

Probabilities of optical transitions in electronic vibration-rotation spectra of diatomic molecules

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This review presents systematized data on absolute probabilities of electronic transitions in diatomic molecules published between the beginning of 1961 and the end of 1973, and relative transition probabilities published between the beginning of 1966 and the end of 1973. The paper reviews theoretical relationships lying at the basis of experimental methods for determining absolute transition probabilities. Individual methods are not reviewed in detail, since the details can be found in the cited literature. The following material is tabulated: absolute probabilities of electronic transitions, the dependence of the dipole moments of electronic transitions on internuclear distances, and the Franck-Condon factors (Tables I, II, and IV, respectively), using all publications known to the authors. In addition to the complete systematization of probability data, the authors attempt to provide a critical analysis of published results with a view to selecting the most reliable. The recommended values of the squares of the matrix elements of the dipole moments of electronic transitions are listed in Table III. The last chapter compares calculations of the Franck-Condon factors obtained for different molecular potentials.

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1. INTRODUCTION

Data on the probabilities of optical transitions in molecular systems have assumed great importance in connection with many problems in science and technology. Such data are essential for calculations of the emissive and absorptive powers of plasmas formed, for example, during electrical discharges in gases, when space vehicles enter the atmosphere, during the operation of quantum-mechanical oscillators, in MHD installations, in plasma chemistry, and so on. The necessary data on the atomic transition probabilities can be found in various reference publications,^[1,18] but no such sources are available for molecular transition probabilities. Moreover, despite the obvious importance of data such as the absolute probabilities of electronic transitions in diatomic molecules, there is a total lack of systematization of such data obtained in the course of the last decade. The last Soviet paper is the review published by Sosnikov^[2] in 1961. It is important to note, however, that data on the absolute probabilities of electronic vibrational transitions were obtained for most molecules during the last decade. A number of generalizing papers^[3,4,7,105-107], appeared during that time both in the USSR and abroad, but none was concerned mainly with atmospheric components at high temperatures. The last summary of data on the relative probabilities of electronic vibrational transitions was given by Ortenberg and Antropov in 1966.^[9]

In the present review, we shall systematize data on the absolute probabilities of electronic transitions in diatomic molecules published between the beginning of 1961 and the end of 1973, and on the relative probabilities published between the beginning of 1966 and end of

1973. Specifically, we shall list values of the absolute probabilities of electronic transitions, the dependence of the electronic transition moments on the distances between the nuclei, and numerical data on the Franck-Condon factors. These data are summarized, respectively, in Tables I, II, and III and incorporate all the published material known to the present authors.¹⁾

In addition to the complete systematization of probability data, we have attempted to provide a critical analysis of the results, designed to establish which are the most reliable. This has been dictated by practical needs and is not at all trivial because of the ambiguity of some of the data. There is no unanimity among the different authors in fields such as the determination of the square of the matrix element, the normalization of the Hanle-London factors, and so on. We shall, therefore, begin by giving a brief summary of the theory of the problem, which will enable us to provide a unified approach to published data on transition probabilities. We shall also briefly review the main experimental techniques for the determination of absolute transition probabilities. The various details of these methods will not be gone into because they can all be found in the published literature. In the last section, we shall compare calculations of the Franck-Condon factors obtained for different molecular potentials.

2. BASIC THEORETICAL RESULTS

A. General Analysis

Transition probabilities are the most important quantum-mechanical characteristics of emission and absorption processes.^[5-7,10] These concepts were first

introduced by Einstein, who discussed them in terms of certain coefficients, now known as the Einstein coefficients. Thus, the probability of spontaneous transition is characterized by A_{nm} and the probability of stimulated emission and absorption is characterized, respectively, by the products of the coefficients B_{nm} and B_{mn} , on the one hand, and the electromagnetic energy density, on the other. The Einstein coefficients are related as follows:

$$g_n B_{nm} = g_m B_{mn}, \quad (1)$$

$$A_{nm} = 8\pi h c \nu_{nm}^3 \frac{g_m}{g_n} B_{mn}; \quad (2)$$

where g_m and g_n are the statistical weights of the energy levels E_m and E_n , ν_{nm} is the wave number for the transition in cm^{-1} , h is Planck's constant, and c the velocity of light. According to the quantum theory of radiation, for a dipole transition

$$A_{nm} = \frac{64\pi^4}{3h} \nu_{nm}^3 \frac{S_{nm}}{g_n}, \quad (3)$$

where S_{nm} is the transition strength, given by

$$S_{nm} = \sum_{k,l} \left| \int \Psi_{nk}^* \mathbf{P} \Psi_{ml} d\tau \right|^2 = \sum_{k,l} |R_{nk, ml}|^2. \quad (4)$$

The quantity $R_{nk, ml}$ is the matrix element of the dipole moment, evaluated for the wave functions for the combining states. The formula given by (4) refers to the general case where the states involved in the transition may be degenerate (degree of degeneracy, respectively, equal to g_n and g_m). The sum is evaluated over all the allowed transitions between states in the upper and lower degenerate levels.

Since the Einstein coefficients are related, the coefficients B_{nm} and B_{mn} can also be expressed in terms of the transition strength:

$$B_{nm} = \frac{8\pi^3}{3h^2 c} \frac{S_{nm}}{g_n}, \quad (5)$$

$$B_{mn} = \frac{8\pi^3}{3h^2 c} \frac{S_{nm}}{g_m}. \quad (6)$$

In addition to the Einstein coefficients, the transition is also frequently characterized by a dimensionless quantity, namely, the oscillator strength f_{mn} for the transition in absorption, which is related to the Einstein coefficient A_{nm} and the strength S_{nm} of the transition as follows:

$$f_{mn} = \frac{m c}{8\pi^2 e^2} \nu_{nm}^{-2} \frac{g_n}{g_m} A_{nm}, \quad (7)$$

$$f_{mn} = \frac{8\pi^2 m c}{3h e^2} \nu_{nm} \frac{S_{nm}}{g_m}. \quad (8)$$

If we express the transition strength in (3) and (8) in terms of atomic units,²⁾ take the wave number in cm^{-1} , and substitute for Planck's constant h , velocity of light c , and electron charge and mass e and m , we obtain the following formulas for the oscillator strength f_{mn} in absorption and for the emission coefficient A_{nm} :

$$f_{mn} = \frac{8\pi^2 m c}{3h e^2} \nu_{nm} \frac{S_{nm}}{g_m} = 3.04 \cdot 10^{-6} \nu_{nm} \frac{S_{nm}}{g_m}, \quad (9)$$

$$A_{nm} = \frac{64\pi^4}{3h} \nu_{nm}^3 \frac{S_{nm}}{g_n} = 2.02 \cdot 10^{-6} \nu_{nm}^3 \frac{S_{nm}}{g_n}. \quad (10)$$

where f_{mn} is dimensionless and A_{nm} has the dimensions of sec^{-1} .

The coefficient A_{nm} is also related to an important excited-state parameter, namely, the lifetime τ_n :

$$\tau_n = \frac{1}{A_n} = \frac{1}{\sum_m A_{nm}}. \quad (11)$$

If we use (10) and (11), we can also express τ_n in terms of the strength of the transition [or, more precisely, in terms of the strengths of the transitions, because (11) includes the sum of the probabilities of all transitions from E_n to E_m]:

$$\frac{1}{\tau_n} = \frac{64\pi^4}{3h} \frac{1}{g_n} \sum_m \nu_{nm}^3 S_{nm}. \quad (12)$$

B. Molecular Transitions

Consider a molecular transition between nondegenerate levels ($e' \Lambda' \Sigma' \nu' J' M'$) and ($e'' \Lambda'' \Sigma'' \nu'' J'' M''$). Here, Λ and Σ are quantum numbers characterizing the components of the orbital and spin angular momenta of electrons along the line joining the nuclei, ν , J , and M are the vibrational, rotational, and magnetic quantum numbers, and the symbols e' and e'' characterize the individual states in Λ -doubling of levels involved in the transitions. The singly primed parameters refer to the upper level and the doubly primed to the lower level. The matrix element of the dipole moment for a given transition is

$$R_{e' \Lambda' \Sigma' \nu' J' M', e'' \Lambda'' \Sigma'' \nu'' J'' M''} = \int \Psi_{e' \Lambda' \Sigma' \nu' J' M'} \mathbf{P} \Psi_{e'' \Lambda'' \Sigma'' \nu'' J'' M''} d\tau, \quad (13)$$

where $\mathbf{P} = \mathbf{P}_e + \mathbf{P}_{\text{nuc}}$ is the electric dipole moment of the electrons (e) and nuclei (nuc), $d\tau = d\tau_e d\tau_n$ is the product of the volume elements in the electronic and nuclear configuration spaces, and Ψ is the resultant wave function of the molecule.

In the first approximation (the Born-Oppenheimer approximation), the resultant wave function for the molecule (without including the nuclear wave function), can be written as the product of the electronic Ψ_e , vibrational Ψ_ν , and rotational Ψ_J wave functions:

$$\Psi_{e \Lambda \Sigma \nu J M} = \Psi_{e \Sigma \Lambda}(\mathbf{r}_e, r) \frac{1}{r} \Psi_e(r) \Psi_{JM}(\theta, \varphi); \quad (14)$$

where \mathbf{r}_e are the coordinates of electrons relative to the nuclear axis of the molecule, r is the distance between the nuclei, and θ and φ are the angular coordinates of the dipole moment.

Substituting (14) in (13), and summing the squares of the matrix elements over the quantum numbers M' and M'' , we obtain the expression for the strength of the line

$$S_{e' \Lambda' \Sigma' \nu' J', e'' \Lambda'' \Sigma'' \nu'' J''} = \sum_{M' M''} |R_{e' \Lambda' \Sigma' \nu' J' M', e'' \Lambda'' \Sigma'' \nu'' J'' M''}|^2 = S_{J' J''} R_{\nu' \nu''}, \quad (15)$$

where $R_{\nu' \nu''}$ is the radial part of the line strength, $S_{J' J''}$ is the Hanle-London factor which, in general, depends on the quantum numbers J , Σ , Λ :

$$S_{J' J''} = \sum_{M' M''} \left| \int \Psi_{J' M'}^* f(\theta, \varphi) \Psi_{J'' M''} \sin \theta d\theta d\varphi \right|^2; \quad (16)$$

and the function $f(\theta, \varphi)$ represents the dependence of the dipole moment on the angular coordinates θ and φ .

The expression for $R_{\nu' \nu''}$ will be found from the general expression for the Einstein coefficient (3).

The Einstein coefficient for a rotational line of an electronic vibration-rotation transition can be obtained by substituting (15) in (3):

$$A_{J' J''} = \frac{64\pi^4}{3h} \nu^3 \frac{S_{J' J''} R_{\nu' \nu''}}{(2J' + 1)}. \quad (17)$$

The Einstein coefficient for an electronic vibrational transition is obtained by summing (17) over all the possible transitions and dividing the result by the statistical weight of the electronic state $g_n = g_{\Lambda'}(2S + 1)$:

$$A_{v'v''}^{nm} = \frac{\sum_{e'e''} \sum_{\Sigma'\Sigma''} \sum_{J'J''} A_{J'J''}}{g_{\Lambda'}(2S+1)} = \frac{64\pi^4}{3h} v^3 \frac{R_{v'v''}^{nm} \sum_{e'e''} \sum_{\Sigma'\Sigma''} \sum_{J'J''} S_{J'J''}}{g_{\Lambda'}(2S+1)(2J'+1)}, \quad (18)$$

where $g_{\Lambda'} = 1$ if $\Lambda' = 0$, and $g_{\Lambda'} = 2$ if $\Lambda' \neq 0$. The factor $2S + 1$ represents the degeneracy in electron spin.

On the other hand, the quantity $A_{v'v''}^{nm}$ can be obtained from the general expressions given by (3) and (4):

$$A_{v'v''}^{nm} = \frac{64\pi^4}{3h} v^3 \frac{\sum_{e'e''} \sum_{\Sigma'\Sigma''} |R_{e'e''}^{nm, \Sigma'\Sigma''}|^2}{g_{\Lambda'}(2S+1)}, \quad (19)$$

where the sums are evaluated over all transitions between the levels degenerate in Λ and Σ' .

The matrix element is given by

$$R_{e'e''}^{nm, \Sigma'\Sigma''} = \int \Psi_{v'} R_{e'e''}^{nm, \Sigma'\Sigma''} \Psi_{v''} dr; \quad (20)$$

where the electronic moment of the transition is given by:

$$R_{e'e''}^{nm, \Sigma'\Sigma''} = \int \Psi_{e'}^* \mathbf{r} \Psi_{e''}(\mathbf{r}, r) P_e \Psi_{\Sigma'}^m(\mathbf{r}, r) d\tau_e. \quad (21)$$

Equating (19) and (18), we obtain

$$R_{v'v''}^{nm} = \frac{(2J'+1) \sum_{e'e''} \sum_{\Sigma'\Sigma''} |R_{e'e''}^{nm, \Sigma'\Sigma''}|^2}{\sum_{e'e''} \sum_{\Sigma'\Sigma''} \sum_{J'J''} S_{J'J''}}. \quad (22)$$

The Hanle-London factors must satisfy the normalization condition

$$\sum_{e'e''} \sum_{\Sigma'\Sigma''} \sum_{J'J''} S_{J'J''} = g_{\Lambda'}(2S+1)(2J'+1). \quad (23)$$

Thus, using (17), (22), and (23), the Einstein coefficients for a rotational line can be written in the form

$$A_{J'J''}^{nm} = \frac{64\pi^4}{3h} v^3 \frac{\sum_{e'e''} \sum_{\Sigma'\Sigma''} |R_{e'e''}^{nm, \Sigma'\Sigma''}|^2}{g_{\Lambda'}(2S+1)(2J'+1)}. \quad (24)$$

This expression was obtained for a line corresponding to a transition between rotational levels degenerate only in the magnetic quantum number M . The statistical weight of a rotational level of this kind is $2J + 1$. If we consider rotational levels which are degenerate in both M and Λ , their statistical weight is $g_{\Lambda}(2J + 1)$. If the rotational levels are degenerate in M , Λ , and S , their statistical weight is $g_{\Lambda}(2S + 1)(2J + 1)$.

