Electronic transition probabilities and lifetimes of electronically excited states of diatomic molecules

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Recent results on the probabilities of electronic transitions of diatomic molecules are reviewed. Experimental methods for determining the absolute (S_e, $|R_e^{mn}|^2$, f_e^{mn}, $\tau_{nv'}$) and relative probabilities, the systematic classification and analysis of the data, and criteria of the reliability of the recommended values are discussed. The absolute and relative probabilities published up to and including 1977 have been collected and used to obtain recommended (most reliable) values of the band strengths $S_e(r_{v'v''})$ and oscillator strengths f_e^{mn} for more than 200 molecular systems. The experimental lifetimes $\tau_{nv'}$ are analyzed for more than 150 electronically excited states. Most reliable values are recommended for these lifetimes.

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1. INTRODUCTION

The probabilities of optical transitions are fundamental physical properties, which quantitatively determine the intensities in absorption and emission spectra. These probabilities are described by several related concepts, such as the Einstein coefficients, the band strengths, the matrix elements of the electronic-transition dipole moments, the oscillator strengths, and the lifetimes of the electronically excited states.

The most extensive systematic classification of the corresponding data for diatomic molecules published up to 1973 was given in the review by Kuznetsova *et al.*[1] In the years since then there has been a sharp increase in the number of papers on optical transition probabilities, because of improved experimental methods for determining the transition probabilities and the increasing importance of these results in such fields as quantum electronics, astrophysics, radiation gas dynamics, and the spectroscopy of flames, plasmas, and shock waves.

Since the publication of the review by Kuznetsova *et al.*,[1] several papers of a generalizing nature have appeared,[2-7] but none can claim to offer a complete systematic classification of the data. In some cases, these papers do not even judge the reliability of the transition probabilities recommended. The recommendations of Hefferlin *et al.*[3] on the oscillator strengths of certain diatomic molecules essentially ignore research over the last decade, and the attempts by this group[2,4] to find correlations among the matrix elements of the electronic transition (dipole) moments are also based on outdated experimental data and on theoretical transition probabilities which must be judged as no more than estimates, as has been pointed out many times in the literature. Hsu and Smith[7] examined the data for only a limited number of molecular transitions of astrophysical interest. In the two-volume handbook by Suchard and Melzer[5,6] there is detailed information on the electronic spectra and molecular constants of diatomic molecules, but the listings on the electronic transition probabilities are fragmentary, chosen at random.

A serious shortcoming of all the reviews which have been published previously is that there has been no joint review of the data on absolute and relative values of the various properties, with the goal of recommending normalized functional dependences of the band strengths on the internuclear distances, for which there is an obvious need in several technical applications. In the present review we attempt to fill this void. Specifically, (1) we have compiled and systematically classified all the factual data from experimental determinations of absolute and relative probabilities for electronic transitions of diatomic molecules published through 1977; (2) on the basis of a joint critical analysis of the data on the absolute and relative probabilities, we have identified most reliable values for the band strengths as functions of the internuclear distance; (3) we have normalized the recommended values to the absolute values, making use of all the reliable work on the absolute transition probabilities.

We emphasize that it is usually not a trivial matter to recommend most reliable values for the transition probabilities. The data in the literature are frequently contradictory, not simply because of the difficulties in ex-

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perimentally determining these probabilities but also because of different points of view regarding several fundamental questions: the concept of the electronic transition moment, the normalization of the Hönl–London factors, the best approximation of the electronic transition moment as a function of the internuclear distance, and several others. Accordingly, in Sec. 2 we will briefly discuss several theoretical points which would benefit most from some clarification, judging by the literature, and we will list the basic theoretical equations which are used to convert the published values of $\tau_{mv'}$, $f_{v'v''}$, f_e, and $|R_e|^2$ into the band strengths S_e.

The probability recommendations are developed by a common method, on the basis of several principles which are stated in Sec. 4. On the basis of our analysis we recommend most reliable values for the electron transition probabilities and the lifetimes of the corresponding electronically excited states for more than 200 molecular systems.

2. BASIC THEORETICAL EQUATIONS

In the Born–Oppenheimer approximation, the Einstein coefficient for an individual rotational line of an electronic-vibrational-rotational transition can be written (in using the term "rotational line" we mean the sum of the Zeeman components) in the form

$$A_{mv''J''}^{nv'J'}=\frac{64\pi^4}{3h}\nu^3\frac{|R_{v'v''}^{nm}|^2 S_{J'J''}}{2J'+1}, \tag{1}$$

$$R_{v'v''}^{nm}=\int \psi_{e'}^{n}\psi_{v'}M_e\psi_{e''}^{m}\psi_{v''}\,d\tau_e\,dr, \tag{2}$$

where $d\tau_e$ is the volume element in the electron configuration space.

Under the assumption that the electronic wave functions of the coupled states are relatively independent of the internuclear distance and under the assumption that the electronic moment operator M_e is independent of the internuclear distance, we obtain

$$|R_{v'v''}^{nm}|^2=|R_e^{nm}|^2 q_{v'v''}, \tag{3}$$

where $(q_{v'v''}=|\int\psi_{v'}\psi_{v''}dr|^2$ is the Franck–Condon factor, and $(R_{e'}^{nm}=\int\psi_{e'}^{n}M_e\psi_{e''}^{m}d\tau_e)$ is the matrix element of the transition dipole moment.

It has been shown in a series of experimental studies (reviewed in Refs. 1 and 8) that the assumption that the dipole-moment matrix element is indpendent of the internuclear distance [in accordance with (3)] turns out to be incorrect in several cases. In such cases there is the problem of taking into account the dependence of the dipole-moment matrix element on the internuclear distance, $R_e(r)$. Essentially no theoretical calculations of $R_e(r)$ have been carried out, and a variety of semiempirical methods have accordingly been proposed for determining $R_e(r)$ (Refs. 9–12, 14, 15, 18, 19). The r-centroid method has been the predominant method.[9-11] The more rigorous approximate approach for finding $R_e(r)$ which was proposed by Jain and Sahni (Ref. 14 and others), Cartwright,[18] and Rapoport *et al.*[19] has yet to be used in practice. The situation can be summed up well by noting that of the more than 190 studies of the function $R_e(r)$ which have been carried out over the past 20 years (see the fifth column in Table I) only a few have used this approximation.[14-19]

In the r-centroid approximation the following equation is used:

$$|R_{v'v''}^{nm}(r)|^2=|R_e^{nm}(r_{v'v''})|^2 q_{v'v''}, \tag{4}$$

where

$$r_{v'v''}=\int\psi_{v'}r\psi_{v''}d\mathbf{r}\Big/\int\psi_{v'}\psi_{v''}dr.$$

Despite the widespread practical use of the r-centroid approximation, doubts persist regarding its applicability.[8,13,19,20] In a recent series of papers,[21-31] there has been a systematic study of the rigorous criteria for the applicability of the r-centroid approximation. The most rigorous measure of the applicability of this approximation is that the following parameter be equal to unity:

$$\Phi_{v'v''}^{k}=\int\psi_{v'}r^k\psi_{v''}dr\Big/r_{v'v''}^{k}\int\psi_{v'}\psi_{v''}dr. \tag{5}$$

Using this criterion, Drake and Nicholls[21] showed that the r-centroid approximation is a good one for describing $R_e(r)$ for many classes of diatomic molecules: oxides, halides, and nitrides. For these molecules, the parameter $\Phi_{v'v''}^{k}$ differs from unity by no more than a few percent. It has been shown that of all the classes of diatomic molecules which have been studied only in the case of hydrides are there large errors in the behavior of $R_e(r_{v'v''})$.

Under the circumstances, all the $R_e(r)$ recommendations in the present paper are based on the r-centroid approximation, with the sole exception of the Br_2 molecule, for which this approximation is not known [because of the considerations explained below Table I shows the band strength as a function of the r-centroid, $S_e(r_{v'v''})$].

When the r-centroid approximation is used, the Einstein coefficient for a rotational line can be written in the form

$$A_{mv''J''}^{nv'J'}=\frac{64\pi^4}{3h}\nu_{J'J''}^{3}|R_e^{nm}(r_{v'v''})|^2 q_{v'v''}\frac{S_{J'J''}}{2J'+1}. \tag{6}$$

The Franck–Condon and Hönl–London factors which are found theoretically must satisfy certain normalization conditions. For the Franck–Condon factors, these conditions are

$$\sum_{v'}q_{v'v''}=\sum_{v''}q_{v'v''}=1. \tag{7}$$

The normalization of the Hönl–London factors has been the subject of a continuing discussion in the literature,[1,32-34,37] because there is no single sum rule for these factors. Various normalization methods have been used in the calculations of these factors:

$$\sum_{\Sigma'\Sigma''}\sum_{p'p''}\sum_{J'}S_{J'J}=K''(2J''+1),\quad \sum_{\Sigma'\Sigma''}\sum_{p'p''}\sum_{J''}S_{J'J''}=K'(2J'+1), \tag{8}$$

where Σ and p represent the components of the spin multiplet and the Λ doublet, while the quantities K are given by

$$K'=(2-\delta_{0,\Lambda'})(2S+1),\quad K''=(2-\delta_{0,\Lambda''})(2S+1), \tag{9a}$$

$$K'=K''=(2-\delta_{0,\bar{\Lambda}})(2S+1), \tag{9b}$$

$$K'=K''=(2-\delta_{0,\Lambda'+\Lambda''})(2S+1), \tag{9c}$$

in accordance with the normalization of Refs. 32, 33, and 37.

