the intensities), positive II, and the systems of Lyman-Borge-Hopfield and Begard-Kaplan. The oscillator strengths of the last three systems were determined from the experimental lifetimes τ . To exclude the possibility of a cascade process, the measured value of τ for $\text{N}_2(2^+)$ and of the ion $\text{N}_2^+(1^-)$ was extrapolated¹⁴⁰ to the energy of the exciting electron beam, an energy corresponding to the excitation threshold of the considered electron levels, but the authors noted that this extrapolation was not sufficiently reliable. The oscillator strength of the ionization continuum was estimated¹³² from data on the dispersion. Measurements were also made^{5,30} of the radiation of air in a shock wave, but these data were insufficient for a final evaluation of the oscillator strength. Many investigations were devoted to the measurement of the coefficient of absorption in the extreme ultraviolet (see Table II). Astoin and Granier¹³⁸ measured the coefficient of absorption in the interval $\lambda = 1000 - 150 \text{ \AA}$ and compared the results of the earlier investigations.

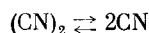
A very crude estimate^{141,144} of the oscillator strengths of the forbidden transitions can be made on the basis of the value of pI necessary to be able to photograph the forbidden electronic bands in absorption. We note also the work of Robin et al.²³⁵ on the measurement of the coefficient of absorption of nitrogen at $\lambda = 2000 - 3000 \text{ \AA}$ and at a pressure $\sim 500 \text{ atm}$.

Nitrogen oxide, NO . Measuring the absorption in the vibrational bands of NO mixed with helium at pressures up to 30 atm, Weber and Penner⁸⁹ obtained the value $f_{ey}^{\text{abs}} = 0.0025$ for the γ system of NO . In an analogous investigation, Bethke¹⁵⁴ obtained $f_e^{\text{abs}} = 0.0015$ and $f_{ey}^{\text{abs}} = 0.0024$ (argon was added, with a

total pressure up to 60 atmospheres). Bethke also measured the intensity of the bands produced by superposition of the γ , β , δ , and ϵ systems. By using their values of the oscillator strengths and by calculating the Franck-Condon factors for the δ and ϵ systems with the aid of the wave functions of the harmonic oscillator, we obtained from his measurements $f_{\epsilon\epsilon}^{\text{abs}} \sim f_{\epsilon\delta}^{\text{abs}} \sim 0.02$. As already noted, however, no complete overlap of the rotational lines was obtained, in spite of the considerable pressure. The actual oscillator strengths may therefore be much greater. Erkovich,⁸⁸ who measured the intensity with a low-resolution instrument, obtained an estimate $f_{\epsilon\gamma}^{\text{abs}} \sim 0.04$ from a calculation of the true contour of the band. A later paper by Erkovich²²⁶ contains data that contradict each other as well as those of his earlier work:⁸⁸ the tables of his article list the values $R_e \sim (0.11 - 0.14)$ atomic units for the β and γ systems, respectively, giving an oscillator strength $\sim 0.002 - 0.003$ for each system. At the same time, the text and the plot refer to a value $R_e \sim 0.7$ atomic units for the β system, corresponding to an oscillator strength ~ 0.1 .

It follows from the shock-wave data⁵ (Figs. 15a and b) that $f_{\epsilon\beta}^{\text{abs}} \approx 0.025^*$ (defining the oscillator strength as $f_e = 8\pi^2 mc R_e^2 G' \nu / 3h$, Keck et al.⁵ obtained $f_{\epsilon\beta} = 0.006 \pm 0.002$ in the interval $\lambda = 3500 - 5000 \text{ \AA}$). This is apparently the most reasonable value. Neglecting the rotational structure we obtain from Bethke's data $f_{\epsilon\beta}^{\text{abs}}/f_{\epsilon\gamma}^{\text{abs}} = 0.6$, while Marmo's data¹⁴⁷ on the ratio of the intensities of the γ - and β -system bands yield $f_{\epsilon\beta}^{\text{abs}}/f_{\epsilon\gamma}^{\text{abs}} = 4$. Taking these and the preceding results into account, as well as the results of a comparison with the data of reference 5, we must apparently assume tentatively $f_{\epsilon\gamma}^{\text{abs}} \lesssim 10^{-2}$.