It is important to emphasize that (24), which gives the Einstein coefficient for an electronic vibration-rotation transition line, has the same form independently of the statistical weight of the rotational levels joined by the transitions. However, the Hanle-London factors, in the first case, refer to a single rotational line, and their normalization is defined by (23). In the second case, the Hanle-London factors refer to the Λ -doublet and must be normalized as follows:

$$\sum_{\Sigma'\Sigma''} \sum_{J'J''} S_{J'J''} = (2S+1)(2J'+1). \quad (25)$$

In the third case, the Hanle-London factors which refer to the rotational multiplet must be normalized as follows:

$$\sum_{J'J''} S_{J'J''} = (2J'+1). \quad (26)$$

Assuming that the electronic moment of the transition, given by (21), is independent of the distance between the nuclei, we obtain the following expression for the matrix element in (24):

$$|R_{e'e''}^{nm, \Sigma'\Sigma''}|^2 = q_{v'v''} |R_{e'e''}^{nm, \Sigma'\Sigma''}|^2; \quad (27)$$

where $q_{v'v''}$ is the Franck-Condon factor which determines the probability of the vibrational transition

$$q_{v'v''} = \left| \int \Psi_{v'} \Psi_{v''} dr \right|^2. \quad (28)$$

The magnitudes of the matrix elements cannot at present be evaluated in the general form given by (20). However, Fraser^[11] has shown empirically that, even when the electron wave function depends on r , the electronic and vibrational parts of the transition strength can be separated by the r -centroid method. For the product of Morse-type vibrational wave functions, we have the approximate expression

$$\Psi_{v'} \Psi_{v''} = \delta(r - r_{v'v''}) q_{v'v''}^{1/2}, \quad (29)$$

where $r_{v'v''}$ is the r -centroid for the transition and δ is the delta function. The former is given by

$$r_{v'v''} = \frac{\int \Psi_{v'} r \Psi_{v''} dr}{\int \Psi_{v'} \Psi_{v''} dr}. \quad (30)$$

Substituting (29) in (20) and integrating with respect to r , we obtain, (a) without the vibration-rotation interaction

$$|R_{e'e''}^{nm, \Sigma'\Sigma''}|^2 = q_{v'v''} |R_{e'e''}^{nm, \Sigma'\Sigma''}(r_{v'v''})|^2, \quad (31)$$

and (b) with the vibration-rotation interaction

$$|R_{e'e''}^{nm, \Sigma'\Sigma''}|^2 = q_{v'v''}^{1/2} |R_{e'e''}^{nm, \Sigma'\Sigma''}(r_{v'v''})|^2; \quad (32)$$

where

$$q_{v'v''}^{1/2} = \left| \int \Psi_{v'} \Psi_{v''} dr \right|^2. \quad (33)$$

Theoretical estimates of the effect of the vibration-rotation interaction have been obtained for the molecules OH^{295} , Mg_2^{325} , and others. The effect of this interaction on $g_{v'v''}$ was found to be substantial. The criterion for estimating, in the first approximation, the magnitude of the vibration-rotation interaction is given in^[295]:

$$\gamma = \frac{2B_e}{\omega_e}, \quad (34)$$

where B_e and ω_e are, respectively, the rotational and vibrational constants of the molecule. For molecules with $\gamma \leq 0.001$, the interaction is unimportant.

Finally, if we substitute (27), (31), or (32) in (24), we can express the Einstein coefficient in terms of the Franck-Condon factor $g_{v'v''}$, the Hanle-London factor $S_{J'J''}$ and the electronic transition strength S_e^{nm} :

$$A_{J'J''} = \frac{64\pi^4}{3h} v^3 \frac{S_e^{nm} q_{v'v''} S_{J'J''}}{g_{\Lambda'}(2S+1)(2J'+1)}, \quad (35)$$

where

$$S_e^{nm} = \sum_{e'e''} \sum_{\Sigma'\Sigma''} |R_{e'e''}^{nm, \Sigma'\Sigma''}|^2. \quad (36)$$

In general, the electronic transition strength S_e^{nm} depends on the r -centroid [see (31)].

In practice, the electronic transition probabilities are frequently characterized not by the electronic transition strength but by the square of the matrix element which, for absorption, is given by

$$|R_e^{mn}|^2 = \frac{S_e^{nm}}{g_{\Lambda'}(2S+1)}. \quad (37)$$

In the case of emission,

$$|R_e^{nm}|^2 = \frac{S_e^{nm}}{g_{\Lambda'}(2S+1)}. \quad (38)$$

The electronic transition strengths in (37) and (38) are equal: $S_e^{mn} = S_e^{nm}$, i.e., they are symmetric with respect to the direction of the transition.

As a rule, original papers give the squares of the matrix elements for absorption, i.e., $|R_e^{mn}|^2$. The

Einstein coefficient (35) is then determined from the formula

$$A_{J'J''} = \frac{64\pi^4}{3h} \nu_{mn}^3 |R_e^{mn}|^2 \frac{g_{A'}}{g_A} \frac{q_{v'v''} S_{J'J''}}{(2J'+1)}. \quad (39)$$

It was shown above [see (9)] that the oscillator strength f_{mn} is related to the transition strength f_{mn} . Substituting for the transition strengths in (9), we obtain the oscillator strength $f_{e\nu J}$ for an electronic vibration-rotation transition line, the oscillator strength $f_{v'v''}$ for the band, and the electronic oscillator strength f_e :

$$f_{e\nu J} = \frac{8\pi^2 mc}{3he^2} \nu_{e\nu J} \frac{S_e}{g_m} q_{v'v''} \frac{S_{J'J''}}{(2J'+1)}, \quad (40)$$

$$f_{v'v''} = \frac{8\pi^2 mc}{3he^2} \langle \nu_{v'v''} \rangle \frac{S_e}{g_m} q_{v'v''}, \quad (41)$$

$$f_e^{mn} = \frac{8\pi^2 mc}{3he^2} \langle \nu_{emn} \rangle \frac{S_e}{g_m}, \quad (42)$$

where $f_{e\nu J}$, $f_{v'v''}$, f_e^{mn} refer to the absorption processes, and $\langle \nu_{v'v''} \rangle$ and $\langle \nu_{emn} \rangle$ are the mean wave numbers for the vibrational band and the electronic transition.

If we suppose that $\nu_{e\nu J} \approx \langle \nu_{v'v''} \rangle$ and use the sum rule (25) and the sum rule for the Franck-Condon factors

$$\sum_{v'} q_{v'v''} = \sum_{v''} q_{v'v''} = 1 \quad (43)$$

we obtain the following relationships between the oscillator strengths of the rotational line $f_{e\nu J}$, the vibrational band $f_{v'v''}$, and the electronic transition f_e^{mn} :

$$f_{v'v''} \approx \sum_{J'} f_{e\nu J}, \quad f_{v'v''} \approx f_e^{mn} q_{v'v''} \frac{\langle \nu_{v'v''} \rangle}{\langle \nu_{emn} \rangle}, \quad (44)$$

$$f_e^{mn} \approx \sum_{v'} f_{v'v''}, \quad \text{if } \frac{\langle \nu_{v'v''} \rangle}{\langle \nu_{emn} \rangle} \approx 1.$$

For the lifetime of the vibrational level v' which is frequently used to determine $|R_e^{mn}|^2$, we have from (12)

$$\frac{1}{\tau_{v'}} = \frac{64\pi^4}{3h} \frac{g_m}{g_n} \sum_{\sigma} \langle \nu_{v'v''} \rangle^3 |R_e^{mn}|^2 g_{v'v''}, \quad (45)$$

where $64\pi^4/3h = 2.02 \times 10^{-6}$, $\nu_{v'v''}$ is in cm^{-1} , and $|R_e^{mn}|^2$ is in atomic units.

It follows from the foregoing discussion of the electronic transition probabilities that these can be calculated only if we know the electronic transition strength, the Franck-Condon factors, and the Hanle-London factors. The Hanle-London factors for diatomic molecules can readily be calculated. For example, the monograph by Covács^[8] gives the necessary formulas for different types of electronic transition. Various methods have been developed for calculating the Franck-Condon factors (see Chap. 5). Theoretical calculations of the electronic transition strength S_e do not yield satisfactory results. The calculated values occasionally differ from the experimental results by as much as an order of magnitude and, therefore, so far, the main source of our data on electronic transition strengths is experiment.

3. EXPERIMENTAL DETERMINATION OF ABSOLUTE TRANSITION PROBABILITIES AND STRENGTHS

The experimental methods for determining the absolute values of $|R_e(r_{v'v''})|^2$ and $S_e(r_{v'v''})$ are based on relationships connecting these quantities with others, some of which are determined experimentally (integrated emission coefficients, integrated absorption coefficients, lifetimes), whilst others can be calculated ($S_{J'J''}$, $q_{v'v''}$). These relationships are as follows.

(1) For the integrated emission coefficient in a rotational line (per unit solid angle), we have

$$\int_{\text{line}} j_\nu d\nu = \frac{7h\nu c}{4\pi} A_{J'J''} N_{n\sigma' \Sigma' v' J'}. \quad (46)$$

where $A_{J'J''}$ is given by (35) and the level population under the conditions of local thermodynamic equilibrium is given by

$$N_{n\sigma' \Sigma' v' J'} = N \frac{g_{J'}^{2J'+1}}{Q_{\text{in}} Q_{\text{nuc}}} \exp\left(-\frac{E_n + E_{nv} + E_{J'}}{kT}\right), \quad (47)$$

$$Q_{\text{in}} = \sum_n Q_n \sum_v Q_{nv} \sum_J Q_{nvJ}, \quad (48)$$

$$Q_n = g_A (2S+1) \exp\left(-\frac{E_n}{kT}\right), \quad (49)$$

$$Q_{nv} = \exp\left(-\frac{E_{nv}}{kT}\right), \quad (50)$$

$$Q_{nvJ} = (2J+1) \exp\left(-\frac{E_{vJ}}{kT}\right) \approx \frac{kT}{hcB_{nv}}, \quad (51)$$

$$Q_{\text{nuc}} = \frac{(2I_1+1)(2I_2+1)}{\sigma}. \quad (52)$$

For heteronuclear molecules $g_{I_1}^{2I_1+1} = Q_{\text{nuc}}$. For homonuclear molecules

$$g_I^2 = I(2I+1), \quad g_I^2 = (I+1)(2I+1). \quad (53)$$

In (47)–(53), the symbols E_n , E_{nv} , E_{nvJ} are the energies of electronic, vibrational, and rotational levels, Q_{in} is the internal partition function for the molecule, Q_{nuc} is the nuclear partition function, $g_{I_1}^{2I_1+1}$ are the nuclear statistical weights for antisymmetric and symmetric rotational levels, σ is the symmetry number equal to 1 for heteronuclear and 2 for homonuclear molecules, I_1 and I_2 are the nuclear spins, and B_{nv} is the rotational constant of the n -th electronic level.

The differences between the statistical weights of symmetric and antisymmetric levels lead to an alternation in the line intensities in the spectra of homonuclear molecules in the case of $\Sigma - \Sigma$, $\Sigma - \Pi$, and $\Pi - \Sigma$ transitions. For the $\Pi - \Pi$, $\Delta - \Delta$, $\Pi - \Delta$, and $\Delta - \Pi$ transitions, the intensity alternation is observed in the Λ components of the doublet in accordance with their nuclear statistical weights.

Using (35), (46), and (47), we obtain the following expression for the integrated emission coefficient in a rotational line:

$$\int_{\text{line}} j_\nu d\nu = \frac{16\pi^3 c}{3} \nu^4 \frac{S_e g_{v'v''} S_{J'J''}}{g_A (2S+1)} \frac{g_{J'}^{2J'+1}}{Q_{\text{in}} Q_{\text{nuc}}} N \exp\left(-\frac{E_n + E_{nv} + E_{nvJ'}}{kT}\right) \quad (54)$$

$$= \frac{16\pi^3}{3} \nu^4 |R_e^{mn}|^2 \frac{g_{A'}}{g_A} q_{v'v''} S_{J'J''} \frac{g_{J'}^{2J'+1}}{Q_{\text{in}} Q_{\text{nuc}}} N \exp\left(-\frac{E_n + E_{nv} + E_{nvJ'}}{kT}\right);$$

where $16\pi^3 c/3 = 3.22 \times 10^{-23}$, ν is in cm^{-1} , and S_e and $|R_e^{mn}|^2$ in atomic units.

(2) For the integrated emission coefficient in a vibrational band we have

$$\int_{\text{band}} j_\nu d\nu = \frac{h\nu c}{4\pi} A_{v'v''}^{\text{int}} N_{nv'}. \quad (55)$$

In accordance with (19), (31), and (36), the Einstein coefficient for a vibrational band is

$$A_{v'v''}^{\text{int}} = \frac{64\pi^4}{3h} \nu^3 \frac{S_e g_{v'v''}}{g_A (2S+1)}. \quad (56)$$

Under the conditions of local thermodynamic equilibrium, the population is given by

$$N_{nv'} = N \frac{g_A (2S+1)}{Q_{\text{in}}} \exp\left(-\frac{E_n + E_{nv'}}{kT}\right) \sum_{J'} (2J'+1) \exp\left(-\frac{E_{J'}}{kT}\right) \quad (57)$$

$$= N \frac{g_A (2S+1)}{Q_{\text{in}}} \frac{kT}{hcB_{nv'}} \exp\left(-\frac{E_n + E_{nv'}}{kT}\right).$$

From (56) and (57), the integrated emission coefficient in an electronic vibrational band is

$$\int_{\text{band}} j_{\nu} d\nu = \frac{16\pi^3 c}{3} \nu_{\nu'}^4 \frac{S_{\nu} g_{\nu'} \nu'}{Q_{\text{in}}} \frac{kT}{hc B_{\nu\nu'}} N \exp\left(-\frac{E_n + E_{n\nu'}}{kT}\right) \quad (58)$$

$$= \frac{16\pi^3 c}{3} \nu_{\nu'}^4 |R_{\nu}^{mn}|^2 g_{\Lambda} (2S+1) q_{\nu\nu'} \frac{kT}{hc B_{\nu\nu'}} \frac{N}{Q_{\text{in}}} \exp\left(-\frac{E_n + E_{n\nu'}}{kT}\right).$$

(3) An analogous expression can be obtained for the electronic vibrational subband corresponding to transitions between individual components of the electronic levels, each of which is characterized by the component of the spin angular momentum:

$$\int_{\text{sub-band}} j_{\nu} d\nu = \frac{16\pi^3 c}{3} \nu_{\nu'}^4 \frac{S_{\nu} g_{\nu'} \nu'}{(2S+1) Q_{\text{in}}} \frac{kT}{hc B_{\nu\nu'}} \exp\left(-\frac{E_n + E_{n\nu'}}{kT}\right) \quad (59)$$

$$= \frac{16\pi^3 c}{3} \nu_{\nu'}^4 |R_{\nu}^{mn}|^2 g_{\Lambda} q_{\nu\nu'} \frac{N}{Q_{\text{in}}} \frac{kT}{hc B_{\nu\nu'}} \exp\left(-\frac{E_n + E_{n\nu'}}{kT}\right).$$

(4) The integrated absorption coefficient in a rotational line and a vibrational band is, respectively,

$$\int_{\text{line}} K_{\nu} d\nu = h\nu_{\nu'} J' B_{J'J''}^{mn} N_{m_e \nu' \Sigma' \nu'' J''}, \quad (60)$$

$$\int_{\text{bands}} K_{\nu} d\nu = h\nu_{\nu'} B_{\nu'}^{mn} N_{m\nu'}, \quad (61)$$

where the stimulated absorption coefficients $B_{J'J''}^{mn}$ and $B_{\nu'}^{mn}$ can be expressed in terms of the Einstein coefficients $A_{J'J''}^{nm}$ and $A_{\nu'}^{nm}$ through the general formula (2).