The single-valued relationship between the Hönl–London factors and the dipole-moment matrix elements deserves special mention. The use of Hönl–London factors normalized in different ways leads to different values of $|R_e(r_{v'v''})|^2$ which are found from measurements of the absolute intensities of rotational lines. It is thus suggested that the band strengths $S_e(r_{v'v''})$, which do not depend on the method used to normalize the Hönl–London factors, be reported instead of the matrix elements as a measure of the transition probabilities. These strengths are given by

$$S_e(r_{v'v''}) = \sum_{\Sigma'\Sigma''} \sum_{p'p''} |R_e(r_{v'v''})|^2 = K\,|R_e(r_{v'v''})|^2, \qquad (10)$$

where $K = K'$ or K'' is given in Eqs. (9a)–(9c).

It is useful to note that in most cases in which the transition matrix elements are used as measures of the probability these matrix elements are related to the band strengths in accordance with (10) and (9a). Here a distinction is made between the matrix elements in emission, R_e^{nm}, and those in absorption, R_e^{mn}:

$$|R_e^{nm}(r_{v'v''})|^2 = \frac{S_e(r_{v'v''})}{(2-\delta_{0,\Lambda'})(2S+1)}, \quad |R_e^{mn}(r_{v'v''})|^2 = \frac{S_e(r_{v'v''})}{(2-\delta_{0,\Lambda''})(2S+1)}. \qquad (11)$$

Several papers (e.g., Refs. 38–43) give transition matrix elements which are related to the band strengths in accordance with (10) and (9c).

In addition to the transition matrix elements, the quanquantities $\tau_{mv'}$, f_e^{mn}, $f_{v'v''}^{mn}$, f_e^{nm}, and $f_{v'v''}^{nm}$ are cited in the original papers as measures of the probability. These quantities can be expressed in terms of the band strength as follows:

$$\tau_{nv'}^{-1} = \frac{64\pi^4}{3h}\,\frac{1}{(2-\delta_{0,\Lambda'})(2S+1)} \sum_m \sum_{v''} S_e(r_{v'v''})\, q_{v'v''} \nu_{v'v''}^3, \qquad (12)$$

$$f_{v'v''}^{mn} = \frac{8\pi^2 mc}{3he^2}\, \nu_{v'v''} q_{v'v''}\, \frac{S_e(r_{v'v''})}{(2-\delta_{0,\Lambda''})(2S+1)}, \qquad (13)$$

$$f_e^{mn} = \frac{8\pi^2 mc}{3he^2}\,\frac{1}{(2-\delta_{0,\Lambda''})(2S+1)} \sum_{v'} S_e(r_{v'v''})\, q_{v'v''} \nu_{v'v''}, \qquad (14)$$

$$f_{v'v''}^{nm} = \frac{8\pi^2 mc}{3he^2}\,\frac{1}{(2-\delta_{0,\Lambda'})(2S+1)}\, S_e(r_{v'v''})\, q_{v'v''} \nu_{v'v''}, \qquad (15)$$

$$f_e^{nm} = \frac{8\pi^2 mc}{3he^2}\,\frac{1}{(2-\delta_{0,\Lambda'})(2S+1)} \sum_{v''} S_e(r_{v'v''})\, q_{v'v''} \nu_{v'v''}. \qquad (16)$$

Here ($64\pi^4/3h = 2.026 \cdot 10^{-6}$, $8\pi^2 mc/3he^2 = 3.037 \cdot 10^{-6}$, $S_e(r_{v'v''})$) is expressed in atomic units, $(a_0 e)^2$, and v is in reciprocal centimeters.

Unfortunately, the subscripts "*mn*" and "*nm*" are frequently omitted in the papers, making it difficult to interpret the results. This situation is yet another argument for describing the transition probabilities in terms of the band strengths $S_e(r_{v'v''})$, since these strengths are symmetric with respect to absorption and emission.

3. EXPERIMENTAL METHODS

The experimental methods for determining the band strengths can be classified arbitrarily into two large groups. The first is based on measurement of the absolute intensities in the electronic–vibrational–rotational spectra of diatomic molecules. The integrated emission coefficient for an isolated spectral line is

$$\int j_\nu\, d\nu = \frac{16\pi^3 c}{3}\, \nu_{J'J''}^4\, |R_e(r_{v'v''})|^2\, q_{v'v''}\, \frac{S_{J'J''}}{2J'+1}\, N_{nv'J'}. \qquad (17)$$

The corresponding equation for the integrated absorption coefficient of an isolated rotational line is

$$\int K_\nu\, d\nu = \frac{8\pi^3}{3hc}\, \nu_{J'J''}\, |R_e(r_{v'v''})|^2\, q_{v'v''}\, \frac{S_{J'J''}}{2J''+1}\, N_{mv''J''}. \qquad (18)$$

In Eqs. (17) and (18), ν is in reciprocal centimeters, $|R_e(r_{v'v''})|^2$ is in atomic units, $16\pi^3 c/3 = 3.22 \cdot 10^{-23}$, and $8\pi^3/3hc = 2.64 \cdot 10^{-18}$.

In these methods in which absolute intensities are measured, local thermodynamic equilibrium must prevail in the source of the molecular spectrum. This requirement is imposed because the overwhelming majority of diatomic molecules can be produced in substantial numbers only at high temperatures and only in mixtures with other atoms and molecules, so that in practice the concentrations of the molecules of interest in the initial state can be calculated only for conditions of local thermodynamic equilibrium. Only a few sources meet this equilibrium requirement: shock tubes, high-temperature furnaces, dc arcs, and certain types of flames, for example. These methods have the advantage that they yield the band strengths directly, and measurements of various electronic–vibrational bands reveal the behavior of S_e as a function of the r-centroid. The basic disadvantage of these methods is that the equilibrium composition in the source of the molecular spectrum must be calculated, and these calculations require thermodynamic functions of all the components of the hot gaseous medium. The reliability of the absolute probabilities determined by this method depends primarily on the validity of treating the plasma formed in the sources as an equilibrium plasma and on the accuracy of the thermodynamic functions used.

The second and largest group of methods for determining the band strengths is based on measurement of the lifetimes of excited states. The lifetime measurements consist essentially of a pulsed (periodic) population of the level of interest, followed by a determination of the parameters of the radiative-decay curve. To analyze the many versions of this method (the delayed-coincidence method, the phase-shift method, the beam–foil method, the Hanle-effect method, the rf-deflection method, and several others[35,36,375]) would go beyond the scope of the present review; we will restrict the discussion to certain aspects of these methods.

In experimental determinations of the lifetimes $\tau_{nv'}$, there are several difficulties peculiar to the methods. In those cases in which an electron beam is used for excitation it is difficult to arrange selective excitation of certain levels, and cascade population effects must be taken into account. A second difficulty is that the measured values of $\tau_{nv'}$ must be extrapolated to zero pressure, since radiative decay is accompanied by relaxation through collisions (the effect is to reduce the actual radiative lifetime) and by "trapping" of radiation (here the effect is to increase the radiative lifetime). Because of the complicated nature of the curves of the lifetime as a function of pressure, it is by no means a trivial problem to extrapolate to zero pressure. These effects make it necessary to carry out the investigations at low absolute concentrations of the molecules of interest, but then it becomes very difficult to measure the signals. In particular, it is not always possible to use spectrometric apparatus of adequate resolution. The superposition on the spectrum of interest of the spectra of other particles may be unavoidable in such cases, and it may lead to important systematic errors, in the same way that the extrapolation to zero pressure and the occurrence of cascade transitions do. In studies of metastable levels the diffusion of molecules out of the excitation zone must also be taken into account. Finally, we should emphasize the fundamental problem of distinguishing between τ_{rad} and τ_{pred}, which arises in a study of predissociation states.

The basic advantage of these methods is that they do not require knowledge of the number of radiating molecules [see (12)], so that it is possible to avoid the primary source of systematic error which afflicts the absolute-intensity methods. This is the reason why it is these methods which have been used recently to determine the transition probabilities of most diatomic molecules. These methods are becoming particularly attractive because of the development of a variety of mutually complementary versions of these methods and the widespread use of laser sources for selective excitation. Unfortunately, the lifetime-measurement methods are also inadequate in certain cases. In particular, the value of $S_e(r_{v'v''})$ for a particular transition can be determined from the measurement of $\tau_{rv'}$ only if the probabilities are known for all other transitions from the given electronic level to lower levels, as is obvious from (12). In such cases the most effective approach seems to be to combine the lifetime method with the more traditional method of measuring absolute intensities.