The radical CN. The oscillator strength of the violet system of CN was determined by White,¹⁶⁰ who measured the absorption in the rotational lines of the violet system of CN, obtained in a short-duration discharge in C_2N_2 , and found $f_e^{\text{abs}} = 0.1 - 0.06$. The concentration of CN was calculated assuming full dissociation of the C_2N_2 . An indeterminacy is introduced here by the possibility of decomposition of the CN during the time of the experiment, which may lead to an overestimate of the CN concentration and accordingly to an overestimate of f_e^{abs} . White also investigated the reaction

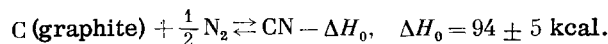


in an electric furnace at 1500°K , and determined with the aid of the value of f_e^{abs} , obtained in the earlier work, the dissociation energy $D(C_2N_2) = 146 - 138 \text{ kcal}$. On the contrary, by specifying a dissociation energy $D(C_2N_2) = 145 \text{ kcal}$,¹⁶⁵ chosen in accordance with the thermochemical data¹⁶⁵ and $D(CO) = 11.11 \text{ ev}$, $D(N_2) = 9.76 \text{ ev}$, $D(CN) = 7.5 \text{ ev}$ (Schmid, Gerö, and Zemplén²²³), White's results yield $f_e^{\text{abs}} = 0.081$ (see

*In the calculations we used the tables of equilibrium concentrations.¹⁵⁶ The calculation was based on formulas (6) and (7).

also reference 82). We can then determine tentatively the oscillator strength of the red CN system, by using the measurements of the relative emission intensity at $T = 2573^\circ \text{K}$ of the $(0, 0)$ band, [$\nu_{0,0} = 25,800 \text{ cm}^{-1}$] of the violet system¹⁶² and the $(2, 0)$ band [$\nu_{2,0} = 12,700 \text{ cm}^{-1}$] of the red system.¹⁶¹ We neglect the rotational structure, and apply formulas (5) and (7b). Taking the Franck-Condon factors from references 160 and 164 we obtain $(f_e^{\text{abs}})_{\text{red}} = 0.0131$ and $(f_e^{\text{abs}})_{\text{v}} \approx 1.1 \times 10^{-3}$, contradicting the estimate* $(f_e^{\text{abs}})_{\text{red}} \sim (f_e^{\text{abs}})_{\text{v}}$, given by Herzberg.^{162*} Thus, the choice of oscillator strengths is determined, in the final analysis, by the dissociation energy of CN and C_2N_2 .

Recently a new value has been proposed, $D(CN) = 8.1 \text{ ev}$ and accordingly $D(C_2N_2) = 116 \text{ kcal}$ (see the discussions in references 166 - 168 and 219). This choice is based principally on the work of Brewer, Templeton, and Jenkins,¹⁶⁸ who made optical measurements of the relative intensity of emission in the most intense portion of the violet $(0, 1)$ band of CN in a graphite tube in equilibrium with a definite amount of nitrogen ($p_{N_2} \sim 0.3 \text{ atm}$). It was assumed that the intensity of emission in the $(0, 1)$ band is proportional to the concentration of the excited CN molecules [formula (7b)]. Measurements in the temperature interval $T = 2500 - 2900^\circ \text{K}$ yielded the following value of the reaction heat



Assuming $D(N_2) = 9.76 \text{ ev}$ (225 kcal) and the sublimation heat of carbon to be $L(C) = 7.37 \text{ ev}$ (170 kcal), we obtain $D(CN) = 8.2 \pm 0.3 \text{ ev}$. On the basis of this work, Gaydon uses in the new edition of his book¹⁶⁶ a new value of dissociation energy for CN, and thereby casts doubts on the results of Schmid, Gerö, and Zemplén.²²³ Doubts are also cast on the accuracy of the experimental measurements of White, since it would follow from $D(C_2N_2) = 116 \text{ kcal}$ that $(f_e^{\text{abs}})_{\text{v}} = 6.5 \times 10^{-4}$. But this value of f_e^{abs} clearly contradicts the theoretical estimate of Mulliken,¹⁶⁰ who obtained $(f_e^{\text{abs}})_{\text{v}} \sim 0.1$. At the same time, if we assume, to the contrary, that White's first work with $(f_e^{\text{abs}})_{\text{v}}$, which agrees with the theoretical estimate, is correct, it becomes difficult to understand how the second work, carried out with the same apparatus, with spectral instruments of the same resolving power, and with approximately the same absorption intensity, can cause a hundred-fold error in the determination of $\int k(\nu) d\nu$.

A major shortcoming of the work of Brewer et al. is the assumed proportionality of the intensity of emission and concentration of CN [formula (7b)]. Owing to self absorption, the intensity of emission changes with the temperature in the rotational lines, more slowly than the concentration of CN, so that the dis-

*The value $(f_e^{\text{abs}})_{\text{red}} = 0.02$, given in references 227 and 229, was not determined experimentally, but proposed on the basis of Herzberg's estimate and an analogy with other molecules.