In accordance with the above relationships, the electronic transition strengths of diatomic molecules are currently measured by the following three main methods:

- (1) emission method,
- (2) absorption method,
- (3) determination of the lifetime of the excited state.

In the first two methods, the source of the spectrum must satisfy the requirement that the plasma is in either complete or local thermodynamic equilibrium because (54), (58), (59), (60), and (61), used for these methods, were obtained on the assumption of a Boltzmann distribution of molecules over the energy levels. The number of such sources is quite small. The following have been used in the experimental determinations of S_e : shock tube, ^[1-14, 30-40, 177-181] high-temperature King furnace, ^[17, 25, 84] dc arc with cooled electrodes, ^[45, 57, 265] flames, ^[49, 50, 102, 215] and spherical bomb. ^[101, 202] In all these methods, the reliability of the final results is determined, above all, by the extent to which the plasma in the source can be regarded as an equilibrium plasma. It follows from (54) or (61) that the composition and temperature of the plasma must be known if the electronic transition strength is to be determined. For example, in the shock tube this involves the calculation of the state of the gas (composition, pressure, and temperature) behind the shock wave front from the values of the initial parameters and the measured shock-wave velocity. ^[204]

We shall not consider in detail the various methods used to determine the electronic transition strength by the emission or absorption techniques, and will only emphasize one important disadvantage of these methods. When the composition of plasma formed in the source is calculated, the concentrations of the molecules may be subject to substantial errors because of the uncertainties in the thermochemical quantities. It follows that the

electronic transition strength obtained by the emission or absorption method is subject to substantial uncertainties. The size of these uncertainties is not, as a rule, quoted in the original papers, and is not included in the uncertainty assigned to the electronic or oscillator transition strength. In some cases, when the concentration of the diatomic molecules at room temperature is sufficient to provide the absorption spectra, there is no need to calculate the composition and, therefore, this source of possible error in S_e is eliminated. ^[75, 85]

If we use the lifetime method to determine the probabilities of electronic transitions, we need not know the number of emitting molecules. This is why this particular method is so widely used (see Table I below). In this method, the molecules are excited by a beam of photons or electrons, and the spectrum is analyzed as a function of time. Excitation by photons produces a much smaller perturbation in the medium under investigation than excitation by electrons, and ensures the maximum possible selectivity of excitation. However, because sufficiently strong pulsed light sources in the required wavelength range are not as yet available, most of the lifetime measurements are carried out with sources excited by electron beams. In recent years, there have been many experiments in which the excitation of molecules was achieved with the aid of laser beams. This is particularly promising in connection with the possibility of using tunable lasers. ^[217, 234, 266, 289] The excitation is produced in a low-pressure gas, which is necessary to ensure that the excited molecules do not undergo a large number of collisions (collision quenching). The pressure dependence is usually taken into account by measuring the lifetime for different pressures and then extrapolating to zero pressure.

Several methods are used to determine the lifetime. In one, after the source is turned on and equilibrium is established between the excited and radiating molecules, the source is turned off at a known time and the duration of afterglow is measured (by investigating the distribution of intensity as a function of time).

This method has been used to determine the lifetimes of C_2 , ^[15] CH , ^[21, 22] N_2 , NO , ^[22, 77] BaO , ^[268] I_2 , ^[264] and so on. The phase shift technique is the most widely used. It is known that, if the upper state is excited at time $t = 0$ by a very short pulse, the intensity of the emitted photons is proportional to $\exp(-t/\tau)$ where τ is the mean lifetime. In this case, one observes the phase lag Θ of the emitted pulses of radiation which is related to the lifetime and the frequency of the exciting pulses by the formula

$$\Theta = \text{tg}^{-1} \omega\tau. \quad (62)$$

Thus, by measuring the delay (phase shift), and knowing ω , we can calculate τ . The lifetimes of most of the diatomic molecules have been obtained by this method (see, for example, ^[23, 30, 46-48, 70, 71, 242, 243]). Knowing the lifetimes of the electronic excited states, we can, whenever necessary, calculate the corresponding electronic transition strengths or oscillator strengths from (41) and (45).

It is important to note, however, that the lifetime method has a number of features which restrict its application. These include: (1) the possibility that the lifetime may be affected by collision quenching, as noted above; (2) cascade transitions are possible from levels lying above the level under investigation, and

(3) the results may be ambiguous when the level under investigation is common to a number of transitions. Because of this, the lifetime method cannot, for example, be used to determine the transition probabilities for molecules with a predissociating upper state.^[23,183]

We have mentioned the most widely used experimental methods for the determination of the electronic transition strengths of diatomic molecules, which are based on measurements of intensities and of the lifetimes of excited states.

There are a number of cases^[76,90,230] in which the interference method can be used to determine S_e . This method was developed by Rozhdestvenskiĭ and is known as the hook method. It is widely used to determine the oscillator strengths for atomic spectral lines.^[297] The hook method has not been widely used for molecules. This is obviously due to the fact that the method yields satisfactory results only in the case of oscillator strengths of allowed rotational lines separated by more than 0.5 Å. This condition is not commonly satisfied in molecular spectra. Moreover, the hook method is subject to the basic disadvantage of all emission and absorption methods, namely, the fact that it requires a knowledge of the equilibrium concentration of the molecules.

4. SUMMARY OF DATA ON TRANSITION PROBABILITIES FOR DIATOMIC MOLECULES. RECOMMENDED VALUE OF $|R_e^{mn}|^2$

All the results of experimental and theoretical determinations of absolute electronic transition probabilities of diatomic molecules which are known to the present authors and were published between 1961 and 1973 are given in Table I. It is important to emphasize that there is no general agreement as to the definition of the matrix element of the dipole moment of an electronic transition. Some authors define $|R_e|$ as the transition strength and use it as a measure of the probability of the entire electronic transition (I) or the transition from one component of the electronic multiplet (II). In the first case, the electronic multiplet state is looked upon as a single state and Λ -doubling and spin splitting are neglected. The statistical weight of a rotational level is then taken to be $g_\Lambda(2S+1)(2J+1)$ and the normalization of the Hanle-London factors is given by (26). The second case obtains when at least one of the electronic states involved can be classified as a or c type Hund coupling. In this procedure, transitions from the individual components of the electronic multiplet are considered separately. The statistical weight of the rotational level is then $g_\Lambda(2J+1)$ and the normalization of the Hanle-London factors is given by (25).

In most published papers, and with the definition adopted here (see Chap. 2), the square of the matrix element of the dipole moment of an electronic transition is given by $|R_e^{mn}|^2 = S_e^{mn}/g_e''$, where g_e'' is the degeneracy of the lower electronic level which is equal to $g_\Lambda(2S+1)$ or g_Λ , depending on whether we are considering a transition of type I or II.

It is also important to note the results reported in^[22,48,58,110,111,243] where the authors use the following definition of the electronic transition probabilities:

$$A_{nm} = \frac{64\pi^4}{3h} \nu^3 G_m D_{nm} = \frac{64\pi^4}{3h} \nu^3 G_m |R_e^{nm}|^2, \quad (63)$$

$$B_{mn} = \frac{8\pi^3}{3h^2c} G_n D_{mn} = \frac{8\pi^3}{3h^2c} G_n |R_e^{mn}|^2, \quad (64)$$

$$f_e^{mn} = \frac{8\pi^2mc}{3h} \nu G_n D_{mn} = \frac{8\pi^2mc}{3h} \nu G_n |R_e^{mn}|^2. \quad (65)$$

In these expressions, G is the Mulliken coefficient which gives the number of final wave functions belonging to a given energy level with which one of the wave functions for the initial state can combine. The Mulliken coefficient for different types of electronic transition is:^[336]

$$\left. \begin{array}{l} \Sigma - \Sigma \\ \Pi - \Pi \end{array} \right\} G_n = G_m = 1, \quad \left. \begin{array}{l} \Pi - \Delta \\ \Delta - \Pi \end{array} \right\} G_n = G_m = 1,$$

$$\Pi - \Sigma : G_n = 2, G_m = 1; \quad \Sigma - \Pi : G_n = 1, G_m = 2.$$

The quantities $|R_e|$ determined from the formula $|R_e|^2 = S_e/g_e$ and (3) and (6) are related to the $|R_e|$ in (63) and (64), as follows:

$$|R_e^{nm}|_{\text{from (3)}}^2 = |R_e^{nm}|_{\text{from (63)}}^2 g_n G_m, \quad (66)$$

$$|R_e^{nm}|_{\text{from (6)}}^2 = |R_e^{nm}|_{\text{from (64)}}^2 g_m G_n. \quad (67)$$

All the foregoing must be remembered when we compare the electronic transition moments determined by different workers. We think it is useful to give the values of the squares of the matrix elements of the dipole moments of electronic transitions in a unified form, in accordance with our definition of $|R_e^{mn}|^2$ given above. These values are listed in the third column of Table I. Whenever the original papers do not quote the value of $|R_e^{mn}|^2$ but list the oscillator strengths f_e or lifetimes τ of excited states, these values are given in columns 4 and 5 of Table I. We note that Table I gives the values of the squares of the matrix elements and oscillator strengths for absorption, i.e., $|R_e^{mn}|^2$ and f_e^{mn} , respectively. Some workers quote the oscillator strengths not for the entire electronic transition but for a particular vibrational band, in which case this is noted in Table I (for example, in^[250] the authors quote the value $f_{0,0} = 1.6 \times 10^{-2}$ for the Swan system C_2). In that case, if the original paper emphasizes which band was used to obtain f_e^{mn} or $|R_e^{mn}|^2$, Table I lists this band. For example, for the γ system of NO, the third column gives "0.018 from (0,0)", which means that $|R_e^{mn}|^2$ was determined using the (0,0) band.^[78] This will be particularly frequently encountered for band systems characterized by a strong dependence of $|R_e^{mn}|^2$ on r .

The fifth column of Table I lists the lifetime data. The numbers in parenthesis after the value of τ indicate the numbers of vibrational levels for which the lifetimes were measured if these levels are indicated in the original paper.

In the seventh column we indicate the methods used to obtain the values of $|R_e^{mn}|^2$, f_e^{mn} , or τ listed in Table I. We use the following notation: a—absorption in the shock tube; d—absorption in the spherical bomb, b—emission in the shock tube, e, r—spectra excited by dc arc or flame, respectively, h—measurements performed on the absorption spectra in the King furnace, sample chambers, etc., c—based on lifetime measurements, c-m—measurements performed in an inert-gas matrix, k—method of hooks was employed, s—measurements were performed on the solar spectrum; o—values recommended on the basis of relative intensity measurements, f—data obtained by theoretical calculations, l—recommended value is based on a critical review of the literature.

Some of the results given in Table I require further explanation. These explanations are listed below.

AlO molecule. The transition $B^2\Sigma - X^2\Sigma$ was previously interpreted as $A^2\Sigma - X^2\Sigma$ (see, for example, [113-115, 218]) but it is shown in [315] that the A-state is, in reality, the previously unknown low-lying $^2\Pi$ state (see also [218]).

BH molecule. The calculation of $|R_e^{mn}|^2$ in [372] is subject to a computational error which is corrected in [162]. The corrected values of $|R_e^{mn}|^2$ and f_e are given in Table I.

BaO molecule. There are two published papers on the lifetime for the $A^1\Sigma - X^1\Sigma$ transition in BaO, [268, 269] and they are very different. In the latest paper by Johnson [269] (one of the authors of [268]), it is shown that the results in [268] are erroneous.

CH molecule. The table gives two values of the lifetime corresponding to the F_1 and F_2 levels of the $C^2\Sigma$ state, taken from [23]. It is suggested in [23] that the anomalously low values of τ_{F_1} and τ_{F_2} are due to the predissociation of the CH molecule in the $C^2\Sigma$ state, and the difference between them is due to the different probability of predissociation of the levels F_1 and F_2 . The value $|R_e^{mn}|^2 = (1.6 \pm 0.3) \times 10^{-2}$ at.u. given in the table for the $C^2\Sigma - X^2\Pi$ transition was obtained from the data in [361] with the correct normalization of the Hanle-London factors. [162]

CN molecule (red system). The value of $|R_e^{mn}|^2$ reported in [31] was subsequently improved in [32] and the improved value, based on [31], is given in the table, namely $|R_e^{mn}|^2 = 0.10$ at.u. Similarly, it is reported in [109] that $\tau(A^2\Pi) = 3.5$ μ sec and this was subsequently corrected by the authors to $\tau(A^2\Pi) = 8.0$ μ sec. [278] We also note that the values of $|R_e^{mn}|^2$ obtained by the emission or absorption methods were found using different values for the dissociation energy of the CN molecule. In [31, 267], the value of D_{CN} was assumed to be 7.5 eV, while in [278] and [326] this value was taken to be 7.89 and 7.6 eV, respectively.

Violet system. Different values of D_{CN} were also used to determine $|R_e^{mn}|^2$: 7.89 eV in [278] and 7.5 eV in [27, 28, 314].

GeO, GeS, SnO, and SnS molecules. The lifetimes of excited states of the intercombination transitions $A^3\Pi - X^1\Sigma$ in these molecules are reported in [51], where a low-temperature matrix was used. The resulting values of τ are not listed in Table I because they depend on the temperature and nature of the matrix.

NH⁺ and SCl molecules. The identification of the molecular systems reported in [70, 48] is doubtful, even according to the authors themselves.

NO and O₂ molecules. Since in the γ and β systems of NO and the Schumann-Runge system of O₂ there is a strong dependence of R_e on r (see Table II), Table I gives the values of $|R_e^{mn}|^2$ and f_e^{mn} with an indication of the bands (whenever possible) used in the determination.