In addition to these two primary groups of experimental methods for determining the probabilities for electronic transitions of molecules, there have been so far a few attempts to use the Rozhdestvenskii hook method,[44-47] which is an interference method, and the method of measuring the energy lost by electrons as they are scattered by the molecules of interest.[48-51]

The experimental methods for determining the electronic transition strengths from the r-centroid can also be divided into two major groups. The first group involves a study of the relative intensities in the emission spectra. The excitation conditions are not necessarily equilibrium conditions in this case, since the populations N_i do not have to be known if the function $S_e(r_{v'v''})$ is determined in a progression of bands with v' =const:

$$S_e(r_{v'v''}) = \frac{16\pi^3 c}{3}\frac{J_{v'v''}\lambda^4_{v'v''}}{q_{v'v''}}N_{v'}^{-1}(2-\delta_{0,\Lambda'})(2S+1). \tag{19}$$

In a simultaneous analysis of the intensities of bands of different progressions, the relative values of $S_e(r_{v'v''})$ are referred to a common coordinate scale through a normalization in a common r-centroid interval by the approach described in Ref. 52. The superposition of bands from different progressions makes it very difficult to find reliable values for the relative intensities. This superposition problem can be alleviated to some extent by obtaining a spectrum under nonequilibrium conditions, with a low rotational temperature and with only a few rotational lines in each of the bands. As an example of this latter approach we can cite Best and Hoffman's study,[53] in which the strength of the $A^1\Sigma - X^1\Sigma$ transition of the BaO molecule as a function of the r-centroid is determined under the low-temperature conditions in the upper atmosphere. Other, extremely promising, approaches are to carry out the measurements at low rotational temperatures in the laboratory[38,54] and to study the resonance fluorescence excited by narrow-band lasers.[55] Yet another method for taking the band superposition into account in measurements of the relative intensities is to use the "synthetic line shape"[55-59] for analyzing the spectra.

A second method for determining how S_e varies with the r-centroid is to measure $\tau_{rv'}$ for various vibrational levels, but the function $S_e(r_{v'v''})$ determined in this way is relatively unreliable, as has been pointed out several times in the literature.[58,60] This method for finding $S_e(r_{v'v''})$ has not been adopted widely, and it is apparently only as an auxiliary method.

We emphasize that the reliability of the results obtained for $S_e(r_{v'v''})$ is governed not only by the accuracy of the experimental data but also by the reliability of the Franck–Condon factors and the r-centroids which are used.

4. GENERAL PRINCIPLES OF ANALYSIS AND RECOMMENDATIONS OF MOST RELIABLE VALUES FOR THE BAND STRENGTHS, THE VARIATION OF THESE STRENGTHS WITH THE INTERNUCLEAR DISTANCE, AND THE LIFETIMES OF ELECTRONICALLY EXCITED STATES

Despite the specific features of each of the molecular systems considered in this review, we have reached our recommendations on the probabilities for all the transitions by a common method, on the basis of several principles which we will now discuss.

First, *we analyzed each original paper on the determination of the transition probabilities* (we analyzed the conditions under which the data were obtained, the methods by which the data were interpreted by the authors, and any criticism of the results which was published subsequently). In the work on lifetime determinations, we took note of the pressure range in which the measurements were made, the perturbations of the levels of interest by other states, and so forth. In the work on absolute-intensity measurements, we took note of the reliability of the thermodynamic functions used and the validity of the assumptions used in calculating the properties of the gas. In analyzing the work on the behavior of the band strengths as a function of the r-centroids we took into account the reliability of the Franck–Condon factors and the r-centroids used in finding the functions $S_e(r_{v'v''})$.

In the next stage, *we selected the most reliable dependence of the band strength on the r-centroid, taking into account the extent to which this dependence agrees with previously selected reliable data on absolute transition probabilities.* The measure of this agreement is the standard deviation of the normalization factor found from the absolute-probability data under the assumption of some particular dependence. In several cases, as

TABLE I. Recommended values of the band strengths and dependence of the strengths on the r-centroid.