Table II. Experimental oscillator strengths

Molecules	Transition	ν_{\max}^{abs}	ν_{\max}^{em}	f_e^{abs}	Experimental value of τ (sec)	Bibliography	Remarks
HI	$1,^3\Pi - X^1\Sigma^+$, continuum	45		0.012		202, 205, 207	d In ref. 205—also D(I). Individual absorption bands at $\nu \sim 55-70$. See ref. 202
HBr	$1,^3\Pi - X^1\Sigma^+$, continuum	55		0.035		202, 206, 208	d In ref. 206—also D(Br). Individual absorption bands at $\nu \sim 65-75$. See ref. 202
HCl	$1,^3\Pi - X^1\Sigma^+$	65		0.044		202, 203	d Continuum
HF	continuum					201	K (ν) in the interval $\nu = 60.5-66.5$
\bar{I}_2	$1,^3\Pi_u - X^1\Sigma_g^+$	18.5		~ 0.015		7, 84, 188, 190-194, 25, 186, 197, 199, 200, 209	d Continuum and bands, in ref. 200, $\int k(\nu) d\nu$ for $\lambda = 9000-4000$ Å. For vibrational analysis see refs. 186, 190, 198, 104
	$^3\Sigma_u^+ - X^1\Sigma_g^+$, continuum	~ 37		$\sim 5.4 \cdot 10^{-4}$		186, 209	d
Br ₂	$1,^3\Pi_u - X^1\Sigma_g^+$, continuum and bands	23		$\sim 4 \cdot 10^{-3}$		7, 84, 21, 25, 187, 189, 191, 195-197	d In ref. 21—from anomalous dispersion in the rotational lines
				0.76		185, 189	d Absorption in interval $\nu = 47-54$
Cl ₂	$1,^3\Pi_u - X^1\Sigma_g^+$	31		$\sim 2 \cdot 10^{-3}$		7, 84, 191, 199	d Continuum
F ₂	$1,^3\Pi_u - X^1\Sigma_g^+$	34.5		$\sim 4 \cdot 10^{-4}$		7, 84	d Continuum
H ₂	Ionization continuum	~ 136		0.69-0.79		114, 169-174	In ref. 169—by dispersion. Transition between the excited states (continuum) etc, see also refs. 7, 43, 109, 175 and 225.
He ₂	$2^3\Sigma_u^+$						> 0.05
Hg ₂	$^3\sigma_u^-$						210, 211 Measurement of lifetime in metastable state
CH	$A^2\Delta^+ - X^2\Pi$	23		0.06 (?)			75, 76 Latest measurements of lifetime in CH and NH, see ref. 241
OH	$A^2\Sigma^+ - X^2\Pi$	33		$1.2 \cdot 10^{-3}$			See discussion
Li ₂	$A^1\Sigma_u^+ - X^1\Sigma_g^+$	15		About 0.3			184 Anomalous dispersion in rotational lines
CN	$B^2\Sigma^+ - X^2\Sigma^+$ (violet system)	26		0.081 (?)			6, 82, 160 f_e^{abs} taken in accordance with $D(C_2N_2) = 145$ kcal
	$A^2\Pi - X^2\Sigma^+$ (red system)	10		$1.1 \cdot 10^{-3}$ (?)			161-164 From ratio of intensities of emission of red and violet systems at $T = 2573^\circ\text{K}$ without allowance for rotational structure.
CO _g	continuum	ORO- JO 190		2.8			158 Absolute measurements for different electronic systems, see also refs. 120, 122, 139, 157, 159.
NO _f	$B^2\Pi - X^2\Pi$ (β -system)	~ 55		0.025 (?)			See discussion See also refs. 4, 227, 130
	$A^2\Sigma^+ - X^2\Pi$ (γ -system) continuum	~ 50		$\leq 10^{-2}$ (??)			The same Measurements of $k(\nu)$. See also refs. 120, 122, 130

Table II. (cont'd)