SO molecule. The value of $f_{0,0}$ for the $A^3\Pi - X^3\Pi$ transition in SO was determined from the lifetime reported in [281]. It is shown in [280] that the measured value of τ given in [281] must be referred to the $A^3\Pi$ state in the A-X transition in the SO and not the SO₂ molecule as previously reported in [281].

S₂ molecule. It is reported in [71] for the $B^3\Sigma - X^3\Sigma$ system that $\sum_{v'=6}^{26} f_{abs} = 6.17 \times 10^{-2}$ and $\sum_{v''=4}^{16} f_{em} = 0.14$.

The difference between these two quantities is explained by the authors by the shift of the intensity maxima in absorption and emission: for absorption $\lambda_{max} = 2600$ Å and for emission $\lambda_{max} = 4200$ Å. The value $\sum f_{abs} = 0.062$ corresponds to $|R_e^{mn}|^2 = 0.58$ at.u., averaged over the interval 2440–2930 Å.

Table II summarizes the results of studies of the dependence of the matrix elements of dipole moments of electronic transitions on the internuclear distance, published between 1966 and 1973. The data reported up to 1966 were systematized by Ortenberg and Antropov. [9] The first and second columns of Table II indicate, respectively, the molecule and type of electronic transition investigated. Column 3 gives analytic expressions for the dependence of the matrix element of the dipole moment of the electronic transitions on the values of the r -centroid. Whenever Table II does not list an analytic expression for $R_e(r)$, this means that the original paper gives $R_e(r)$ graphically or in tabular form. In all cases, the r -centroid interval for which $R_e(r)$ is given is indicated (fourth column).

As already noted, Table I lists the results of all the determinations, known to the present authors, of the absolute probabilities of electronic transitions published between 1961 and 1973, but it is important to emphasize that these results differ very substantially among themselves. It was therefore decided to recommend the most reliable values of the square of the matrix element of the dipole moments of electronic transitions. These recommended values of $|R_e^{mn}|^2$ were chosen on the basis of a critical analysis of all the published results listed in Table I, and the most reliable determinations, in the opinion of the present authors, were used to choose the recommended values of $|R_e^{mn}|^2$. These are listed in Table III. Column 7 of Table III indicates the original papers upon which the recommended values of $|R_e^{mn}|^2$ are based. When a number of such papers were used in the selection of the recommended value of $|R_e^{mn}|^2$, this value was obtained as the arithmetic mean.

In order to characterize the reliability of the recommended values, each probability was assigned an accuracy class in accordance with the scheme adopted in [337]. If the uncertainty in $|R_e^{mn}|^2$ is less than 3%, the results are in class A; if the uncertainty is less than 10%, they are in class B; if less than 25%, they are in class C; and up to 50% in class D. The uncertainty in the recommended values is determined as the random error in the arithmetic mean, [338] calculated using the root mean square errors of the individual measurements.

Since, in general, $|R_e^{mn}|^2$ depends on the internuclear distance (see Table II), we have tried to recommend values of $|R_e^{mn}|^2$ for vibrational bands [using the (0, 0) band whenever possible]. Whenever the corresponding values are not available, we recommend the mean $|\bar{R}_2^{mn}|^2$ for the entire electronic transition.

The fifth column in Table III lists the $v' = 0$ lifetimes of vibrational levels in the upper electronic states for the corresponding transitions, determined from the recommended values of $|R_e^{mn}|^2$ using (45). It follows from (45) that the calculations of $\tau_{v'=0}$ were carried

transition in BeO was determined in^[248,266]. The results obtained in these two papers are very different. Since the determination of the concentration of the BeO molecules in^[248] may be subject to substantial error, we think that the more reliable value of $|R_e^{mn}|^2$ is that reported in^[266] and this is, in fact, listed in the table.

CF molecule. The probability of the $A^2\Sigma - X^2\Pi$ transition was determined from the lifetimes^[19,243] and from the emission behind the shock wave front.^[298,293] The results obtained in these two papers are in good agreement if the improved thermodynamic data reported in^[292] for CF and CF₂ are employed in the calculation of the composition and gas-dynamic parameters behind the shock wave front. We also note that, in their determination of $|R_e^{mn}|^2$, the authors of^[292] introduced a computational error which was subsequently corrected in^[293]. The table recommends the mean value of $|R_e^{mn}|^2$ based on^[243,293].

CN molecule. As already noted, different values of D_{CN} were used in determinations of $|R_e^{mn}|^2$ for the red and violet systems by the absorption and emission methods. We have converted all these results to the dissociation energy $D_{CN} = 7.5$ eV, since this gives the best correlation with lifetime data.

CO molecule. The mean value of $|R_e^{mn}|^2$ for the third positive $b^3\Sigma - a^3\Pi$ system is recommended for the wavelength band 2980–3900 Å. The value of $|R_e^{mn}|^2$ for the $a^3\Pi - X^1\Sigma$ Cameron system is based on absorption in sample-holders and shock tubes. Lifetime data are contradictory and are not taken into account.

NO molecule. The recommended value of $|R_e^{mn}|^2$ for the $\delta(C^2\Pi - X^2\Pi)$ system was obtained by analyzing the data on absorption in air behind a reflected shock wave.^[334]

SiO molecule. The value of $|R_e^{mn}|^2$ for the $A^1\Pi - X^1\Sigma$ transition is recommended on the basis of the lifetime of the $A^1\Pi$ state reported in^[220] for the wavelength range 2340–2820 Å. The values of $|R_e^{mn}|^2$ determined on the basis of thermodynamic data given in^[99-102,202] differ among themselves to within an order of magnitude. This may be connected with uncertainties in the calculated concentrations of SiO and the unreliability of data on the thermodynamic properties of highly heated components of the gas (in particular, SiCl₃, SiCl, etc.; see, for example,^[339]).

5. FRANCK-CONDON FACTORS

According to (28), the probability of a vibrational transition is determined by the Franck-Condon factor $q_{v'v''}$, i.e., the square of the overlap integral for the vibrational wave functions. These factors are calculated by choosing a suitable potential $U(r)$ in the vibrational Schrödinger equation

$$\frac{d^2\Psi_v}{dr^2} + \frac{2\mu}{\hbar^2} [E_v - U(r)] \Psi_v = 0, \quad (68)$$

the solution of which yields the vibrational wave functions Ψ_v . The next step is to substitute the resulting Ψ_v into (28) and evaluate the overlap integral.

The accuracy with which the Franck-Condon factors are calculated increases with increasing accuracy of the vibrational wave functions. The accuracy of these functions, on the other hand, is determined by the extent to which the potential used in the Schrödinger equation truly represents the potential of the molecule, and

by the approximations used in solving the Schrödinger equation.

The various potentials used to calculate the Franck-Condon factors have been examined in^[9,382] and, therefore, we shall simply list the various molecular potentials: the harmonic oscillator and modifications of it, the Lennard-Jones potential, the Hulbert-Hirschfelder potential, the Morse potential, and, finally, various "true" potentials deduced from spectroscopic data. In recent years, calculations of $q_{v'v''}$ have been largely based on the Morse potential or the true potentials obtained by the Rydberg-Klein-Rees method^[300] modified by Vanderslice^[301] and Jarman^[302] (these methods are reviewed in detail in^[303]). The Morse potential leads to an exact solution of the Schrödinger equation. The corresponding wave functions Ψ_v are expressed in terms of Laguerre polynomials with alternating signs, and integration of (28) turns out to be quite difficult. However, such difficulties have been overcome through the use of computers. Various programs have been developed for the numerical integration, using the Morse potential. Descriptions of the algorithms for these programs can be found both in foreign and Soviet literature. A large number of papers concerned with calculations of the Franck-Condon factors using the Morse potential is available in the literature (Table IV).

We note in connection with the above difficulty of numerical integration of (28), especially when computers are not available, that there are very useful approximate methods for calculating the overlap integral for the Morse potential. The most widely used of these approximate methods is the α -averaging method^[304] (see also^[167] for further details). The α -averaging method leads to a relatively simple integration of (28) in analytic form, and to simple working formulas for calculating the Franck-Condon factors. The α -averaging method is widely used in parallel with the method of numerical integration of the Morse potential and is found to yield good results (see, for example, the series of recent papers^[118,119,148,167,168]).

We have discussed in some detail the existing methods of numerical integration of the Morse potential and the α -averaging method because it has been a popular view that only the use of the RKR method will result in reliable values for the Franck-Condon factors. Thus, Ortenberg and Antropov^[9] state that the use of the Morse potential may lead to substantial errors in $q_{v'v''}$ and recommend that the "true" potential be used whenever possible.

We have carefully examined this problem. The fact is that the use of the RKR potentials involves substantial difficulties: (1) the Schrödinger equation (68) cannot be solved exactly for the RKR potentials and, therefore, approximate methods of solution are always employed (see, for example,^[305,306]) and this, of course, introduces uncertainties into the wave functions, but there is practically no information in the literature on the errors in $q_{v'v''}$ due to the approximate solution of (68); (2) a sufficient volume of reliable spectroscopic data is not always available for the determination of the "true" potential (especially for large v).

In recent years, the true potential curve has been constructed on the basis of spectroscopic data and has been compared with Morse curves^[61,285] and others. In practically all cases, there is good agreement between the true and the Morse potential curves (using the turn-

Table IV continued

Molecule	Transition	v'_{\max}	v''_{\max}	Method	Ref.		
SiH	$C^2\Sigma - X^2\Pi$ $B^2\Sigma - A^2\Sigma$ $A^2\Delta - X^2\Pi$	2	3	α	117		
		2	4	M	167		
		5	14	M	117		
		4	4	α	172		
		4	11	M	117		
SiH ⁺	$A^1\Pi - X^1\Sigma$	3	3	R	71		
		2	2	R	213		
		2	2	α	214		
SiO	$A^1\Pi - X^1\Sigma$	1	5	R	236		
		5	4	M	262		
		13	19	R	236		
SnF	$A^2\Sigma - X^2\Pi$	2	4	α	168		
		3	3	α	173		
SnO	$A - X^1\Sigma$ $D^1\Pi - X^1\Sigma$	2	6	α	200		
		5	5	α	174		
SrH	$D^2\Sigma - X^2\Sigma$	12	18	R	120		
		13	18	R	120		
ThO	$A^1\Sigma - X^1\Sigma$ $B^1\Pi - X^1\Sigma$ $C^1\Pi - X^1\Sigma$ $D^1\Pi - X^1\Sigma$ $E^1\Sigma - X^1\Sigma$ $G^1\Delta - H^1\Phi$ $I^1\Pi - X^1\Sigma$	5	10	M	285		
		6	9	M	285		
		5	9	M	285		
		5	8	M	285		
		5	9	M	285		
		6	9	M	285		
		5	7	M	285		
		TiO	$b^1\Pi - a^1\Delta$ $b^1\Pi - d^1\Sigma$ $c^1\Phi - a^1\Delta$	6	6	M	175
				6	6	M	175
				6	6	M	175
YO	$B^2\Sigma - X^2\Sigma$	2	3	B	176		
		22	22	R	120		
ZrO	$B^1\Sigma - A^1\Sigma$ $C^3\Pi - X^3\Pi$	2	2	R	120		
		21	21	R	120		

ing points) although, in some cases, there are, of course, considerable discrepancies. For example, a discrepancy is observed in the $B^2\Sigma$ state of $CH^{[302]}$ and $B^2\Sigma$ state of $AlO^{[114]}$.

There is a smaller number of papers on the calculation of the Franck-Condon factors for both the Morse and the true RKR functions. Let us consider some of them in greater detail. Thus, Flinn et al.^[307] have calculated $q_{v'v''}$ for the γ system of N using the RKR curves. Despite the fact that the shapes of the RKR and Morse curves are in good agreement, especially for small v , Flinn et al. found that, even for the (0, 0) band, the factor $q_{v'v''}$ differed by about 40% from the Morse value of $q_{0,0}$. They explained this discrepancy by saying that the true wave functions occupied the regions beyond the classical turning points for the given vibrational level. Subsequent papers concerned with the study of $R_e(r)$ for the γ system of $NO^{[77,198]}$ have cast doubt on the results of Flinn et al. Finally, Jain and Sahni^[157] state directly that the results of Flinn et al. are incorrect because of the errors admitted into the calculations. Extensive tables are reported in^[157] of the values of $q_{v'v''}$ for the γ ($v' = 5$, $v'' \leq 23$) and β ($v' \leq 24$, $v'' \leq 23$) systems of NO . Comparison of these values with the Morse values of $q_{v'v''}^{[308]}$ shows that the agreement between them is fully satisfactory. We note that the authors of the review paper given in^[9] used mainly a comparison of the results in^[308] with the erroneous data given by Flinn et al.^[307] to reach the doubtful conclusion that the agreement between the approximate and true potentials for a given vibrational level cannot serve as an adequate criterion for the accuracy with which the wave functions and the factors $q_{v'v''}$ are calculated. The results reported in all the papers known to us in which the Morse and RKR calculations of $q_{v'v''}$ are reported and compared suggest the very opposite. Zare et al.^[309-311] use the RKR method to calculate $q_{v'v''}$ for the $B^3\Pi_0 - X^1\Sigma$ transition in I_2 and the $B^3\Pi - A^3\Sigma$ transition in N_2 , and show that they are substantially different from the Morse values of the factor $q_{v'v''}^{[312,313]}$. How-

ever, the Morse values for the B-X system of $I_2^{[144]}$ and the first positive system of $N_2^{[61]}$ were later recalculated, using improved molecular constants for these systems, since it was pointed out in^[61,144] that the previously adopted vibrational identifications for both molecular systems (and that used in^[312,315] in constructing the Morse potential) were erroneous. The value of $q_{v'v''}$ calculated in this way for the B-X system of $I_2^{[144]}$ are found to be in good agreement with the RKR calculations^[309] (see the comparative Table I in^[144]). The Morse $q_{v'v''}$ obtained in^[61] are also in satisfactory agreement with the RKR factors calculated by Benesch^[151] and Zare^[311] (see Table II in^[61]). The last table is interesting since it clearly shows that the differences between the RKR factors given in^[151] and^[311] are almost the same as the differences between the Morse and RKR factors. It is important to note that it is emphasized in^[61] and^[151] that such differences can be due not so much to the differences between the potentials as to the differences caused by the approximate method used to solve the Schrödinger equation. Moreover, the fact that the vibration-rotation interaction has not been taken into account (this may reach 10% for $J = 0-30^{[151]}$) may affect the results.