Molecule	Electronic transition, Δλ, nm	$S_e(r_{v'v''})$, $(a_0e)^2$, range of $r_{v'v''}$, Å	f_e^{mn}; $S_e(r_{00})$, $(a_0e)^2$; r_{00}, Å *	References on relative probabilities	References on absolute probabilities
AlO	$B^2\Sigma^+-X^2\Sigma^+$ 405—571	$(19.0\pm5.9)(1-0.46\,r_{v'v''})^2$ 1.50—1.85	$3.92\cdot10^{-2}$ 1.12 ± 0.35 1.6465	70, 71	62—64
BBr	$A^1\Pi-X^1\Sigma^+$ 286—310	0.99	$1.0\cdot10^{-1}$		65
BCl	$A^1\Pi-X^1\Sigma^+$ 261—298	1.04	$1.2\cdot10^{-1}$		41
BF	$A^1\Pi-X^1\Sigma^+$ 186—210	2.88	$4.5\cdot10^{-1}$		41
BH	$A^1\Pi-X^1\Sigma^+$ 395—460	0.5	$3.5\cdot10^{-2}$		66
BO	$A^2\Pi-X^2\Sigma^+$ 310—850	$0.024(1-0.4584\,r_{v'v''})^2$ 1.24—1.33	$2.0\cdot10^{-4}$ 0.0042 1.2760	72	67
	$B^2\Sigma^+-X^2\Sigma^+$ 210—370	$\mathrm{const}\cdot(1-1.434\,r_{v'v''})^2$ 1.30—1.50		73	
BaBr	$C^2\Pi-X^2\Sigma^+$ 514—543	$^{\mathrm{a,\,b}}$ 37.6	~1		69
BaCl	$C^2\Pi-X^2\Sigma^+$ 505—532	$^{\mathrm{a,\,b}}$ 15 ± 25	$4.4\cdot10^{-1}$		68, 69
BaF	$C^3\Pi-X^2\Sigma^+$ 484—514	$^{\mathrm{b}}$ 10.32	$3.2\cdot10^{-1}$		68
BaI	$C^2\Pi-X^2\Sigma^+$ 528—570	$^{\mathrm{a,\,b}}$ 18.96	$5.1\cdot10^{-1}$		68
BaO	$A^1\Sigma-X^1\Sigma$ 230—840	$1.10[1-41.3(r_{v'v''}-2.0268)^2]^2$ 1.88—2.12	$3.3\cdot10^{-2}$ 1.09 2.0321	53	74
BeO	$B^1\Sigma-X^1\Sigma$ 418—570	$903(1-2.416\,r_{v'v''}+1.905\,r^2_{v'v''}-0.502\,r^3_{v'v''})^2$ 1.10—1.70	$3.6\cdot10^{-2}$ 0.56 1.3521	85	75
Br_2	$B^3\Pi_{0_u^+}-X^1\Sigma_g^+$ 511—867	$0.0074(-1+1.2087\,r)^2$ 2.10—2.55	—	76	76
	$^1\Pi_{1u}-X^1\Sigma_g^+$	$0.115(1-0.1798\,r)^2$ 2.10—2.55	—	76	76
C_2	$d^3\Pi_g-a^3\Pi_u$ 340—785	$(33\pm17)(1-0.52\,r_{v'v''})^2$ 1.120—1.488	$3.3\cdot10^{-2}$ 3.6 1.2937	59	78—84
	$b^3\Sigma_g^--a^3\Pi_u$ 1100—2700	0.65	$2.0\cdot10^{-3}$		81
	$c^3\Pi_g-a^3\Pi_u$ 237—328	0.40			81
	$A^1\Pi_u-X^1\Sigma_g^+$ 672—1549	0.38	$1.1\cdot10^{-2}$		81
	$D^1\Sigma_u^+-X^1\Sigma_g^+$ 231—241	0.38 ± 0.50	$5.0\cdot10^{-2}$		82, 83
	$C^1\Pi_g-A^1\Pi_u$ 339—411	1.73	$7.0\cdot10^{-2}$		83
	$E^1\Sigma_g^+-A^1\Pi_u$ 207—222	2.26	$1.6\cdot10^{-1}$		81
C_2^-	$B^2\Sigma-X^2\Sigma$ 500—590	0.6	$1.7\cdot10^{-2}$		87
CF	$A^2\Sigma^+-X^2\Pi$ 220—296	0.84 ± 0.16	$3.0\cdot10^{-2}$		41, 88
	$B^2\Delta-X^2\Pi$	0.88	$3.3\cdot10^{-2}$		41
CH	$A^2\Delta-X^2\Pi$ 431—489	0.322 ± 0.024	$5.6\cdot10^{-3}$		36, 66, 89—95
	$B^2\Sigma^--X^2\Pi$ 363—449	0.166 ± 0.013	$3.2\cdot10^{-3}$		89, 90, 92, 96, 97
	$C^2\Sigma^+-X^2\Pi$ $\lambda_{00}=314,4$	0.288	$7.0\cdot10^{-3}$		e 98, This paper
CD	$A^2\Delta-X^2\Pi$ 431—489	0.33 ± 0.04	$5.6\cdot10^{-3}$		66, 92
CH^+	$A^1\Pi-X^1\Sigma$ 373—480	0.24 ± 0.20	$1.7\cdot10^{-2}$	99, 100	90, 99, 100
	$B^1\Delta-A^1\Pi$ 340—350	0.20 ± 0.12	$8.8\cdot10^{-3}$		92, 99, 100
CN	$A^2\Pi-X^2\Sigma^+$ 437—1500	$(0.144\pm0.041)(1+0.5717\,r_{v'v''})^2$ 1.05—1.27	$6.4\cdot10^{-3}$ 0.41 ± 0.12 1.2060	17	39, 101, 102
	$B^2\Sigma^+-X^2\Sigma^+$ 344—460	$(1.00\pm0.08)(1-0.03\,r_{v'v''})^2$ 0.95—1.32	$3.6\cdot10^{-2}$ 0.93 ± 0.07 1.1658	109	103, 104, 106—108
CO	$A^1\Pi-X^1\Sigma^+$ 114—280	$(1.68\pm0.05)10^4(1-3.1357\,r_{v'v''}+3.6922\,r^2_{v'v''}-1.9205\,r^3_{v'v''}+0.3716\,r^4_{v'v''})^2$ 1.00—1.50	$1.2\cdot10^{-1}$ 0.58 ± 0.02 1.1816	This paper	41, 50, 111—116
	$B^1\Sigma^+-X^1\Sigma^+$ 110—115	$^{\mathrm{d}}$ 0.030 ± 0.006	$7.9\cdot10^{-3}$		e 50, 115, 118—123, 376, This paper
	$B^1\Sigma^+-A^1\Pi$ 412—668	$^{\mathrm{d}}$ $(0.133\pm0.025)(1+1.745\,r_{v'v''}-0.768\,r^2_{v'v''})^2$ 1.12—1.19	$2.1\cdot10^{-2}$ 0.52 ± 0.09 1.177	127	
	$C^1\Sigma^+-X^1\Sigma^+$ 104—111	$^{\mathrm{d}}$ 0.37 ± 0.08	$1.2\cdot10^{-1}$		e 41, 50, 115, 118, 376, This paper
	$C^1\Sigma^+-A^1\Pi$ 368—521	$^{\mathrm{d}}$ 0.54 ± 0.12	$2.2\cdot10^{-2}$		
	$E^1\Pi-X^1\Sigma^+$ 105—108	0.22	$6.2\cdot10^{-3}$		e 50, This paper
	$a^3\Pi-X^1\Sigma^+$ 176—258	$f_{00}=(1.7\pm0.2)\cdot10^{-7}$	—		364—370
	$b^3\Sigma-a^3\Pi$ 266—383	$(4.21\pm0.25)\cdot10^2(1-0.943\,r_{v'v''})^2$ 1.08—1.16	— 2.94 ± 0.17 1.149	127	117, 120, 124
	$e^3\Sigma^--a^3\Pi$ 427—543	const 1.23—1.30		128	
	$a'^3\Sigma^+-a^3\Pi$ 390—860	0.405 ± 0.089	$2.2\cdot10^{-3}$		117, 125, 126
	$c^3\Pi-a^3\Pi$ 230—271	3.4	$7.8\cdot10^{-2}$		117
	$d^3\Delta-a^3\Pi$ 377—750	0.65 ± 0.43 1.18—1.26	$5.7\cdot10^{-3}$ 0.65 ± 0.43 1.2855	143	117, 125, 129, 130
CO^+	$A^2\Pi-X^2\Sigma^+$ 308—850	$(1.24\pm0.38)10^3(-1+1.738\,r_{v'v''}-0.7454\,r^2_{v'v''})^2$ 1.07—1.20	$6.2\cdot10^{-2}$ 0.209 ± 0.064 1.1782	14	131—136
	$B^2\Sigma^+-X^2\Sigma^+$ 180—316	$^{\mathrm{d}}$ $(1.39\pm0.10)(1-0.5301\,r_{v'v''})^2$ 1.07—1.34	$1.6\cdot10^{-2}$ 0.218 ± 0.016 1.1449	60	41, 94, 118, 123, 131, 137—141
	$B^2\Sigma^+-A^2\Pi$ 330—420	$^{\mathrm{d}}$ 0.104 ± 0.016	$2.1\cdot10^{-3}$		
CS	$A^1\Pi-X^1\Sigma^+$ 240—330	$(0.6\pm1.4)(1-0.40\,r_{v'v''})^2$ 1.35—1.75	$1.1\cdot10^{-2}$ $(0.86\pm2.00)\cdot10^{-1}$ 1.5576	144	43, 142
CaO	$^1\Sigma-{}^1\Sigma$ 730—923	$\mathrm{const}\cdot\exp(-3.58\,r_{v'v''})$ 1.74—1.92		145	
CaBr	$A^2\Pi-X^2\Sigma^+$ 614—640	$^{\mathrm{a}}$ 14.3	$3.5\cdot10^{-1}$		68
	$B^2\Sigma^+-X^2\Sigma^+$ 600—613	$^{\mathrm{a,\,b}}$ 5.2	$1.3\cdot10^{-1}$		68
	$C^2\Pi-X^2\Sigma^+$ 380—411	$^{\mathrm{a,\,b}}$ 3.7	$1.4\cdot10^{-1}$		68
CaCl	$A^2\Pi-X^2\Sigma^+$ 605—637	$^{\mathrm{a}}$ 16.3	$4.0\cdot10^{-1}$		68
	$B^2\Sigma^+-X^2\Sigma^+$ 582—608	$^{\mathrm{a,\,b}}$ 5.40	$1.4\cdot10^{-1}$		68
	$C^2\Pi-X^2\Sigma^+$ 364—395	$^{\mathrm{a,\,b}}$ 4.2	$1.7\cdot10^{-1}$		68
CaF	$A^2\Pi-X^2\Sigma^+$ 583—630	$^{\mathrm{a}}$ 21.9	$5.9\cdot10^{-1}$		68
	$B^2\Sigma^+-X^2\Sigma^+$ 515—542	$^{\mathrm{a,\,b}}$ 5.9	$1.7\cdot10^{-1}$		68
CaI	$A^2\Pi-X^2\Sigma^+$ 622—670	$^{\mathrm{a}}$ 12.4	$2.9\cdot10^{-1}$		68
	$B^2\Sigma^+-X^2\Sigma^+$ 627—666	$^{\mathrm{a,\,b}}$ 5.0	$1.2\cdot10^{-1}$		68
CdH (CdD)	$A^2\Pi-X^2\Sigma$ 370—570	2.4	$8.1\cdot10^{-2}$		146, 147
ClO	$A^2\Pi-X^2\Pi$ 260—450	1.4 ± 2.5 (in the interval 277—295)	—		148, 149
F_2	$A^1\Pi_u-X^1\Sigma_g$ 220—440	0.0038	$3.2\cdot10^{-4}$		150
Cu_2	$A^1\Pi_u-X^1\Sigma_g^+$ 485—575	$^{\mathrm{a}}$ 1.7	$1.1\cdot10^{-1}$		151
	$B^1\Sigma^+-X^1\Sigma_g^+$ 449—472	$^{\mathrm{b}}$ 3.8	$2.3\cdot10^{-1}$		151
GeO	$D^1\Pi-X^1\Sigma$ 225—332	$\mathrm{const}\cdot(1-0.476\,r_{v'v''}-0.061\,r^2_{v'v''})^2$ 1.62—1.82		161	
H_2	$B^1\Sigma_u^+-X^1\Sigma_g^+$ $\nu_{00}=90203$ cm^{-1}	$(0.027\pm0.002)(1+6.707\,r_{v'v''})^2$ 0.55—0.96	$3.0\cdot10^{-1}$ 1.38 ± 0.12 0.918	157	48, 152—159
	$C^1\Pi_u-X^1\Sigma_g^+$ $\nu_{00}=99081.7$ cm^{-1}	$(0.382\pm0.033)(1+0.748\,r_{v'v''})^2$ 0.58—0.85	$3.2\cdot10^{-1}$ 1.04 ± 0.09 0.871	157	48, 154—157
	$B'^1\Sigma^+-X^1\Sigma_g^+$ $\nu_{00}=110478.5$ cm^{-1}	0.12	—		157
	$D^1\Pi_u-X^1\Sigma_g^+$ $\nu_{00}=112871$ cm^{-1}	0.16	$5.4\cdot10^{-2}$		157
	$d^3\Pi_u-a^3\Sigma_g^+$ $\nu_{00}=16619.8$ cm^{-1}	9.9	$1.7\cdot10^{-1}$		160
HBr^+	$A^2\Sigma^+-X^2\Pi$ 326—392	$4.84\cdot10^4\exp(-9\,r_{v'v''})$ 1.58—1.78	— 0.031 1.5854	171	162
HCl^+	$A^2\Sigma^+-X^2\Pi$ 280—400	$1.14\cdot10^3\exp(-7.2\,r_{v'v''})$ 1.44—1.82	$1.6\cdot10^{-3}$ 0.041 1.4216	171	163
HgBr	$B^2\Sigma-X^2\Sigma$ 320—508	$^{\mathrm{a}}$ 3.4	$1.2\cdot10^{-1}$		164
I_2	$B^3\Pi_{0_u^+}-X^1\Sigma_g^+$ 430—840	0.16 For λλ (430—600)	—		165, 166
	$E^3\Pi_{0_g^+}-B^3\Pi_{0_u^+}$ 400—440	$^{\mathrm{a}}$ 1.1	$1.4\cdot10^{-1}$		167
	$D^1\Sigma_u^+-X^1\Sigma_g^+$ 195—346	$^{\mathrm{a}}$ 0.3	$3.57\cdot10^{-2}$		168
K_2	$B^1\Pi-X^1\Sigma^+$ 625—695	26 ± 41	~1		169, 170
LaO	$B^2\Sigma^+-X^2\Sigma^+$ 501—645	$2.422\cdot10^5(-1.0+1.74275\,r_{v'v''}-0.99636\,r^2_{v'v''}+0.18803\,r^3_{v'v''})^2$ 1.60—2.10	$1.6\cdot10^{-1}$ 5.3 1.8424	172	110

*The first row gives the value of f_e^{mn}; the second gives $S_e(r_{00})$; and the third gives r_{00}. Where the function $S_e(r_{v'v''})$ has not been studied, the fourth column gives only f_e^{mn}. The value of f_e^{mn} is not given if the information of the Franck-Condon factors required for the calculation is not available.