Molecules	Transition	ν_{\max}^{abs}	ν_{\max}^{em}	f_e^{abs}	Experimental value of τ (sec)	Bibliography	Remarks
N_2^e	$C^3\Pi_u - B^3\Pi_g$	32	28	0.048	$4.48 \cdot 10^{-8}$	140, cf. also ref. 5	Positive system II. Excitation by electron impact
	$A^3\Sigma_u^+ - X^1\Sigma_g^+$	67	36 (cf. ref. 142)	$< 6.6 \cdot 10^{-7}$	$> 10^{-2}$	139, 142	Vegard-Kaplan system. Excitation with electron impact. See Lichten's correction ¹³⁹
				$2.9 \cdot 10^{-5}$	$2.3 \cdot 10^{-4}$	135	
				$1.23 \cdot 10^{-7}$		141, 144	b
	$a^4\Pi_g - X^1\Sigma_g^+$	75 (cf. ref. 137)	54	$8.8 \cdot 10^{-6}$	$1.7 \cdot 10^{-4}$	139	Lyman-Berge-Hopfield system. Excitation with electron impact; magnetic dipole transition. See also refs. 105 and 137
				$1.36 \cdot 10^{-6}$		141, 144	b Electric quadrupole transition
				$4.4 \cdot 10^{-8}$		141, 144	b
	$a^1\Sigma_u^- - X^1\Sigma_g^+$	80 (cf. ref. 139)		$6.6 \cdot 10^{-8}$		141, 144	b
	$B^3\Sigma_u^- - X^1\Sigma_g^+$	80 (cf. ref. 139)		$6.6 \cdot 10^{-8}$		141, 144	b
	$X^1\Sigma_g^+$	89 (cf. ref. 139)		$1.6 \cdot 10^{-6}$		141, 144	b
	$C^3\Pi_u - X^1\Sigma_g^+$	cf. ref. 139		$1.6 \cdot 10^{-6}$		141, 144	b
	continuum	~ 140		3.3		120, 121, 128, 132, 134, 138, 109	The dispersion was measured in ref. 132.
						93, 94, 101, 104, 105, 108, 109, 114, 116, 120, 122, 125, 126, 133, 134, 137, 138, 143	Measurements of the coefficient of absorption $k(\nu)$
N_2^+	$B^2\Sigma_u^+ - X^2\Sigma_g^+$	27	25	0.040	$6.5 \cdot 10^{-8}$	140, cf. also ref. 5	Negative system I. Excitation with electron impact

Molecules	Transition	ν_{\max}^{abs}	ν_{\max}^{em}	f_e^{abs}	Experimental value of τ (sec)	Bibliography	Remarks
O_2^e	$B^3\Sigma_u^- - X^3\Sigma_g^-$, Schumann-Runge system	~ 69		0.16-0.20		5, 12, 16, 91, 92, 110, 112, 102, 124, 103, 106, 113, 232, 236	Emission, absorption, dispersion. In refs. 111 and 112—calculation of the probability of emission from individual bands (see also refs. 105, 120, 122)
	Ionization and dissociation continuums	~ 180		6-6.9		16, 92, 100, 113, 115, 124, 127	Absorption and dispersion (see also refs. 105, 120, 130)
	$b^1\Sigma_g^+ - X^3\Sigma_u^-$, atmospheric bands	13.1	13.1	$\sim 4.2 \cdot 10^{-10}$ $\sim 3 \cdot 10^{-10}$	~ 7 ~ 10	128, 129, 123	See also refs. 212-214

Remarks to Table II. a) See remark a) of Table I. b) Approximate estimate from the value of pl , necessary for photography of the bands. c) In the calculation we used the Franck-Condon factors which were graciously supplied to us by I. T. Yakubov. d) f_e^{abs} was estimated from $\int k(\nu)d\nu$. e) See also refs. 131, 143, 237. f) See also refs. 143, 237. g) In ref. 231 there is also an estimate of the lifetime of the metastable state $a^3\Pi$.

sociation energy is overestimated. Our own calculation has shown that when $D(\text{CN}) = 7.5 \text{ eV}$ and $(f_e^{\text{abs}})_v = 0.081 - 0.04$, calculation by means of the approximate formula (7b) instead of the exact formula (7) leads precisely to an overestimate of $D(\text{CN})$ by $\sim 0.7 - 0.4 \text{ eV}$ respectively. The data on the doublet splitting have been taken here from reference 160, and the impact half width has been calculated from the gas-kinetic cross section $\sigma = \pi r^2$ at $r = 2 \text{ \AA}$. The value of the latter hardly influences the final results, and the deviation from the case $\sigma \sim 0$ can in general be neglected. When $D(\text{CN}) = 8.2 \text{ eV}$ and $(f_e^{\text{abs}})_g = 6.5 \times 10^{-4}$, the overestimate is merely $\sim 0.1 \text{ eV}$. Thus, the results of Brewer et al. are not decisive in the choice of $D(\text{CN})$, although they furnish definite evidence in favor of $D(\text{CN}) = 7.5 \text{ eV}$, $(f_e^{\text{abs}})_v = 0.081$, and accordingly $(f_e^{\text{abs}})_{\text{red}} = 1.06 \times 10^{-3}$.