There are very few comparisons of the values of $q_{v'v''}$ for electronic transitions with a large difference between the equilibrium internuclear distances. It is therefore interesting to note the paper by Harris et al.^[160] which gives extensive tables of values of these factors for the Schumann-Runge system of O_2 ($v' \leq 20$, $v'' \leq 23$). Their results are in satisfactory agreement with the Morse factors $q_{v'v''}^{[323]}$.

Linton and Nicholls^[115] used the shock tube to produce the emission spectrum of AlO . They investigated the function $R_e(r)$ for the $B^2\Sigma - X^2\Sigma$ system and recalculated the Morse factors $q_{v'v''}$. The function $R_e(r)$ was found to be practically the same for both the Morse and the RKR values of $q_{v'v''}^{[114]}$.

A recent paper by Wentink and Spindler^[215] reports calculations of the RKR and Morse values of $q_{v'v''}$ for the $A^1\Sigma - X^1\Sigma$ transition in BaO and again show very good agreement between them even for high v [for example, $q_{0,0}(M) = 0.1038 \times 10^{-1}$, $q_{0,0}(RKR) = 0.1019 \times 10^{-1}$, $q_{6,17}(RKR) = 0.1178$, $q_{6,17}(M) = 0.1182$ and so on]. In^[215] it is reported that $R_e(r)$ is of the form $\text{const} \cdot (1 - k_2 r)$ and it is emphasized that the numerical value of k_2 is practically independent of whether the Morse or the RKR values are used for $q_{v'v''}$. We note that, both in these and in other papers where averages over the vibrational structure are employed, approximate values of $q_{v'v''}$ are frequently successfully used (see, for example,^[201]).

The above comparison of the data obtained as a result of the calculation of $q_{v'v''}$ by the RKR and Morse methods shows, in our opinion, that the two sets of results are practically equivalent for most molecular systems. This does not mean that the Morse potential is better than the RKR potentials (or vice versa). It is, in fact, important to emphasize that, to be able to conclude which particular molecular potential is "correct," it is necessary to compare the results of calculations with reliable experimental data in each specific case. For example, it may be suggested that a criterion of this kind can be obtained by comparing the rotational constant B_v for each vibrational level^[303] where

$$B_v = \frac{\hbar}{8\pi^2\mu c} \int_0^\infty \frac{\Psi_v(r)}{r} dr = \frac{\hbar}{8\pi^2\mu c} \left(\frac{1}{r^2} \right). \quad (69)$$

Unfortunately, comparisons of this kind are not very frequent in the literature..

All the calculations on the Franck-Condon factors for diatomic molecules known to the present authors are listed in Table IV.⁴⁾ Since^[9] contains all work up to 1965 inclusive, Table IV summarizes data on $q_{v'v''}$ between 1966 and the end of 1973. The order in which the material is given in Table IV is as follows: the first column indicates the molecule, the second the electronic transition, and the third and fourth the maximum vibrational quantum numbers v' and v'' up to which (inclusive) the factors $q_{v'v''}$ have been calculated. The fifth column shows the molecular potential used to investigate $q_{v'v''}$ and the last column indicates the reference to the original source. The symbol M in the fifth column indicates that the $q_{v'v''}$ are calculated using the Morse potential and a direct evaluation of the integral, the symbol α signifies that the factors $q_{v'v''}$ were calculated using the average Morse potential (the α -averaging method), R indicates that the factors were calculated using a potential determined from the spectroscopic constants, B indicates the use of various modifications of the harmonic oscillator, W shows that the factors are calculated by the WKB method, q represents a quantum-mechanical calculation, and j shows that the vibration-rotation interaction was taken into account.

It is clear from Table IV that there are at present practically no values for the $q_{v'v''}$ factors with vibrational quantum numbers $v > 20-25$. However, data on these factors and on transitions near the dissociation limit are essential for calculations of the emissivities of gases at high temperatures (up to 10 000°K) and for large optical depths. There is no theory that could be used to calculate $q_{v'v''}$ for vibrational transition between highly excited states ($v > 25$).

¹⁾We have scanned the abstracting journal Referativnyi Zhurnal—"Fizika" and original papers in the following journals: Zh. Prikl. Spektrosk., Teplofiz. Vys. Temp., Tr. Fiz. Inst. Akad. Nauk SSSR, Vestn. Mosk. Univ. Fiz. Astron., Usp. Fiz. Nauk, J. Quantitative Spectrosc. and Radiative Transfer, J. Chem. Phys., J. Mol. Spectrosc., J. Phys. (Proc. Phys. Soc. Lond.), Indian J. Pure Appl. Phys., Indian J. Phys., Can. J. Phys., Can. J. Chem., Trans. Faraday Soc., Chem. Phys. Lett., Phys. Rev., J. Res. Nat. Bureau Stand., Astrophys. J., At. Data, Phys. Rev. Lett., Physica, Combustion and Flames, Phys. Lett., Z. Phys., and Z. Naturforsch.

²⁾The atomic unit is $(ea_0)^2 = 6.459 \times 10^{-36} \text{ g-cm}^5 \text{ sec}^{-2}$, where a_0 is the radius of the Bohr orbit in cm and e is the charge of the electron in esu.

³⁾Data on the function $R_e(r)$ for some molecules are also given in a recent paper by Klemsdal. [³⁴⁰]

⁴⁾Extensive data on the factors $q_{v'v''}$ calculated by the RKR method in the Klein-Dunham-Jarman version with molecular constants taken mainly from the Herzberg monograph [⁵] are also given in the not very accessible publication of the York University in Canada. [³⁴¹] The data are given for a number of systems of the following molecules: AlCl, AlH, AlO, B₂, BaH, BaO, BeH, BN, Br₂, CH, CCl, CuH, GeO, HCl⁺, He₂, K₂, FeO, etc.

⁵⁾C. H. Corliss and W. R. Bozman, Experimental Probabilities for Spectral Lines of Seventy Elements, NBS Monograph No. 53 (Russ. Transl., Mir. M. 1968).

²⁾V. N. Soshnikov, Usp. Fiz. Nauk 74, 61 (1961) [Sov. Phys.-Usp. 4, 425 (1961)].

³⁾R. W. Nicholls, Can. J. Chem. 47, 1847 (1969).

⁴⁾R. Anderson, At. Data 3, 227 (1971).

⁵⁾G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 1, N. Y., 1960.

⁶⁾M. A. El'yashevich, Atomnaya i molekulyarnaya spektroskopiya (Atomic and Molecular Spectroscopy), Fizmatgiz, M. 1962.

⁷⁾S. S. Penner, Quantitative Molecular Spectroscopy and Gas Emissivities (Russ. Transl., IL, M. 1963).

⁸⁾I. Covács, Rotational Structure in the Spectra of Diatomic Molecules, Académic Kiadó, Budapest, 1969.

⁹⁾F. S. Ortenberg and E. T. Antropov, Usp. Fiz. Nauk 90, 237 (1966) [Sov. Phys.-Usp. 9, 717 (1967)].

¹⁰⁾V. A. Kamenshchikov, Yu. A. Plastinin, V. M. Nikolaev, and L. A. Novitskiĭ, Radiatsionnye svoĭstva gazov pri vysokikh temperaturakh (Radiation Properties of Gases at High Temperatures), Mashinstroenie, M. 1971.

¹¹⁾P. A. Fraser, Can. J. Phys. 32, 515 (1954).

¹²⁾A. G. Sviridov, N. N. Sobolev, and M. Z. Novgorodov, J. Quantit. Spectr. Rad. Transfer 6, 337 (1966).

¹³⁾A. G. Sviridov, N. N. Sobolev, and V. M. Sutovskii, J. Quantit. Spectr. Rad. Transfer 5, 525 (1965).

¹⁴⁾A. G. Sviridov, Tr. Fiz. Inst. Akad. Nauk SSSR 51, 124 (1970).

¹⁵⁾M. Jeunehomme and R. P. Schwenker, J. Chem. Phys. 42, 2406 (1965).

¹⁶⁾A. R. Farbrain, J. Quantit. Spectr. Rad. Transfer 6, 325 (1966).

¹⁷⁾R. L. Barger and H. P. Broida, J. Chem. Phys. 37, 1159 (1962).

¹⁸⁾B. M. Mils and W. L. Wiese, Bibliography on Atomic Transition Probabilities, Gov. Print, Washington, 1970.

¹⁹⁾J. E. Hesser and K. Dressler, J. Chem. Phys. 45, 3149 (1966).

²⁰⁾T. Wentink and L. Isaakson, J. Chem. Phys. 46, 3149 (1966).

²¹⁾R. G. Bennet and F. W. Dalby, J. Chem. Phys. 32, 1716 (1960).

²²⁾M. Jeunehomme and A. B. F. Duncan, J. Chem. Phys. 41, 1692 (1964).

²³⁾J. E. Hesser and B. L. Lutz, Astrophys. J. 159, 703 (1970).

²⁴⁾N. E. Kuz'menko, Yu. Ya. Kuzyakov, L. A. Kuznetsova, I. N. Kurdyumova, and B. N. Chuev, Teplofiz. Vys. Temp. 9, 905 (1971).

²⁵⁾M. J. Linevsky, J. Chem. Phys. 47, 3485 (1967).

²⁶⁾R. G. Bennett and F. W. Dalby, J. Chem. Phys. 36, 399 (1962).

²⁷⁾E. M. Kudryavtsev, E. F. Gippius, A. N. Pechenov, and N. N. Sobolev, Teplofiz. Vys. Temp. 1, 73, 376 (1963).

²⁸⁾E. A. Ambartsumyan, N. V. Popov, and A. A. Kon'kov, sbornik "Issledovaniya po fizicheskoi gazodinamike (in: Studies on Physical Gas Dynamics), Nauka, M. 1966, p. 72.

²⁹⁾H. J. Hurtfuss and A. Schmillner, Z. Naturforsch. 23a, 726 (1968).

³⁰⁾H. S. Liszt and J. E. Hesser, Astrophys. J. 159, 1101 (1970).

³¹⁾E. F. Gippius, E. M. Kudryavtsev, A. N. Pechenov, N. N. Sobolev, and V. P. Fokeev, Teplofiz. Vys. Temp. 2, 181 (1964).