TABLE I. *(Continued)*

Molecule	Electronic transition, Δλ, nm	$S_e(r_{v'v''})$, $(a_0e)^2$, range of $r_{v'v''}$, Å	f_e^{mn}; $S_e(r_{00})$, $(a_0e)^2$ r_{00}, Å *)	References on relative probabilities	References on absolute probabilities
	$C^2\Pi-X^2\Sigma$ 435—462	6.08	$2.1\cdot10^{-1}$		110
Li_2	$A^1\Sigma^+-X^1\Sigma^+$ 655—770	12.2	$5.4\cdot10^{-1}$		173
MgH	$A^2\Pi-X^2\Sigma^+$ 470—610	2.0	$5.9\cdot10^{-2}$		174
MgO	$B^1\Sigma^+-X^1\Sigma^+$ 367—380	$0.34\,(-1+3.381\,r_{v'v''}-1.48\,r^2_{v'v''})^2$ 1.750—1.835	$3.0\cdot10^{-3}$ 0.05 1.7500	200	105, This paper
	$C^1\Sigma-A^1\Pi$ 483—520	0.056	$2.2\cdot10^{-3}$		105
	$D^1\Delta-A^1\Pi$	0.065	$2.6\cdot10^{-3}$		105
	$d^3\Delta-a^3\Pi$	0.10	$1.8\cdot10^{-3}$		e 372, This paper
MnO	480—670	const $(1-3.192\,r_{v'v''}+1.99\,r^2_{v'v''})^2$ 1.74—1.90		201	
N_2	$B^3\Pi_g-A^3\Sigma_u$ 470—1200	$(92\pm16)\,(1-1.278\,r_{v'v''}+0.410\,r^2_{v'v''}+0.02\,r^3_{v'v''})^2$ 1.1—1.6	$6.1\cdot10^{-3}$ 0.61±0,10 1.2536	38	38, 40, 56, 177–186
	$C^3\Pi_u-B^3\Pi_g$ 268—545	$(2.49\pm0.19)10^2\,(-1+1.9583\,r_{v'v''}-0.8602\,r^2_{v'v''})^2$ 1.03—1.30	$5.0\cdot10^{-2}$ 3.17±0.24 1.1843	202	41, 42, 118, 122, 131, 177, 185, 187–199, 203
	$A^3\Sigma_u-X^1\Sigma_g^+$ 210—506	$1.724\cdot10^{-6}\,(-1.173+r_{v'v''})^2$ 1.08—1.14	$1.5\cdot10^{-9}$ $S_e(r_{03})=3.0\cdot10^{-9}$	203	
		$3.08\cdot10^{-6}\,(-1.206+r_{v'v''})^2$ 1.236—1.413	$r_{03}=1.8373$	363	e 204, This paper
	$a^1\Pi_g-X^1\Sigma_g^+$ 109—260	^{b} $(0.34\pm0.09)\cdot10^{-4}$	$6.5\cdot10^{-6}$	205	205–209
	$b'^1\Sigma^+-X^1\Sigma_g^+$ 83—96	~ 0.6	~ $1.7\cdot10^{-1}$		211, This paper
	$b^1\Pi_u-X^1\Sigma_g^+$ 85—99	~ 0.8	~ $1.7\cdot10^{-1}$		211, This paper
	$D^3\Sigma_u^+-B^3\Pi_g$ 225—291	1.68	—		212
	$c'^1\Sigma-X^1\Sigma_g^+$ $\lambda_{00}=95{,}8$	^{a} 0.37	$1.2\cdot10^{-1}$		41, 210, 211
	$a'^1\Sigma_u^--X^1\Sigma_g^+$ 108—200	$2.2\cdot10^{-7}$	$6.7\cdot10^{-8}$		e 213, This paper
	$c^1\Pi_u-X^1\Sigma_g^+$ 86—96	^{a} ~0.12	~ $3.8\cdot10^{-2}$		210, 211
	$E^3\Sigma-A^3\Sigma$ 213—274	~ $4.3\cdot10^{-5}$	~ $2\cdot10^{-6}$		e 209, 214, This paper
	$E^3\Sigma-B^3\Pi$ $\nu_{00}=36691$	~ $1.4\cdot10^{-5}$	~ $2.6\cdot10^{-7}$		
	$E^3\Sigma-C^3\Pi$ $\nu_{00}=6841$	~ $0.9\cdot10^{-2}$	~ $2.9\cdot10^{-5}$		
	$B'^3\Sigma_u-B^3\Pi$ 606—892	0.32	$1.2\cdot10^{-3}$		e 373, This paper
N_2^+	$A^2\Pi-X^2\Sigma$ 610—950	$(1.14\pm0.28)\,(1-0.463\,r_{v'v''})^2$ 0.9—1.40	$4.2\cdot10^{-3}$ 0.25±0.06 1.149	18	132, 178, 181, 184, 215–221
	$B^2\Sigma-X^2\Sigma$ 280—590	$(289\pm3)\,(1-1.631\,r_{v'v''}+0.704\,r^2_{v'v''})^2$ 0.974—1.265	$3.8\cdot10^{-2}$ 0.97±0.01 1.097	233 234	38, 41, 93, 118, 131, 139, 140, 177, 185, 188, 189, 191, 192, 194, 196, 198, 219, 222, 223, 225–228
NH	$A^3\Pi-X^3\Sigma^-$ 302—368	0.263±0.012	$7.9\cdot10^{-3}$		91, 193, 222, 229–231, 360
	$b^1\Sigma-X^3\Sigma^-$ ~ 471	^{a} $2.7\cdot10^{-6}$	$5.0\cdot10^{-8}$		232
	$c^1\Pi-b^1\Sigma$ ~ 450	^{b} 0.23	$1.6\cdot10^{-2}$		193, 229, 230
	$c^1\Pi-a^1\Delta$ 303—365	^{b} 0.09	$4.2\cdot10^{-3}$		193, 229, 230
	$d^1\Sigma-c^1\Pi$ ~ 253	^{b} 0.35	$2.1\cdot10^{-2}$		235
NH^+	$A^2\Sigma^--X^2\Pi$ 431—466	^{a} 0.09	$1.5\cdot10^{-3}$		236
	$B^2\Delta-X^2\Pi$ ~ 436	$^{a,\,b}$ 0.17	$2.9\cdot10^{-3}$		236
	$C^2\Sigma^+-X^2\Pi$ 273—290	$^{a,\,b}$ 0.06	$1.6\cdot10^{-3}$		236
NO	$A^2\Sigma^+-X^2\Pi$ 195—340	$(3.14\pm0.35)\cdot10^3\,(1-2.8986\,r_{v'v''}+2.74995\,r^2_{v'v''}-0.8597\,r^3_{v'v''})^2$ 1.00—1.20	$2.1\cdot10^{-3}$ 0.079±0.009 1.1090	This paper	44, 46, 175, 237–249
	$B^2\Pi-X^2\Pi$ 200—650	$(1.82\pm0.12)\cdot10^3\,(1-2.2352\,r_{v'v''}+1.6551\,r^2_{v'v''}-0.4024\,r^3_{v'v''})^2$ 1.16—1.58	$3.5\cdot10^{-3}$ 0.078±0.05 1.2692	This paper	47, 237, 238, 240, 250, 251
	$C^2\Pi-A^2\Sigma$ 1205—1235	53.2±45.7	$6.6\cdot10^{-1}$		252, 253
	$C^2\Pi-X^2\Pi$ 184—210	0.36±0.14	$1.5\cdot10^{-2}$		135, 240, 245, 248, 254–256
	$B'^2\Delta-X^2\Pi$ 140—200	^{b} 0.116	$5.4\cdot10^{-3}$		245
	$D^2\Sigma^+-A^2\Sigma^+$ 1085—1130	12.0±3.3	$1.7\cdot10^{-1}$		41, 245, 248, 257