Hydroxyl, OH. Measurements on OH, by a method similar to that used by White for CN, were made by Avramenko and Kondrat'ev²³⁰ and, using better apparatus, by Oldenberg, Rieke, and Dwyer.^{177,178} A high-resolution spectrophotograph was used to measure the absorption in the rotational lines of the (0, 0) band of OH, the concentration of which in the mixture of water vapor and oxygen was calculated theoretically. By processing the results of the measurements obtained under different temperatures and concentrations of the initial components, Dwyer and Oldenberg¹⁷⁸ determined simultaneously f_e^{abs} and the heats of the different reactions in which OH was formed. The final values they give are $f_e^{\text{abs}} = 1.26 \times 10^{-3}$ and $D(\text{OH}) = 100.1 \pm 0.9 \text{ kcal}$ (4.34 eV). Repeating the measurements of Oldenberg et al., Dyne¹⁸¹ obtained only half the value of the oscillator strength, and raised doubts concerning the accuracy of the Oldenberg measurements (a more detailed report of his work is given in reference 227). Analyzing the measurement results, he also found that the impact broadening a (where $a = \Delta\nu_{\text{imp}} \sqrt{\ln 2} / \Delta\nu_{\text{Doppl}}$) should be less than the value obtained by Oldenberg et al. Were we to assume the value $D(\text{OH}) = 103 \text{ kcal}$,^{165,166,179,218} obtained by using the Borge-Sponer extrapolation, in the method of electronic impacts, etc.¹⁶⁶ and to recognize that the Oldenberg measurements were made at $T \sim 1750^\circ \text{K}$, we would obtain a suitably modified value $f_e^{\text{abs}} = 5.4 \times 10^{-4}$. Analyzing the photographs of a discharge produced in water vapor, Barrow^{216,217} investigated bands which he ascribed to the transitions $B^2\Sigma^+ - A^2\Sigma^+$ in OH. From this he found the $A^2\Sigma^+$ vibrational levels from $v = 0$ to a level with energy different from the dissociation limit by less than 300 cm^{-1} , from which follows that $D(\text{OH}) = 101.3 \text{ kcal}$. This value agrees with the measurement of Oldenberg et al. and is quite likely, since it leads to $f_e^{\text{abs}} = 8.9 \times 10^{-4}$. Hornbeck,¹⁸⁰ on the basis of a spectroscopical investigation of nine lower vibrational levels of OH, obtained by extrapolation $D(\text{OH}) = 106.7 \text{ kcal}$. This extrapolation, however, is quite indeterminate (only up to the dissocia-

tion limit of 19 levels) and can therefore not be regarded as final. Recently Carrington¹⁸² repeated the measurements with absorption of OH in a flame, in order to resolve the indeterminacy in the oscillator strength and the impact width. Using the most intense rotational lines, he determined by the growth-curve method an impact parameter $a = 0.06 \pm 0.06$ for $T \sim 2600^\circ \text{K}$, $p = 1 \text{ atm}$, at a molar composition 60% O_2 , 20% H_2O , and 20% CO_2 . At the same time he determined from the low-intensity rotational lines, corresponding to the linear portion of the growth curve, an oscillator strength $f_e^{\text{abs}} = 1.2 \times 10^{-3}$, which agreed within the limits of errors with the value of Oldenberg et al. In calculating the concentration of OH, he assumed the dissociation energy value determined by Barrow. Thus, the value $f_e^{\text{abs}} = 1.2 \times 10^{-3}$ can be regarded as final. We note that it is in good agreement with the theoretical estimates (Table I).

Halogens and hydrogen halides. There have been many measurements of the coefficient of absorption in the continuous spectra of halogens (Table II), both in the gaseous state and in solution. The oscillator strength is determined from the value of the integral coefficient of absorption $\int k(\nu) d\nu$. The principal difficulty in this case is that the continuous spectrum is the result of superposition of several electronic systems, to each of which corresponds an upper electronic state with a repulsion potential curve. The most intense in this case are the transitions that violate the spin conservation rule, $^3\Pi - ^1\Sigma_g^+$. The experimental absorption coefficients of individual components of the electronic bands, as well as the analysis of the potential curves I_2 , are contained in references 186 and 190. An analogous situation obtains for the continuous spectra in hydrogen halides, the oscillator strengths of which are listed in Table II.

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