³²⁾E. F. Gippius, E. M. Kudryavtsev, A. N. Pechenov,

- and N. N. Sobolev, *Teplofiz. Vys. Temp.* 5, 32 (1967).
- ³³ J. Rogers and R. Anderson, *J. Quantit. Spectr. Rad. Transfer* 10, 515 (1970).
- ³⁴ R. P. Schwenker, *J. Chem. Phys.* 42, 1895 (1965).
- ³⁵ R. G. Fowler and T. M. Holzberlein, *J. Chem. Phys.* 45, 1123 (1966).
- ³⁶ W. M. Huo, *J. Chem. Phys.* 49, 1482 (1968).
- ³⁷ J. H. Moore and W. W. Robinson, *J. Chem. Phys.* 48, 4870.
- ³⁸ E. H. Fink and K. H. Welge, *Z. Naturforsch.* 23a, 358 (1968).
- ³⁹ A. R. Farbairn, *J. Quantit. Spectr. Rad. Transfer* 10, 1321 (1970); 11, 1289 (1971).
- ⁴⁰ V. Hasson and R. W. Nicholls, *J. Phys.* B4, 681 (1971).
- ⁴¹ W. L. Borst and E. Zipf, *Phys. Rev.* A3, 979 (1971).
- ⁴² V. D. Meyer and E. M. Lassetre, *J. Chem. Phys.* 54, 1608 (1971).
- ⁴³ E. M. Lassetre and A. Skerbele, *J. Chem. Phys.* 54, 1597 (1971).
- ⁴⁴ W. C. Wells and R. C. Isler, *Phys. Rev. Lett.* 24, 705 (1970).
- ⁴⁵ A. N. Vargin, L. M. Pasynkova, and E. S. Trekhov, *Zh. Prikl. Spektrosk.* 13, 662 (1970).
- ⁴⁶ K. C. Ioshi, V. D. P. Sastri, and S. Parthasarathi, *J. Quantit. Spectr. Rad. Transfer* 6, 205, 215 (1966).
- ⁴⁷ L. Isaacson, E. P. Marram, and T. Wentank, *J. Quantit. Spectr. Rad. Transfer* 7, 691 (1967).
- ⁴⁸ W. H. Smith, *J. Quantit. Spectr. Rad. Transfer* 9, 1191 (1969).
- ⁴⁹ R. P. Main, D. J. Carlson, and P. A. Du Pusi, *J. Quantit. Spectr. Rad. Transfer* 7, 805 (1967).
- ⁵⁰ R. P. Main and A. Schadee, *J. Quantit. Spectr. Rad. Transfer* 9, 713 (1969).
- ⁵¹ B. Meyer, J. J. Smith, and K. Spitzer, *J. Chem. Phys.* 53, 3616 (1970).
- ⁵² J. E. Hesser, N. H. Brooks, and G. M. Lawrence, *J. Chem. Phys.* 49, 5388 (1968).
- ⁵³ G. N. Haddad, K. N. Lokan, A. J. D. Farmer, and J. H. Carver, *J. Quantit. Spectra. Rad. Transfer* 8, 1193 (1968).
- ⁵⁴ A. C. Allison and A. Dalgarno, *At. Data* 1, 289 (1970).
- ⁵⁵ W. J. Tango and R. N. Zare, *J. Chem. Phys.* 53, 3094 (1970).
- ⁵⁶ V. N. Egorov, L. N. Tunitskiĭ, and E. M. Cherkasov, *Zh. Prikl. Spektrosk.* 8, 479 (1968).
- ⁵⁷ A. N. Vargin, L. M. Pasynkova, and E. S. Trekhov, in: *Fizika gazorazryadnoi plazmy (Physics of Gas Discharge Plasma)*, No. 2, Atomizdat, M., 1969, p. 77.
- ⁵⁸ E. B. Kupriyanova, V. N. Kolesnikov, and N. N. Sobolev, *J. Quantit. Spectra. Rad. Transfer* 9, 1025 (1969).
- ⁵⁹ D. E. Shemansky and A. L. Broadfoot, *J. Quantit. Spectr. Rad. Transfer* 11, 1385 (1971).
- ⁶⁰ R. G. Greene, *J. Quantit. Spectr. Rad. Transfer* 11, 169 (1971).
- ⁶¹ R. E. W. Jansson and B. E. Cunio, *J. Quantit. Spectr. Rad. Transfer* 8, 1747 (1968).
- ⁶² E. H. Fink and K. H. Welge, *Z. Naturforsch.* 19a, 1193 (1964).
- ⁶³ T. Wentink and L. Isaacson, *J. Chem. Phys.* 46, 822 (1967).
- ⁶⁴ D. E. Shemansky, *J. Chem. Phys.* 51, 682, 689 (1969).
- ⁶⁵ D. E. Shemansky, *J. Chem. Phys.* 51, 5487 (1969).
- ⁶⁶ K. L. Wray and T. J. Connolly, *J. Quantit. Spectr. Rad. Transfer* 5, 633 (1965).
- ⁶⁷ V. N. Egorov and L. N. Tunitskiĭ, *Zh. Prikl. Spektrosk.* 7, 227 (1967).
- ⁶⁸ L. I. Kisilevskii and V. D. Shimanovich, *Opt. Spektrosk.* 24, 506 (1968) [*Opt. Spectrosc.* 24, 266 (1968)].
- ⁶⁹ J. A. Harrington, A. P. Modica, and D. R. Libby, *J. Quantit. Spectr. Rad. Transfer* 6, 799 (1966).
- ⁷⁰ W. H. Smith, *J. Chem. Phys.* 51, 520 (1969).
- ⁷¹ W. H. Smith and H. S. Liszt, *J. Quantit. Spectr. Rad. Transfer* 11, 45 (1971).
- ⁷² J. W. Driber and M. J. Williams, *J. Quantit. Spectr. Rad. Transfer* 1, 135 (1961).
- ⁷³ E. T. Antropov, A. P. Dronov, and N. N. Sobolev, *Opt. Spektrosk.* 17, 654 (1964) [*Opt. Spectrosc.* 17, 355 (1964)].
- ⁷⁴ S. P. Erkovich and F. S. Ageshin, *Opt. Spektrosk.* 18, 979 (1965) [*Opt. Spectrosc.* 18, 553 (1965)].
- ⁷⁵ E. T. Antropov, N. N. Sobolev, and V. P. Cheremisinov, *Opt. Spektrosk.* 16, 208 (1964) [*Opt. Spectrosc.* 16, 115 (1964)].
- ⁷⁶ A. Pery-Thorne and F. P. Banfield, *J. Phys.* B3, 1011 (1970).
- ⁷⁷ M. Jeunehomme, *J. Chem. Phys.* 45, 4433 (1966).
- ⁷⁸ E. T. Antropov, *Tr. Fiz. Inst. Akad. Nauk SSSR* 35, 3 (1966).
- ⁷⁹ H. A. Ory, *J. Chem. Phys.* 40, 562 (1964).
- ⁸⁰ W. Groth, D. Kley, and U. Schurath, *J. Quantit. Spectr. Rad. Transfer* 11, 1475 (1971).
- ⁸¹ M. McClintoch, W. Demtröder, and R. N. Zare, *J. Chem. Phys.* 51, 5509 (1969).
- ⁸² N. I. Krindach, N. N. Sobolev, and L. N. Tunitskiĭ, *Opt. Spektrosk.* 15, 298, 601 (1969) [sic!].
- ⁸³ V. H. Reis, *J. Quantit. Spectr. Rad. Transfer* 5, 585 (1965).
- ⁸⁴ R. D. Hudson and V. L. Carter, *J. Opt. Soc. Am.* 58, 1621 (1968).
- ⁸⁵ A. J. Farmer, W. Fabion, D. K. Lewis, K. H. Lokan, and G. H. Hadad, *J. Quantit. Spectr. Rad. Transfer* 8, 1739 (1968).
- ⁸⁶ V. Hasson, G. R. Hebert, and R. W. Nicholls, *J. Phys. B* 3, 1188 (1970).
- ⁸⁷ R. G. Breene, *J. Quantit. Spectr. Rad. Transfer* 11, 37 (1971).
- ⁸⁸ D. E. Buttrey, *J. Quantit. Spectr. Rad. Transfer* 9, 1527 (1969).
- ⁸⁹ V. Hasson, R. W. Nicholls, and V. Degen, *J. Phys. B* 3, 1192 (1970).
- ⁹⁰ J. Anketell and A. Pery-Thorne, *Proc. R. Soc.* A301, 343 (1967).
- ⁹¹ W. H. Smith, *J. Chem. Phys.* 53, 792 (1970).
- ⁹² J. F. Bott and T. A. Jacobs, *J. Chem. Phys.* 52, 3545 (1970).
- ⁹³ Yu. Ya. Kuzyakov, I. E. Ovcharenko, N. E. Kuz'menko, and I. N. Kurdyumova, *Zh. Prikl. Spektrosk.* 12, 555 (1970).
- ⁹⁴ N. E. Kuz'menko, Yu. Ya. Kuzyakov, and A. D. Smirnov, *Zh. Prikl. Spektrosk.* 13, 616 (1970).
- ⁹⁵ A. J. Sauval, *Solar, Phys.* 10, 319 (1969).
- ⁹⁶ A. Schadee, *Bull. Astron. Inst. Neth.* 17, 311 (1964).
- ⁹⁷ D. L. Lambert and E. A. Mallia, *Mon. Not. RAS* 148, 313 (1970).
- ⁹⁸ N. Grevesse and A. J. Sauval, *J. Quantit. Spectr. Rad. Transfer* 11, 65 (1971).
- ⁹⁹ R. P. Main, A. L. Morsell, and W. J. Hooker, *J. Quantit. Spectr. Rad. Transfer* 8, 1527 (1968).
- ¹⁰⁰ W. J. Hooker and R. P. Main, *Physica* 41, 35 (1969).
- ¹⁰¹ A. D. Rusin, *Vestn. Mosk. Univ. Fiz. Khim.* 5, 526 (1970).
- ¹⁰² A. Czernichowski and W. Zyrnicni, *Acta Phys. Pol.* A37, 865 (1970).
- ¹⁰³ M. L. Price, K. G. P. Sulzmann, and S. S. Penner,

- J. Quantit. Spectr. Rad. Transfer 11, 427 (1971).
- ¹⁰⁴G. E. Copeland, J. Chem. Phys. 54, 3482 (1971).
- ¹⁰⁵L. M. Biberman and A. Kh. Mnatsakanyan, Teplofiz. Vys. Temp. 2, 148 (1966).
- ¹⁰⁶Yu. A. Plastinin and G. G. Baula, as^[28], p. 41.
- ¹⁰⁷A. A. Kon'kov, V. Ya. Neiland, V. M. Nikolaev, and Yu. A. Plastinin, Teplofiz. Vys. Temp. 7, 140 (1969).
- ¹⁰⁸B. Hexter, J. Chem. Phys. 37, 1347 (1962).
- ¹⁰⁹T. Wentink, L. Isaacson, and J. Morreal, J. Chem. Phys. 41, 278 (1964).
- ¹¹⁰M. Jeunehomme, J. Chem. Phys. 42, 4086 (1965).
- ¹¹¹M. Jeunehomme, J. Chem. Phys. 45, 1805 (1966).
- ¹¹²B. Huron, Physica 41, 58 (1969).
- ¹¹³D. V. A. Rao, K. P. Nair, and D. K. Dai, Current Sci. (India) 36, 372 (1967).
- ¹¹⁴A. Sharma, J. Quantit. Spectr. Rad. Transfer 7, 289 (1967).
- ¹¹⁵C. Linton and R. W. Nicholls, J. Quantit. Spectra. Rad. Transfer 9, 1 (1969).
- ¹¹⁶S. V. J. Laksman and T. V. Ramakrishna, J. Phys. B 4, 269 (1971).
- ¹¹⁷T. Wentink and R. J. Spindler, J. Quantit. Spectr. Rad. Transfer 10, 609 (1970).
- ¹¹⁸R. K. Mishra and B. N. Khanna, J. Quantit. Spectr. Rad. Transfer 10, 703 (1970).
- ¹¹⁹A. N. Pathak and R. C. Maneshwari, Indian J. Pure Appl. Phys. 5, 138 (1967).
- ¹²⁰H. S. Liszt and W. H. Smith, J. Quantit. Spectr. Rad. Transfer 11, 1043 (1971).
- ¹²¹A. P. Walvekar, Indian J. Phys. 43, 742 (1969).
- ¹²²M. R. Katti, Indian J. Pure Appl. Phys. 3, 499 (1965).
- ¹²³H. Mohanty, J. C. Mohanty, and B. S. Mohanty, Indian J. Pure Appl. Phys. 8, 423 (1970).
- ¹²⁴A. P. Walvekar and V. M. Korwar, J. Phys. B2, 115 (1969).
- ¹²⁵M. R. Katti and H. D. Sharma, Indian J. Pure Appl. Phys. 6, 458 (1968).
- ¹²⁶R. K. Mishra and B. N. Khanna, Indian J. Pure Appl. Phys. 7, 63 (1969).
- ¹²⁷R. G. Fowler, P. R. Skwerski, R. A. Anderson, G. E. Copeland, and T. M. Holzberlein, J. Chem. Phys. 50, 4133 (1969).
- ¹²⁸T. V. R. Ramakrishna and S. V. Lakshman, Current Sci. (India) 40, 316 (1971).
- ¹²⁹R. J. Spindler, J. Quantit. Spectr. Rad. Transfer 5, 165 (1965).
- ¹³⁰J. D. Singh and R. C. Maneshwari, Indian J. Pure Appl. Phys. 9, 296 (1971).
- ¹³¹A. N. Pathak and P. D. Singh, Indian J. Pure Appl. Phys. 5, 139 (1967).
- ¹³²D. Sharma, P. D. Singh, and A. N. Pathak, Indian J. Pure Appl. Phys. 6, 443 (1968).
- ¹³³P. H. Krupenie and W. Benesh, J. Res. NBS A72, 495 (1968).
- ¹³⁴R. W. Nicholls, J. Phys. B1, 1192 (1968).
- ¹³⁵D. C. Jain and R. C. Sahni, J. Quantit. Spectr. Rad. Transfer 6, 705 (1966).
- ¹³⁶P. D. Singh and A. N. Pathak, Indian J. Pure Appl. Phys. 7, 132 (1969).
- ¹³⁷N. I. Zhirnov and L. A. Kronrod, in: Voprosy radiofiziki i spektroskopii (Problems of Radiophysics and Spectroscopy), No. 3, Sovetskoe Radio, M. (1967), p. 6.
- ¹³⁸J. A. Coxon, J. Quantit. Spectr. Rad. Transfer 11, 1355 (1971).
- ¹³⁹R. T. V. Ramakrishna and S. V. J. Lakshman, J. Quantit. Spectr. Rad. Transfer 11, 1157 (1971).
- ¹⁴⁰T. Gulab and K. P. R. Nair, J. Sci. Res. Banaras Hindu Univ. 17, 260 (1966/67).
- ¹⁴¹Don Villarejo, R. Stockbaner, and M. C. Inghram, J. Chem. Phys. 50, 1754 (1969).
- ¹⁴²D. Singh and M. M. Shukla, J. Quantit. Spectr. Rad. Transfer 12, 1249 (1972).
- ¹⁴³R. I. Spindler, J. Quantit. Spectr. Rad. Transfer 9, 597, 627, 1041 (1969).
- ¹⁴⁴M. Halmann, I. Laulicht, and J. T. Steinfeld, J. Mol. Spectrosc. 21, 328 (1966).
- ¹⁴⁵M. Halmann and I. Laulicht, J. Chem. Phys. 46, 2684 (1967).
- ¹⁴⁶J. D. Singh, M. M. Shukla, and R. C. Maneshwari, J. Quantit. Spectr. Rad. Transfer 9, 533 (1969).
- ¹⁴⁷T. V. R. Ramakrishna and S. V. J. Lakshman, J. Quantit. Spectr. Rad. Transfer 10, 945 (1970).
- ¹⁴⁸N. A. Nazimova, Zh. Prikl. Spektrosk. 7, 169 (1967).
- ¹⁴⁹G. Gandare, J. Schamps, and M. Bécart, C. R. Acad. Sci. B270, 1213 (1970).
- ¹⁵⁰P. S. Dube, A. V. Chandury, G. D. Baruah, and D. U. Rai, Appl. Spectrosc. 25, 554 (1971).
- ¹⁵¹W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 144, 408 (1966).
- ¹⁵²A. Kh. Mnatsakanyan, Teplofiz. Vys. Temp. 6, 236 (1968).
- ¹⁵³W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 143, 236 (1966).
- ¹⁵⁴G. R. Hebert and R. W. Nicholls, J. Phys. B 2, 626 (1969).
- ¹⁵⁵A. M. Jorns-Bony, F. Vincent, and R. Grant-Montagen, C. R. Acad. Sci. B270, 491 (1970).
- ¹⁵⁶R. J. Spindler, T. Wentink, and L. Isaacson, J. Quantit. Spectr. Rad. Transfer 10, 621 (1970).
- ¹⁵⁷D. C. Jain and R. C. Sahni, Trans. Faraday Soc. 64, 3169 (1968).
- ¹⁵⁸J. I. Generosa and R. A. Harris, J. Chem. Phys. 53, 3147 (1970).
- ¹⁵⁹M. Jeunehomme, J. Chem. Phys. 44, 2672 (1966).
- ¹⁶⁰R. Harris, M. Blackledge, and J. Generosa, J. Mol. Spectrosc. 30, 506 (1969).
- ¹⁶¹R. K. Asundi and C. V. S. Ramachandrarao, Chem. Phys. Lett. 4, 89 (1969).
- ¹⁶²F. N. Putilin, Candidate's dissertation, MGU, 1973.
- ¹⁶³P. S. Dube, K. N. Upadhyaya, and D. K. Rai, J. Quantit. Spectr. Rad. Transfer 10, 1191 (1970).
- ¹⁶⁴V. M. Korwar, Proc. Phys. Soc. Lond. 92, 523 (1967).
- ¹⁶⁵D. C. Jain and R. S. Sahni, Proc. Phys. Soc. Lond. 88, 495 (1966).
- ¹⁶⁶W. M. Smith, J. Quantit. Spectr. Rad. Transfer 8, 1437 (1968).
- ¹⁶⁷N. E. Kuz'menko, Yu. Ua. Kuzyakov, N. N. Kabankova, and G. E. Tokeris, L. Z. Fridlyand, and A. B. Bolotin, Lit. Fiz. Sb. 11, 433 (1971).
- ¹⁶⁸J. Singh and P. S. Dube, Indian J. Pure Appl. Phys. 9, 164 (1971).
- ¹⁶⁹N. E. Kuz'menko, A. D. Smirnov, and Yu. Ya. Kuzyakov, Vestn. Mosk. Univ. Fiz. Khim. 11, 357 (1970).
- ¹⁷⁰N. E. Kuz'menko, A. D. Smirnov, and Yu. Ya. Kuzyakov, Vestn. Mosk. Univ. Fiz. Khim. 11, 478 (1970).
- ¹⁷¹V. S. Mohanty and O. N. Singh, Indian J. Pure Appl. Phys. 7, 109 (1969).
- ¹⁷²J. D. Singh and R. C. Maneshwari, Indian J. Pure Appl. Phys. 7, 708 (1969).
- ¹⁷³N. A. Nazimova and L. V. Zhdanova, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 8, 146 (1971).
- ¹⁷⁴P. D. Singh and Y. P. Srivastava, J. Quantit. Spectr. Rad. Transfer 8, 1443 (1968).