Molecule	Electronic transition, Δλ, nm	$S_e(r_{v'v''})$, $(a_0e)^2$, range of $r_{v'v''}$, Å	f_e^{mn}; $S_e(r_{00})$, $(a_0e)^2$ r_{00}, Å *)	References on relative probabilities	References on absolute probabilities
	$D^2\Sigma^+-X^2\Pi$ 170—190	0.32	$1.4\cdot10^{-2}$		258, 259
	$F^2\Delta-X^2\Pi$ 145—162	^{a} 0.09	$4.4\cdot10^{-3}$		245
	$b^4\Sigma-a^4\Pi$ 750—980	0.06	$2.3\cdot10^{-4}$		260
	$a^4\Pi-X^2\Pi$ 320—490	$3.6\cdot10^{-7}$	$2.6\cdot10^{-8}$		224
NO^+	$A^1\Pi-X^1\Sigma$ 120—170	$1.82\,(1-0.68\,r_{v'v''})^2$	$4.9\cdot10^{-2}$ 0.101±0.062 1.1248	268	41, 111
Na_2	$A^1\Sigma_u^+-X^1\Sigma_g^+$ 600—860	16.2	$6.4\cdot10^{-1}$		261
	$B^1\Pi_u-X^1\Sigma$ 456—504	$((2.43\pm0.04)+(0.17\pm0.02)\,r_{v'v''})^2$ 2.5—6.0	$5.5\cdot10^{-1}$ 8.9 3.2440	262	262
NiH	$A^2\Delta-X^2\Delta$ 642—665	^{a} 0.42	$5.0\cdot10^{-3}$		267
	$B^2\Delta-X^2\Delta$ 490—626	^{a} 0.49	$5\ 8\cdot10^{-3}$		267
O_2	$A^3\Sigma_u^+-X^3\Sigma_g^-$ 243—488	$(10.2\pm2.3)\cdot10^{-6}\cdot r_{v'v''}^{-7.6}$ 1.31—1.53	— $(1.04\pm0.23)10^{-6}$ 1.3500	303	269, 270,
	$B^3\Sigma^--X^3\Sigma^-$ 130—535	$(23.3\pm1.0)\exp(-1.832\,r_{v'v''})$ 1.30—1.75	— 1.88±0.08 1.37443	This paper	49, 148, 271–282
	$^1\Pi_u-a^1\Delta_g$ 143	0.15	$1.6\cdot10^{-2}$		284
O_2^+	$A^2\Pi-X^2\Pi$ 194—653	$(3.01\pm0.94)\cdot10^{-3}\,(1-6.934\,r_{v'v''})^2$ 1.20—1.40	$5.9\cdot10^{-3}$ 0.175±0.055 1.245	285	285, 359
	$b^4\Sigma_g^--a^4\Pi_u$ 499—853	$(9.03\pm0.78)\,(1-0.587\,r_{v'v''})^2$ 1.05—1.44	$2.1\cdot10^{-3}$ 0.43±0.04 1.3320	285	196, 285, 286, 359
OH	$A^2\Sigma^+-X^2\Pi$ 261—411	$(0.706\pm0.017)\,(1-0.75\,r_{v'v''})^2$ 0.8—1.2	$1.2\cdot10^{-3}$ 0.042±0.001 1.0080	55	45, Ref. 293 300, 354
	$D^2\Sigma^--X^2\Pi$ 122	^{a} 0.06	$4.0\cdot10^{-3}$		302
OD	$A^2\Sigma^+-X^2\Pi$ 270—340	0.040±0.004	$9.6\cdot10^{-4}$		288, Ref. 293 295–297, 299, 301
OH^+	$A^3\Pi-X^3\Sigma^-$ 333—398	0.25	$7.0\cdot10^{-3}$		233
OD^+	$A^3\Pi-X^3\Sigma^-$ 346—399	0.21	$5.9\cdot10^{-3}$		305
PH	$A^3\Pi-X^3\Sigma$ 318—360	^{a} 0.002	$5.9\cdot10^{-5}$		222
PN	$A^1\Pi-X^1\Sigma^+$ 257—300	$0.0425\cdot\exp(0.3568\,r_{v'v''})$ 1.426—1.630	$8.7\cdot10^{-3}$ 0.073 1.5215	312	306
PbO	$B1-X^1\Sigma$ 398—577	$8.2\,(1-0.5408\,r_{v'v''})^2$ 2.020—2.148	$1.1\cdot10^{-3}$ 0.046 1.9880	313	307
S_2	$B^3\Sigma^--X^3\Sigma^-$ 240—711	5.5±3.0	$1.95\cdot10^{-1}$		43, 308–310
SH	$A^2\Sigma^+-X^2\Pi$ 292—349	0.034	$7.9\cdot10^{-4}$		298
SO	$A^3\Pi-X^3\Sigma^-$ 240—263	5.5	$2.1\cdot10^{-1}$		311
	$B^3\Sigma-X^3\Sigma$ 190—457	$3.182\cdot10^3\,(1-1.08\,r_{v'v''}+0.282\,r^2_{v'v''})^2$ 1.651—1.942	— 0.29 1.6197	314	43
ScO	$A^2\Pi-X^2\Sigma$ 574—730	^{a} 12.0	$3.0\cdot10^{-1}$		110
	$B^2\Sigma-X^2\Sigma$ 450—577	^{a} 3.4	$1.0\cdot10^{-1}$		110
SiBr	$B^2\Sigma-X^2\Pi$ 287—323	$\mathrm{const}\cdot\exp(8.22\,(1-0.4672\,r_{v'v''}))$ 2.10—2.28		323	
SiCl	$B^2\Sigma-X^2\Pi$ 285—310	$\mathrm{const}\cdot\exp(12.62\,(1-0.4836\,r_{v'v''}))$ 1.92—2.08		323	
SiF	$A^2\Sigma-X^2\Pi$ 423—497	3.5 1.626—1.735	$5.7\cdot10^{-2}$ 3.5 1.627	324	64, 315
	$B^2\Sigma-X^2\Pi$ 264—321	$10.82\exp(12.7\,(1-0.6457\,r_{v'v''}))$ 1.454—1.635	$1.9\cdot10^{-1}$ 8.8 1.574	323	64
	$a^4\Sigma^--X^2\Pi$ 334—337	$4\cdot10^{-5}$	$9\cdot10^{-7}$		64
SiH	$A^2\Delta-X^2\Pi$ 414,2(0.0)	0.19±0.08	$3.5\cdot10^{-3}$		229, 316–318
SiH^+	$A^1\Pi-X^1\Sigma$ 390—480	0.08	$6.1\cdot10^{-3}$		318
SiN	$B^2\Sigma-X^2\Sigma$ 380—520	$\mathrm{const}\cdot(1-1.27\,r_{v'v''}+0.412\,r^2_{v'v''})^2$ 1.38—1.71		325	
SiO	$A^1\Pi-X^1\Sigma$ 210—293	1.3±3.8	$1.6\cdot10^{-1}$		319, 320
	$E^1\Sigma-X^1\Sigma$ 171—200	$3.16\,(1-0.1353\,r_{v'v''})^2$ 1.45—1.61	$3.3\cdot10^{-1}$	321	321
SnF	$A^2\Sigma-X^2\Pi_{1/2}$ 460—630	$\mathrm{const}\cdot(1-0.5307\,r_{v'v''})^2$ 1.9—2.2		326	
	$A^2\Sigma-X^2\Pi_{3/2}$ 510—660	$\mathrm{const}\cdot(1-0.5208\,r_{v'v''})^2$ 1.9—2.2		326	
SnO	$D^1\Pi-X^1\Sigma$ 307—466	$\mathrm{const}\cdot(1-1.119\,r_{v'v''}+0.356\,r^2_{v'v''})^2$ 1.8—2.2		327	
SrBr	$A^2\Pi-X^2\Sigma$	^{a} 17.8	$4.0\cdot10^{-1}$		68

TABLE I. *(Continued)*

Molecule	Electronic transition, Δλ, nm	$S_e(r_{v'v''})$, $(a_0e)^2$, range of $r_{v'v''}$, Å	f_e^{mn}, $S_e(r_{00})$, $(a_0e)^2$ r_{00}, Å*)	References on relative probabilities	References on absolute probabilities
	629—690				
	$B^2\Sigma-X^2\Sigma$ 631—670	^{a,b}6.44	$1.5\cdot10^{-1}$		68
	$C^2\Pi-X^2\Sigma$ 399—484	^{a,b}4.60	$1.7\cdot10^{-1}$		68
SrCl	$A^2\Pi-X^2\Sigma$ 646—690	^{a}19.02	$4.3\cdot10^{-1}$		68
	$B^2\Sigma-X^2\Sigma$ 623—660	^{a,b}6.54	$1.6\cdot10^{-1}$		68
	$C^2\Pi-X^2\Sigma$ 390—405	^{a,b}4.68	$1.8\cdot10^{-1}$		68
SrF	$A^2\Pi-X^2\Sigma$ 628—687	^{a}24.04	$5.6\cdot10^{-1}$		68
SrI	$A^2\Pi-X^2\Sigma$ 618—709	^{a}14.92	$3.3\cdot10^{-1}$		68
	$B^2\Sigma-X^2\Sigma$ 437—448	^{a,b}6.06	$1.4\cdot10^{-1}$		68
	$C^2\Pi-X^2\Sigma$ 425—434	^{a,b}4.32	$1.5\cdot10^{-1}$		68
TiO	$C^3\Delta-X^3\Delta$ 404—630	$S_e(r_{00})=12.3$ $S_e(r_{10})=17.6$ $S_e(r_{01})=23.7$	$1.2\cdot10^{-1}$ 12.3 1.6590	328	328
	$A^3\Phi-X^3\Delta$ 570—865	$S_e(r_{00})=43.7$ $S_e(r_{10})=65.1$ $S_e(r_{01})=92.6$	$3.1\cdot10^{-1}$ 43.7 1.6450	328	328
	$c^1\Phi-a^1\Delta$ 490—580	10.1 1.50—1.65	$2.75\cdot10^{-1}$ 10.1 1.6313		329
VO	$C^4\Sigma-X^4\Sigma$	1.1	$1.4\cdot10^{-2}$		5, 332
ZnH	$A^2\Pi-X^2\Sigma$ 360—522	2.16	$7.8\cdot10^{-2}$		147
YO	$A^2\Pi-X^2\Sigma$ 570—680	13.4	$3.3\cdot10^{-1}$		110
	$B^2\Sigma-X^2\Sigma$ 440—560	3.7	$1.2\cdot10^{-1}$		110

Notes. ^{a}The calculation was carried out under the assumption $q_{v'v''}=\delta_{v'v''}$. ^{b}The conversion from $\tau_{nv'}$ to S_e is made under the assumption that the probabilities for all allowed transitions other than that under consideration are zero. ^{d}The error cited does not take into account the error in the branching ratio used in the calculations. ^{e}The value from the corresponding paper, obtained from relative measurements, is renormalized in accordance with the recommendations of the present review.

TABLE II. Recommended values of the experimental lifetimes.