- ¹⁷⁵C. Linton and R. W. Nicholls, *J. Phys.* **B2**, 490 (1969).
- ¹⁷⁶N. S. Murthy and B. N. Murthy, *Proc. Phys. Soc.* **A 91**, 489 (1967).
- ¹⁷⁷A. P. Dronov, N. N. Sobolev, and F. S. Faizullof, *Opt. Spektrosk.* **21**, 267, 538 (1966). [*Opt. Spectros.* **21**, 158, 301 (1966)].
- ¹⁷⁸Yu. A. Plastinin, in: *Svoistva gazov pri vysokikh temperaturakh (Properties of Gases at High Temperatures)*, Nauka, M. 1967, p. 82.
- ¹⁷⁹W. H. Wurster, *J. Quantit. Spectr. Rad. Transfer* **3**, 355 (1963).
- ¹⁸⁰J. C. Keck, P. A. Allen, and R. L. Taylor, *J. Quantit. Spectr. Rad. Transfer* **3**, 335 (1963).
- ¹⁸¹P. A. Allen, J. C. Camm, and J. C. Keck, *J. Quantit. Spectr. Rad. Transfer* **1**, 269 (1961).
- ¹⁸²A. Chutjian and T. C. James, *J. Chem. Phys.* **51**, 1242 (1969).
- ¹⁸³K. Sakuray, G. Capelle, and H. P. Broida, *J. Chem. Phys.* **54**, 1220 (1971).
- ¹⁸⁴N. R. Tawde and V. M. Korwar, *J. Phys.* **B2**, 753 (1969).
- ¹⁸⁵K. Prasad and S. S. Prasad, *J. Phys.* **B2**, 725 (1969).
- ¹⁸⁶A. N. Vargin and E. S. Trekhov, collection cited in^[57], p. 93.
- ¹⁸⁷B. G. Elmergreen and W. H. Smith, *Astophys. J.* **178**, 557 (1972).
- ¹⁸⁸I. V. Avilova, L. M. Biberman, V. S. Vorob'ev, V. M. Zamalin, G. A. Kobzev, A. Kh. Mnatsakanyan, and G. E. Norman, *Teplofiz. Vys. Temp.* **8**, 1 (1970).
- ¹⁸⁹V. S. Afanas'ev, A. N. Vargin, and E. S. Trekhov, collection cited in^[57], p. 62.
- ¹⁹⁰V. E. Cunio and R. E. W. Jansson, *J. Quantit. Spectr. Rad. Transfer* **8**, 1763 (1968).
- ¹⁹¹G. Chandraith and G. G. Shepherd, *Can. J. Phys.* **46**, 221 (1968).
- ¹⁹²A. L. Broadfoot and S. P. Maran, *J. Chem. Phys.* **51**, 678 (1969).
- ¹⁹³D. C. Jain and R. C. Sahni, *J. Quantit. Spectr. Rad. Transfer* **7**, 475 (1967).
- ¹⁹⁴A. N. Vargin, L. M. Pasynkova, and E. S. Trekhov, collection cited in^[57], p. 87.
- ¹⁹⁵W. A. Brown and R. K. Landshoff, *J. Quantit. Spectr. Rad. Transfer* **11**, 1143 (1971).
- ¹⁹⁶V. T. Koppe, A. G. Koval', V. V. Gritsina, and Ya. M. Fogel', *Opt. Spektrosk.* **21**, 821 (1968) [**21**, 440 (1968)].
- ¹⁹⁷A. N. Vargin, R. I. Serikov, and E. S. Trekhov, collection cited in^[57], p. 72.
- ¹⁹⁸A. B. Callear, M. J. Pilling, and J. W. M. Smith, *Trans. Faraday Soc.* **62**, 2997 (1966).
- ¹⁹⁹J. Anketell and R. C. M. Icarner, *Proc. R. Soc. A* **301**, 355 (1967).
- ²⁰⁰P. S. Dube and D. K. Rai, *J. Phys.* **B4**, 579 (1971).
- ²⁰¹A. Kh. Mnatsakanyan, *Opt. Spektrosk.* **30**, 1015 (1971) [**30**, 544 (1971)].
- ²⁰²A. D. Rusin, *Vestn. Mosk. Univ. Fiz. Khim.* **13**, 196 (1972).
- ²⁰³J. C. Mohanty and B. S. Mohanty, *Indian J. Pure Appl. Phys.* **9**, 487 (1971).
- ²⁰⁴T. C. James, *J. Mol. Spectrosc.* **40**, 545 (1971).
- ²⁰⁵B. Chakraborty and Y. K. Pan, *J. Chem. Phys.* **56**, 3722 (1972).
- ²⁰⁶D. C. Jain, *J. Phys. B* **5**, 199 (1972).
- ²⁰⁷N. S. Murthy and B. N. Murthy, *J. Phys.* **B5**, 714 (1972).
- ²⁰⁸V. Degen and R. W. Nicholl, *J. Phys. B* **2**, 1240 (1969).
- ²⁰⁹B. Chakraborty, Y. K. Pan, and T. Y. Chang, *J. Chem. Phys.* **55**, 5147 (1971).
- ²¹⁰V. Hasson and R. W. Nicholls, *J. Phys.* **B4**, 1778 (1971).
- ²¹¹G. E. Copeland, *J. Chem. Phys.* **56**, 689 (1972).
- ²¹²V. Hasson and R. W. Nicholls, *J. Phys.* **B4**, 1769 (1971).
- ²¹³T. V. R. Ramakrishna and S. V. J. Lakshman, *Physica* **56**, 322 (1971).
- ²¹⁴J. D. Singh and M. Prasad, *Current Sci. (India)* **40**, 625 (1971).
- ²¹⁵T. Wentink and R. J. Spindler, *J. Quantit. Spectr. Rad. Transfer* **12**, 129 (1972).
- ²¹⁶M. Van Pee, W. R. Kineyko, and R. Caruso, *Combustion and Flame* **14**, 381 (1970).
- ²¹⁷S. E. Johnson, G. Capelle, and H. P. Broida, *J. Chem. Phys.* **56**, 663 (1972).
- ²¹⁸H. H. Mishels, *J. Chem. Phys.* **56**, 665 (1972).
- ²¹⁹R. J. Donovan and D. Husain, *Trans. Faraday Soc.* **63**, 2879 (1967).
- ²²⁰W. H. Smith and H. S. Liszt, *J. Quantit. Spectr. Rad. Transfer* **12**, 505 (1972).
- ²²¹J. Desequelles, M. Du Fay, and M. C. Pulizac, *Phys. Lett. A* **27**, 96 (1968).
- ²²²R. E. Imhoff, F. H. Read, and S. T. Beckett, *J. Phys.* **B5**, 896 (1972).
- ²²³R. F. Holland and W. B. Maier, *J. Chem. Phys.* **56**, 5229 (1972).
- ²²⁴M. Hollstein, D. C. Lorents, J. R. Peterson, and J. R. Sheridan, *Can. J. Chem.* **47**, 1858 (1969).
- ²²⁵R. S. Freund, *J. Chem. Phys.* **51**, 1979 (1969).
- ²²⁶D. Gray, J. L. Morack, and T. D. Roberts, *Phys. Lett. A* **37**, 25 (1971).
- ²²⁷H. Anton, *Ann. Phys. (N.Y.)* **18**, 178 (1966).
- ²²⁸J. Olmstead, A. S. Newton, and K. Street, *J. Chem. Phys.* **42**, 2321 (1965).
- ²²⁹H. Bubert and F. W. Froben, *Chem. Phys. Lett.* **8**, 242 (1971).
- ²³⁰A. J. D. Former, V. Hasson, and R. W. Nicholls, *J. Quantit. Spectr. Rad. Transfer* **12**, 627 (1972).
- ²³¹A. J. D. Former, V. Hasson, and R. W. Nicholls, *J. Quantit. Spectr. Rad. Transfer* **12**, 635 (1972).
- ²³²R. L. de Zafra, A. Marshall, and H. Metcalf, *Phys. Rev. A* **3**, 1557 (1971).
- ²³³P. S. Dube, *Indian J. Pure Appl. Phys.* **10**, 70 (1972).
- ²³⁴G. Capelle, K. Sakurai, and H. P. Broida, *J. Chem. Phys.* **54**, 1728 (1971).
- ²³⁵R. T. V. Ramakrishna and S. V. J. Lakshman, *Indian J. Pure and Appl. Phys.* **10**, 69 (1972).
- ²³⁶H. S. Liszt and W. H. Smith, *J. Quantit. Spectr. Rad. Transfer* **12**, 947 (1972).
- ²³⁷J. F. M. Aarts and F. J. De Heer, *Physica* **54**, 609 (1971).
- ²³⁸J. A. Coxon, *J. Quantit. Spectr. Rad. Transfer* **12**, 639 (1972).
- ²³⁹W. R. Jarman, *J. Quantit. Spectr. Rad. Transfer* **12**, 603 (1972).
- ²⁴⁰P. S. Dube, D. K. Rai, and N. L. Singh, *Indian J. Pure Appl. Phys.* **10**, 87 (1972).
- ²⁴¹T. C. James, *J. Chem. Phys.* **55**, 4118 (1971).
- ²⁴²B. L. Lutz and J. E. Hesser, *J. Chem. Phys.* **48**, 3042 (1968).
- ²⁴³J. E. Hesser, *J. Chem. Phys.* **48**, 2518 (1968).
- ²⁴⁴J. E. Hesser and K. Dressler, *J. Chem. Phys.* **47**, 3443 (1967).
- ²⁴⁵W. H. Smith, *J. Chem. Phys.* **54**, 1384 (1971).
- ²⁴⁶J. Geiger and H. Schmoranzner, *J. Mol. Spectrosc.* **32**, 39 (1969).

- ²⁴⁷ H. E. Porkie and N. H. Henneker, *J. Chem. Phys.* 55, 617 (1971).
- ²⁴⁸ G. W. F. Drake, D. C. Tyte, and R. W. Nicholls, *J. Quantit. Spectr. Rad. Transfer* 7, 639 (1967).
- ²⁴⁹ J. O. Arnold, *J. Quantit. Spectr. Rad. Transfer* 8, 1781 (1968).
- ²⁵⁰ E. H. Fink and K. H. Welge, *J. Chem. Phys.* 46, 4315 (1967).
- ²⁵¹ J. Geiger, *Z. Phys.* 181, 413 (1964).
- ²⁵² J. Geiger and M. Topschowsky, *Z. Naturforsch.* 21a, 626 (1966).
- ²⁵³ R. G. Bennett and R. W. Dalby, *J. Chem. Phys.* 31, 434 (1959).
- ²⁵⁴ D. J. Sebacher, *J. Chem. Phys.* 42, 1368 (1965).
- ²⁵⁵ L. L. Nicholls and W. F. Wilson, *Appl. Opt.* 7, 167 (1968).
- ²⁵⁶ K. H. Wagner, *Z. Naturforsch.* 19a, 716 (1964).
- ²⁵⁷ A. Chutjian, J. K. Link, and L. Brewer, *J. Chem. Phys.* 46, 2666 (1967).
- ²⁵⁸ R. L. Brown and W. Klemperer, *J. Chem. Phys.* 41, 3072 (1964).
- ²⁵⁹ L. Brewer, R. A. Berg, and G. M. Rosenblatt, *J. Chem. Phys.* 38, 1381 (1963).
- ²⁶⁰ G. Baumgartner, W. Demtröder, and M. Stock, *Z. Phys.* 232, 462 (1970).
- ²⁶¹ W. Demtröder, M. McClintock, and R. N. Zare, *J. Chem. Phys.* 51, 5495 (1969).
- ²⁶² S. E. Johnson, K. Sakurai, and H. P. Broida, *J. Chem. Phys.* 52, 6441 (1970).
- ²⁶³ S. J. Silvers and Chin Chi-Lian, *J. Chem. Phys.* 56, 5663 (1972).
- ²⁶⁴ K. C. Shotton and G. D. Chapman, *J. Chem. Phys.* 56, 1012 (1972).
- ²⁶⁵ E. B. Brusyanova, V. N. Kolesnikov, and N. N. Sobolev, *Opt. Spektrosk.* 19, 819 (1965) [*Opt. Spectrosc.* 19, 453 (1965)].
- ²⁶⁶ G. A. Capelle, S. E. Johnson, and H. P. Broida, *J. Chem. Phys.* 56, 6264 (1972).
- ²⁶⁷ A. P. Dronov, N. N. Sobolev, F. S. Faizullof, and V. A. Boiko, *Opt. Spektrosk.* 21, 727 (1966) [*Opt. Spectrosc.* 21, 397 (1967)].
- ²⁶⁸ K. Sakurai, S. E. Johnson, and H. P. Broida, *J. Chem. Phys.* 52, 1625 (1970).
- ²⁶⁹ S. E. Johnson, *J. Chem. Phys.* 56, 149 (1972).
- ²⁷⁰ R. F. Holland, *J. Chem. Phys.* 51, 3940 (1969).
- ²⁷¹ A. Skerbele and E. N. Lassetre, *J. Chem. Phys.* 53, 3806 (1970).
- ²⁷² A. W. Johnson and R. G. Fowler, *J. Chem. Phys.* 53, 65 (1970).
- ²⁷³ R. S. Freund, *J. Chem. Phys.* 50, 3734 (1969).
- ²⁷⁴ D. M. Golden, F. P. Del Greco, and F. Kaufman, *J. Chem. Phys.* 39, 3034 (1963).
- ²⁷⁵ K. R. German and R. N. Zare, *Phys. Rev. Lett.* 23, 1207 (1969).
- ²⁷⁶ R. G. Bennett and F. W. Dalby, *J. Chem. Phys.* 40, 1414 (1964).
- ²⁷⁷ R. T. Thomson and R. G. Fowler, *J. Quantit. Spectr. Rad. Transfer* 12, 117 (1972).
- ²⁷⁸ J. O. Arnold and R. W. Nicholls, *J. Quantit. Spectr. Rad. Transfer* 12, 1435 (1972).
- ²⁷⁹ N. R. Tawde and V. G. Tulasigeri, *J. Phys. B* 5, 1681 (1972).
- ²⁸⁰ W. H. Smith, *Astrophys. J.* 176, 265 (1972).
- ²⁸¹ W. H. Smith, *J. Chem. Phys.* 54, 4169 (1971).
- ²⁸² G. C. Singh, *J. Quantit. Spectr. Rad. Transfer* 12, 1343 (1972).
- ²⁸³ B. Maier and R. F. Holland, *J. Phys. B* 5, L118 (1972).
- ²⁸⁴ L. Schoonveld, *J. Quantit. Spectr. Rad. Transfer* 12, 1139 (1972).
- ²⁸⁵ T. Wentink and R. L. Spindler, *J. Quantit. Spectr. Rad. Transfer* 12, 1569 (1972).
- ²⁸⁶ T. G. Slinger and G. Black, *J. Phys. B*, 5, 1988 (1972).
- ²⁸⁷ T. L. Stephens and A. Dalgarno, *J. J. Quantit. Spectr. Rad. Transfer* 12, 569 (1972).
- ²⁸⁸ V. Hasson, A. J. D. Farmer, R. W. Nicholls, and J. Ankettel, *J. Phys. B* 5, 1248 (1972).
- ²⁸⁹ P. S. Dube, *Indian J. Pure Appl. Phys.* 10, 167 (1972).
- ²⁹⁰ V. S. Kushwana and B. P. Asthana, *Indian J. Pure Appl. Phys.* 10, 346 (1972).
- ²⁹¹ D. Lambert, *J. Quantit. Spectr. Rad. Transfer* 8, 1265 (1968).
- ²⁹² J. A. Harrington, A. P. Modica, and D. R. Libby, *J. Chem. Phys.* 44, 3380 (1966).
- ²⁹³ J. A. Harrington, A. P. Modica, and D. R. Libby, *J. Chem. Phys.* 45, 2720 (1966).
- ²⁹⁴ L. A. Kuznetsova and Yu. Ya. Kuzyakov, *Tr. Inst. Mekh. Mosk. Univ. No. 20*, 68 (1973).
- ²⁹⁵ T. C. James, *J. Chem. Phys.* 32, 1770 (1960).
- ²⁹⁶ J. A. Coxon, *J. Mol. Spectrosc.* 41, 566 (1972).
- ²⁹⁷ N. P. Penkin, in: *Spektroskopiya gazorazryadnoi plazmy (Spectroscopy of Discharge Plasma)*, Nauka, L. 1970, p. 63.
- ²⁹⁸ S. P. Sinha and C. L. Chatterjee, *Indian J. Pure Appl. Phys.* 10, 494 (1972).
- ²⁹⁹ B. P. Asthana, V. S. Kushawaha, J. S. Yadava, and K. P. R. Nair, *Indian J. Pure Appl. Phys.* 10, 463 (1972).
- ³⁰⁰ A. G. Gaydon, *Dissociation Energies and the Spectra of Diatomic Molecules (Russ. Transl., IL, M. 1949)*.
- ³⁰¹ J. T. Vanderslice, E. A. Mason, and W. G. Maisch, *J. Chem. Phys.* 32, 515 (1960).
- ³⁰² W. R. Jarman, *Can. J. Phys.* 38, 217 (1960).
- ³⁰³ W. R. Jarman, *J. Quantit. Spectr. Rad. Transfer* 11, 421 (1971).
- ³⁰⁴ P. A. Fraser and W. R. Jarman, *Proc. Phys. Soc. A* 66, 1145 (1953).
- ³⁰⁵ J. W. Cooley, *Math. Comp.* 15, 363 (1961).
- ³⁰⁶ D. R. Hartree, *The Calculation of Atomic Structures*, 1957 (Russ. Transl., IL, M. 1960).
- ³⁰⁷ D. J. Flinn, R. J. Spindler, S. Fifer, and M. Kelly, *J. Quantit. Spectr. Rad. Transfer* 4, 271 (1964).
- ³⁰⁸ R. W. Nicholls, *J. Res. NBS A* 68, 535 (1964).
- ³⁰⁹ R. N. Zare, *J. Chem. Phys.* 40, 1934 (1964).
- ³¹⁰ J. T. Steinfeld, R. N. Zare, L. Lesk, and W. Klemperer, *J. Chem. Phys.* 42, 25 (1966).
- ³¹¹ J. T. Steinfeld, R. N. Zare, L. Lesk, and W. Klemperer, *J. Chem. Phys.* 42, 25 (1966).
- ³¹² N. N. Sobolev, *Éksperimental'noe opredelenie sil élektronnykh perekhodov dvukhatomnykh molekul (Experimental Determination of the Electronic Transition Strengths for Diatomic Molecules)*, FIAN SSSR, M. 1966 (preprint).
- ³¹³ E. M. Weinstock and R. N. Zare, *J. Chem. Phys.* 56, 3456 (1972).
- ³¹⁴ E. M. Kudryavtsev, *Tr. Fiz. Inst. Akad. Nauk SSSR* 35, 74 (1966).
- ³¹⁵ J. K. McDonald and K. K. Innes, *J. Mol. Spectrosc.* 32, 501 (1969).
- ³¹⁶ T. V. Ramakrishna Rao and S. V. J. Lakshman, *J. Quantit. Spectr. Rad. Transfer* 12, 1063 (1972).
- ³¹⁷ W. J. Balfour, *Can. J. Phys.* 50, 1082 (1972).
- ³¹⁸ T. S. Wanchop and H. P. Broida, *J. Chem. Phys.* 56, 330 (1972).

- ³¹⁹ G. M. Lawrence, *J. Quantit. Spectr. Rad. Transfer* 5, 359 (1965).
- ³²⁰ A. Schadee, *J. Quantit. Spectr. Rad. Transfer* 7, 169 (1967).
- ³²¹ R. W. Nicholls, *J. Chem. Phys.* 38, 1029 (1963).
- ³²² R. W. Nicholls, *J. Res. NBS A* 65, 451 (1961).
- ³²³ H. A. Ory and A. P. Gittleman, *Astrophys. J.* 139, 357 (1964).
- ³²⁴ T. J. Cook and D. H. Levy, *J. Chem. Phys.* 57, 5059 (1972).
- ³²⁵ W. J. Balfour and R. F. Whitlock, *Can. J. Phys.* 50, 1648 (1972).
- ³²⁶ A. R. Fairbairn, *AIAA J.* 2, 1004 (1964).
- ³²⁷ C. E. Head, *Phys. Lett. A* 34, 92 (1971).
- ³²⁸ W. B. Maier and R. F. Holland, *Bull. Am. Phys. Soc.* 17, 695 (1972).
- ³²⁹ J. R. Peterson and J. T. Moseley, *J. Chem. Phys.* 58, 172 (1973).
- ³³⁰ A. A. Kon'kov, A. P. Razin, and V. S. Rudnev, *J. Quantit. Spectr. Rad. Transfer* 7, 345 (1967).
- ³³¹ K. R. German, R. N. Zare, and D. R. Crosley, *J. Chem. Phys.* 54, 4039 (1971).
- ³³² O. P. Shadrin and N. I. Zhirnov, *Opt. Spektrosk.* 34, 590 (1973).
- ³³³ K. L. Wray, *J. Quantit. Spectr. Rad. Transfer* 9, 255 (1969).
- ³³⁴ I. I. Galaktionov and Yu. N. Kolpakov, *Trudy III Vsesoyuznoi teplofizicheskoi konferentsii po svoistvam veshchestv pri vysokikh temperaturakh, Baku, 1968 (Proc. Third All Union Conf. on the Thermophysical Properties of Materials at High Temperatures Baku, 1968).*
- ³³⁵ D. C. Cartwright, *J. Chem. Phys.* 58, 178 (1973).
- ³³⁶ R. S. Mulliken, *J. Chem. Phys.* 714, 20 (1939).
- ³³⁷ W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities (A Critical Data Compilation)*, NBS4, 1966.
- ³³⁸ V. V. Nalimov, *Prilozhenie matematicheskoi statistiki k analizu veshchestva (Application of Mathematical Statistics to the Analysis of Matter)*, Fizmatgiz, M. 1961.
- ³³⁹ A. D. Rusin and O. P. Yakovlev, *Vestn. Mosk. Univ. Ser. Khim.* 13, 716 (1972).
- ³⁴⁰ H. Klemsdal, *J. Quantit. Spectr. Rad. Transfer* 13, 517 (1973).
- ³⁴¹ J. C. McCallum, W. R. Jarman, and R. W. Nicholls, *CRESS Spectroscopic Reports No. 1 (1970)*, No. 2 (1971), No. 3-5 (1972), York University, Toronto.
- ³⁴² J. O. Arnold and R. W. Nicholls, *J. Quantit. Spectr. Rad. Transfer* 13, 115 (1973).
- ³⁴³ J. G. Chervenak and R. A. Anderson, *J. Opt. Soc. Am.* 61, 952 (1971).
- ³⁴⁴ T. G. Slanger and G. Black, *J. Chem. Phys.* 55, 2164 (1971).
- ³⁴⁵ M. J. Mumma, J. E. Stone, and E. C. Zipf, *J. Chem. Phys.* 54, 2627 (1971).
- ³⁴⁶ J. Rogers and R. Anderson, *J. Opt. Soc. Am.* 60, 278 (1970).
- ³⁴⁷ J. E. Mentall and H. D. Morgan, *J. Chem. Phys.* 56, 2271 (1972).
- ³⁴⁸ D. C. Jain, *J. Quantit. Spectr. Rad. Transfer* 12, 759 (1972).
- ³⁴⁹ D. D. Gray, T. D. Roberts, and J. L. Morack, *J. Chem. Phys.* 57, 4190 (1972).
- ³⁵⁰ R. Anderson, R. Sutherland, and N. Frey, *J. Opt. Soc. Am.* 62, 1127 (1972).
- ³⁵¹ M. Jeunehomme, *J. Chem. Phys.* 44, 4253 (1966).
- ³⁵² J. Dufayrad, M. Lombard, and O. Nedelec, *C. R. Acad. Sci. B* 276, 461 (1973).
- ³⁵³ W. S. Cathro and J. C. Mackie, *J. Chem. Soc. Faraday Trans.* 69, 237 (1973).
- ³⁵⁴ J. F. M. Aarts and F. J. De Heer, *Physica* 49, 425 (1970).
- ³⁵⁵ J. C. Rich, *Astrophys. J.* 153, 327 (1968).
- ³⁵⁶ M. J. Pilling, A. M. Bass, and W. Braun, *J. Quantit. Spectr. Rad. Transfer* 11, 1593 (1971).
- ³⁵⁷ H. S. Kiszt and W. H. Smith, *J. Quantit. Spectr. Rad. Transfer* 12, 1591 (1972).
- ³⁵⁸ G. M. Lawrence and S. C. Seitel, *J. Quantit. Spectr. Rad. Transfer* 13, 713 (1973).
- ³⁵⁹ G. A. Capella and H. P. Broida, *J. Chem. Phys.* 58, 4212 (1973).
- ³⁶⁰ R. A. Sutherland and R. A. Anderson, *J. Chem. Phys.* 58, 1226 (1973).
- ³⁶¹ F. N. Putilin, A. L. Evseenko, L. A. Kuznetsova, and Yu. Ya. Kuzyakov, *Zh. Fiz. Khim.* 47, 759 (1973).
- ³⁶² G. T. Best and H. S. Hoffman, *J. Quantit. Spectr. Rad. Transfer* 13, 69 (1973).
- ³⁶³ M. Yoshimine, A. D. McLean, and B. Lin, *J. Chem. Phys.* 58, 4412 (1973).
- ³⁶⁴ M. Marchetti, P. S. Julienne, and M. Krauss, *J. Res. NBS A* 76, 665 (1972).
- ³⁶⁵ D. L. Judge and L. G. Lee, *J. Chem. Phys.* 57, 455 (1972).
- ³⁶⁶ M. Yoshimine, S. Green, and P. Thaddeus, *Astrophys. J.* 183, 899 (1973).
- ³⁶⁷ S. Green, S. Hornstein, and C. F. Bender, *Astrophys. J.* 179, 671 (1973).
- ³⁶⁸ G. Berbig, *Z. Astrophys.* 68, 243 (1968).
- ³⁶⁹ T. Wentink and R. J. Spindler, *J. Quantit. Spectr. Rad. Transfer* 13, 595 (1973).
- ³⁷⁰ P. E. Rouse and R. Engleman, *J. Quantit. Spectr. Rad. Transfer* 13, 297 (1973).
- ³⁷¹ W. H. Smith and R. Chevalier, *Astrophys. J.* 177, 835 (1972).
- ³⁷² F. N. Putilin, O. D. Khramova, L. A. Kuznetsova, and Yu. Ya. Kuzyakov, *Zh. Fiz. Khim.* 47, 1339 (1973).
- ³⁷³ L. Kurzweg, G. T. Egbert, and D. J. Burns, *J. Chem. Phys.* 59, 2641 (1973).
- ³⁷⁴ M. B. Moeller and S. J. Silver, *Chem. Phys. Lett.* 19, 78 (1973).
- ³⁷⁵ P. N. Sinha and C. L. Chatterjee, *Indian J. Pure Appl. Phys.* 11, 57 (1973).
- ³⁷⁶ C. A. Van de Runstraat, T. R. Govers, W. B. Maier, and R. F. Holland, *Chem. Phys. Lett.* 18, 549 (1973).
- ³⁷⁷ W. M. Jackson, *J. Chem. Phys.* 59, 960 (1973).
- ³⁷⁸ J. Le Calve, M. Bourene, M. Schmidt, and M. Clerc, *J. Phys. (Paris)* 30, 807 (1969).
- ³⁷⁹ A. J. Smith, R. E. Imhof, and F. H. Read, *J. Phys.* B 6, 1333 (1973).
- ³⁸⁰ L. C. Lee and D. L. Judge, *J. Phys. B* 6, L121 (1973).
- ³⁸¹ R. Anderson, D. Wilcox, and R. Sutherland, *Nucl. Instrum. Methods* 110, 167 (1973).
- ³⁸² B. Chakraborty and Y. K. Pan, *Appl. Spectr. Rev.* 7, 283 (1973).

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