Molecule	Electron state	τ, nsec	References
AlO	$B^2\Sigma^+$	110±180	62, 63
Ar_2	$^3\Sigma_u^+$	3100±400	265, 333–336
	$^1\Sigma_u^+$	5±11	333, 334
BBr	$A^1\Pi$	25.6(0.1)	65
BCl	$A^1\Pi$	19.1(0—2)	41
BF	$A^1\Pi$	2.8(0—2)	41
BH	$A^1\Pi$	159	66
BaBr	$C^2\Pi$	8	69
BaCl	$C^2\Pi$	20±32	68, 69
BaF	$C^2\Pi$	23.6	68
BaI	$C^2\Pi_{1/2}$	17.9(25)	68
	$C^2\Pi_{3/2}$	16.5	68
BaO	$A^1\Sigma$	356	74
	$A'\Pi$	9400	337
	$a^3\Pi$	~ 10 000	374
BeO	$B^1\Sigma$	90	75
Br_2	$B^3\Pi_{0u}^+$	280(1), 500(5) 420(20), 1200(27)	338
		110(16). 310(19)	339
BrCl	$B^3\Pi_{0u}$	$18.5\cdot10^3$	77
C_2	$d^3\Pi_g$	122±19	83, 84
	$C^1\Pi_g$	31.1	83
	$D^1\Sigma_u^+$	16±22(0—3)	82, 83
CF	$A^2\Sigma^+$	19.0(1)	41
	$B^2\Delta$	18.8	41
CH	$A^2\Delta$	497±38	36, 66, 89–95
	$B^2\Sigma^-$	364±28	89, 90, 92, 96, 97
	$C^2\Sigma^+$	(6–26) as a function of *J*	90, 92
CD	$A^2\Delta$	470±50	66, 92
CH^+	$A^1\Pi$	360±210	90, 99, 100
	$B^1\Delta$	230±140	92, 99, 100
	$b^3\Sigma^-$	480	99
CN	$A^2\Pi$	8000	101
	$B^2\Sigma^+$	61.7±4.3	104, 106–108
CO	$A^1\Pi$	10.42 ±0.59 (1)	41, 111, 112, 116
	$B^1\Sigma^+$	23.7±1.8	118–123, 376
	$C^1\Sigma^+$	1.9±1.0	41, 118, 376
	$a^3\Pi$	(7.7 $\pm2.0)\cdot10^6$	367, 369, 370
	$b^3\Sigma^+$	55.7±5.0	117, 120, 124
	$e^3\Sigma^-$	2000(4)	86
	$a'^3\Sigma^+$	10300 ±800(4)	117, 125, 126
	$c^3\Pi$	16	117
	$d^3\Delta$	7300(1)	117
	$D^1\Delta$ (?)	97000	130
CO^+	$B^2\Sigma^+$	52.0±3.9	41, 94, 118, 123, 131, 137, 139, 140
	$A^2\Pi$	3820(0) 3610±360(1)	132, 134, 136
CS	$A^1\Pi$	215±508	43, 142
CaBr	$A^2\Pi$	34.2(1) $^2\Pi_{1/2}$	68
		33.7(1) $^2\Pi_{3/2}$	68
	$B^2\Sigma^+$	42.9	68
	$C^2\Pi$	33.2 $^2\Pi_{1/2}$	68
		31.8(1) $^2\Pi_{3/2}$	68
CaCl	$A^2\Pi$	29.4(2) $^2\Pi_{1/2}$	68
		28.4(2) $^2\Pi_{3/2}$	68
	$B^2\Sigma^+$	38.2	68
	$C^2\Pi$	25.0	68
CaF	$A^2\Pi$	21.9 $^2\Pi_{1/2}$	68
		18.4 $^2\Pi_{3/2}$	68
	$B^2\Sigma^+$	25.1	68
CaI	$A^2\Pi$	41.7(3) $^2\Pi_{1/2}$	68
		41.6(5) $^2\Pi_{3/2}$	68
	$B^2\Sigma^+$	50.9(4)	68
CdH	$A^2\Pi$	70	146, 147
	$B^2\Sigma$	60—300	147
Cl_2	$^3\Pi_{0u}^+$	10000	341
FeO	$A^5\Sigma$, $B^5\Sigma$	450	342
Cu_2	$A^1\Pi$	70	151
	$B^1\Sigma^+$	30	151
GeO	$a^3\Pi$	^{c}(420 $-2100)\cdot10^3$	322
GeS	$a^3\Pi$	^{c}(625 $-3000)\cdot10^3$	322
H_2	$B^1\Sigma_u^+$	0.8(3)	41
	$C^1\Pi_u$	0.6	41
	$a^3\Sigma_g^+$	11.1±1.7	197, 343, 344
	$d^3\Pi_u$	68	160
	$c^3\Pi_u$	$1\cdot10^6$	345
HBr^+	$A^2\Sigma^+$	4400	162
HCl^+	$A^2\Sigma^+$	2600	163
HgBr	$B^2\Sigma$	23	164
I_2	$B^3\Pi_{0u}^+$	Depends on *J* for $v'<13$ $10^3\cdot0.88(20)$ $10^3\cdot0.98(32)$ $10^3\cdot1.62(40)$ $10^3\cdot9.0(62)$	346–349
	$E^3\Pi_{0g}^+$	27	167
	$D^1\Sigma^+$	15.5	168
ICl	$A^3\Pi_1$	10^5	350
IF	$B^3\Pi$	10^6	351
K_2	$B^1\Pi$	11±17	169, 170
Kr_2	$^3\Sigma^+$	350	265
LaO	$B^2\Sigma$	34.8	110
	$C^2\Pi_{1/2}$	26.9	110
	$C^2\Pi_{3/2}$	28.3	110
Li_2	$A^1\Sigma_u^+$	18 ($v'>6$)	173
LiH	$A^1\Sigma^+$	31.6±12.7(5)	263, 352
N_2	$B^3\Pi_g$	6500±1500	40, 186
	$C^3\Pi_u$	41.0±2.9	41, 42, 118, 122, 131, 185, 187–198, 340
	$a^1\Pi_g$	(115 $\pm46)\cdot10^3$	206–209
	$D^3\Sigma_u^+$	14.1	212
	$c'^1\Sigma_u^+$	0.9	41
	$E^3\Sigma_g^+$	$190\cdot10^3$	209, 214
N_2^+	$A^2\Pi_u$	$13.9\cdot10^3$ (1)	216
	$B^2\Sigma_u^+$	63.1±1.7	36, 41, 93, 118, 131, 139, 140, 185, 188, 189, 191, 192, 194, 196, 198, 219, 222, 226–228
	$C^2\Sigma_u^+$	77(1)	353
NH	$A^3\Pi$	434±28	91, 193, 222, 229, 230
	$b^1\Sigma^+$	$17.8\cdot10^6$	232
	$c^1\Pi$	441±92	193, 229, 230
	$d^1\Sigma^+$	46	235
ND	$d^1\Sigma^+$	62	235
NH^+	$A^2\Sigma^-$	1090	236
	$B^2\Delta$	930	236
	$C^2\Sigma^+$	400	236
NO	$A^2\Sigma^+$	170±44	241–249
	$B^2\Pi$	3100	42, 243
	$C^2\Pi$	25.7±15.1	135, 245, 248
	$B'\ ^2\Delta$	110	245
	$D^2\Sigma^+$	21.9±6.0	41, 245, 248, 257
	$F^2\Delta$	90	245
	$b^4\Sigma$	6430(1)	260
	$a^4\Pi$	^{c} $160\cdot10^6$	224
NO^+	$A^1\Pi$	54±33	41, 111
Na_2	$A^1\Sigma_u^+$	12.2(1)	261
	$B^1\Pi_u$	7.5	262
NaH	$A^1\Sigma^+$	24.0(3)	264
Ne_2	$^3\Sigma^+$	5.9±9.1	265, 266
O_2	$a^1\Sigma_u^+$	$25\cdot10^3$	283
O_2^+	$A^2\Pi_u$	693±216	285, 359
	$b^4\Sigma_g^-$	1130±100	196, 285, 286, 359
OH	$A^2\Sigma^+$	773±47	287–289, 291, 292, 295–299, 354
	$C^2\Sigma^+$	6.1	301
OD	$A^2\Sigma$	770±60	288, 295–297, 299, 304
OH^+	$A^3\Pi$	850	236
OD^+	$A^3\Pi$	1010	305
PH	$A^3\Pi$	$440\cdot10^3$	222
PN	$A^1\Pi$	227	306
PbO	*B*1	1500	307
S_2	$B^3\Sigma_u^-$	18.6±14.0	43, 309, 310
SCl	$^2\Pi$	10.2 (?)	43
SH	$A^2\Sigma^+$	280	298
SD	$A^2\Sigma^+$	280	208, 355
SH^+	$A^3\Pi$	1080	236
SO	$A^3\Pi$	12.4	311
	$B^3\Sigma^-$	17.3	43
ScF	$E^1\Pi$	$1.1\cdot10^5$	371
	$^3\Phi$	$1\cdot10^5$	371
ScO	$A^2\Pi_{1/2}$	35.9	110
	$A^2\Pi_{3/2}$	27.0	110
	$B^2\Sigma$	33.3	110
SiF	$A^2\Sigma^+$	230	356, 357
SiH	$A^2\Delta$	700	229
SiD	$A^2\Delta$	680	229
SiO	$A^1\Pi$	9.6	319
	$E^1\Sigma$	10.5(1—7)	321
	$a^3\Pi$	^{c} $4.8\cdot10^6$	322
SiO^+	?	8.3 (?)	319
SiS	$a^3\Pi$	^{c} $29\cdot10^6$	322
SnO	$a^3\Pi$	^{c} (110— $-320)\cdot10^3$	322
SnS	$a^3\Pi$	^{c} (230— $-570)\cdot10^3$	322
SrBr	$A^2\Pi_{1/2}$	34.3(3)	68
	$A^2\Pi_{3/2}$	33.2(2)	68
	$B^2\Sigma$	42.2(3)	68
	$C^2\Pi_{1/2}$	30.3(1)	68
	$C^2\Pi_{3/2}$	28.2(1)	68
SrCl	$A^2\Pi_{1/2}$	31.3(1)	68
	$A^2\Pi_{3/2}$	30.4(1)	68
	$B^2\Sigma$	38.8(1)	68
	$C^2\Pi_{1/2}$	26.1(1)	68
	$C^2\Pi_{3/2}$	26.0(1)	68
SrF	$A^2\Pi_{1/2}$	31.3(1)	68
	$A^2\Pi_{3/2}$	30.4(1)	68
SrI	$A^2\Pi_{1/2}$	43.3(6)	68
	$A^2\Pi_{3/2}$	41.9(10)	68
	$B^2\Sigma$	46.0	68
	$C^2\Pi_{3/2}$	36.0(8)	68
TiO	$c^1\Phi$	17.5	329
	$C^3\Delta$	37	176
Xe_2	$a^3\Sigma_u^+(1_u)$	60	330, 331
	$A^1\Sigma_u^+(0_u^+)$	2	330, 331
	$b^3\Sigma_g^+(1_g)$	150	330, 331
	$B^1\Sigma_g^+(0_g^+)$	500	330, 331
XeF	$C(1/2)$	18±13	361, 362
XeO	1*S*	100	358
VO	$C^4\Sigma^-$	415	5, 332
ZnH	$A^2\Pi_{1/2}$	77	147
	$A^2\Pi_{3/2}$	73	147
ZnD	$A^2\Pi_{1/2}$	76	147
	$A^2\Pi_{3/2}$	75	147
YO	$A^2\Pi_{1/2}$	33.0	110
	$A^2\Pi_{3/2}$	32.3	110
	$B^2\Sigma$	30.0	110

Note. ^{c}The lifetime is determined in a low-temperature matrix.

the result of a joint analysis of the data on the absolute and relative probabilities, we have found new functions $S_e(r_{v'v''})$, which we believe are more reliable than those in the literature [for the (4+) system of CO, for the Schumann–Runge system of O_2, and for the γ and β systems of NO].

Since different quantities are used in the original papers as measures of the absolute probabilities $[f_{v'v''}^{nm}, f_{v'v''}^{mn}, \tau_{nv'}, S_e(r_{v'v''}), |R_e^{nm}(r_{v'v''})|^2, |R_e^{mn}(r_{v'v''})|^2]$, we converted everything to values of $S_e(r_{00})$ on the basis of the function adopted. At this point *we examined the validity of converting the lifetimes into values of $S_e(r_{00})$.* In particular, the reciprocal of the lifetime was adopted as the Einstein coefficient of the transition only if the selection rules permit only a single transition from the level of interest to all lower levels. In calculating the quantities $\sum_{v''} S_e(r_{v'v''}) q_{v'v''} \nu_{v'v''}^3$ in (12), we tried to carry out the summation in accordance with the requirement $\sum_{v''} q_{v'v''} = 1$. In those cases in which the conversion from $\tau_{nv'}$ to $S_e(r_{00})$ required an extrapolation of the function outside the range in which it had been determined, we considered whether this extrapolation might lead to a physically meaningless result.

For each study, we calculated a single value of $\bar{S}_e(r_{00})$, averaged over all the measurements of that study. In other words, regardless of the number of electronic–vibrational bands used in determining the absolute probabilities in the given study, or regardless of the number of vibrational levels used in determining $\tau_{nv'}$, we converted all these values to values of $S_e(r_{00})$. These values were averaged, and the result was ascribed to the given study. In those cases in which a given author was involved in obtaining several experimental results on the probability for some transition, and there was a significant difference in the results, we considered only the most recent result.

Our experience with the literature on electronic transition probabilities have convinced us that the variation in the nature of the errors from study to study makes it impossible to construct any scale of statistical weights by year, by experimental method used, or whatever. Accordingly, *in recommending absolute probabilities for electronic transitions we assigned equal weights to the results of all the selected studies, and we assumed that these results were in a normal distribution with respect to the actual value.* We found that the discrepancy between the results of different studies frequently does well beyond the errors cited; in other words, these cited errors do not tell us the actual accuracy of the data, so they cannot be used to introduce statistical weights.

The values of $S_{e_{\rm rec}}(r_{00})$ were calculated from

$$S_{e_{\rm rec}}(r_{00}) = \frac{1}{n} \sum_{i=1}^{n} \bar{S}_{e_i}(r_{00}), \tag{20}$$

where n is the number of original papers which we used.

If the results of certain studies differed from the average value found by more than 2σ (σ is the standard deviation), these results were discarded. The resulting values of $S_{e_{\rm rec}}(r_{00})$ are shown in the fourth column of Table I, and the papers used in finding these results are listed in the sixth column.

The errors of the recommended values, ε, were calculated with the help of Student's coefficients[61] t_{n-1}^{α} for a confidence interval $\alpha = 0.95$:

$$\varepsilon = \sqrt{\frac{\sum_{i=1}^{n} \Delta_i^2}{n(n-1)}}\, t_{n-1}^{\alpha}, \tag{21}$$

where $\Delta_i = S_{e_{\rm rec}}(r_{00}) - S_{e_i}(r_{00})$.

If a normalized function $S_e(r_{v'v''})$ is recommended, the corresponding error ε is also given for the normalization factor (in the third column in Table I). Where the recommendation is based on a single study, no error is indicated for the recommended values in Table I. In the third column, underneath the recommended dependence, is the r-centroid interval over which this dependence is determined. In the fourth column, underneath the recommended value of $S_e(r_{00})$ is the r-centroid for the 0, 0 band.

In all cases in which the function $S_e(r_{v'v''})$ was not studied, or no recommendation could be made, the corresponding values of $\tau_{nv'}$ were converted to values of S_e under the assumption $S_e(r_{v'v''}) = \text{const}$, and the third column shows the recommended value of S_e, which is an average for the entire electronic transition.

We have also felt it useful to show (in the fourth column of Table I) the recommended values of the electronic transition oscillator strengths f_e^{mn}, as calculated from Eq. (14).

Since data on the lifetimes of the excited states are in large demand, we give recommended values in Table II. The recommendations regarding $\tau_{nv'}$ are based solely on an analysis of papers reporting experimental measurements of the lifetimes: No theoretical calculations and no measurements of absolute intensities have been used here. As a rule, Table II shows lifetimes for the zero vibrational level. If this level has not been studied, we recommend a value of $\tau_{nv'}$ for the lowest-lying level which has been studied, and this level is specified in parentheses along with the recommended value of $\tau_{nv'}$.

In conclusion we note that in the course of writing this review it was necessary to compile a system of comments regarding the particular features of each of the molecular transitions considered. Because of space limitations, we cannot reproduce all these comments here, even in a very abbreviated form. For the same reason, we do not give the complete bibliography of all the papers which we read (more than 1000); the only papers cited are those from which we used data in generating the recommendations in Tables I and II. The comments and references which we have omitted here are all included in a monograph by the authors, *Probabilities for Optical transitions of Diatomic Molecules*, which is to be published (in Russian) by the Nauka publishing house in 1979.

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NOTATION

A_{nm} - Einstein coefficient for emission, sec^{-1}

$a_0=\frac{h^2}{4\pi^2 me^2}$ - first Bohr radius, $0.529\cdot 10^{-8}$ cm

a_0e - product of the first Bohr radius and the electron charge, $2.5416\cdot 10^{-18}\ \mathrm{g}^{1/2}\cdot\mathrm{cm}^{5/2}/\mathrm{sec}$

$f_e^{mn}, f_e^{nm}, f_{v'v''}^{mn}, f_{v'v''}^{nm}$ - oscillator strengths for the entire electron transition (in absorption and emission) and oscillator strengths of the individual electronic–vibrational bands (in absorption and emission), dimensionless quantities

v, J, S - vibrational, rotational, and spin quantum numbers

Λ, Σ - quantum numbers giving the projection of the orbital angular momentum and spin of the electrons onto the internuclear axis

$\bar{\Lambda}$ - the smaller of the two values of Λ of the coupled electronic states

j_ν - spectral emission coefficient, $\mathrm{erg}/(\mathrm{sec}\cdot\mathrm{cm}^3\cdot\mathrm{sr})$

K_ν - spectral absorption coefficient, cm^{-1}

N_i - population of level i, molecules/cm^3

$q_{v'v''}$ - Franck–Condon factor, dimensionless

$|R_e^{mn}|^2, |R_e^{nm}|^2$ - square of the dipole-moment matrix element of the electronic transition in absorption and emission, atomic units, $(a_0e)^2$

δ - Kronecker delta

ν - transition wave number, cm^{-1}

$\tau_{nv'}$ - lifetime of the excited electronic–vibrational state; all lifetimes in this review are given in nsec

Ψ_e, Ψ_v, Ψ_J - electronic, vibrational, and rotational wave functions

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