

Problems in the description of the intensities of electronic spectra of diatomic molecules in the adiabatic approximation

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A review is given of the current state of research into the radiative properties of diatomic molecules. Problems that arise in the theoretical description of intensity distributions in molecular spectra are discussed, possible ways of solving these problems are examined, and progress achieved in overcoming such problems is surveyed. It is shown that it is possible to provide a reliable quantitative description of the intensity distribution in the electronic spectra of diatomic molecules by using the adiabatic Born-Oppenheimer model, provided the appropriate "corrections" are introduced for the electron-vibration (EV) and vibration-rotation (VR) interactions. Particular attention is devoted to the current state of research into the effect of these interactions on Franck-Condon factors, and to a possible way of taking into account the VR interaction, which has not been adequately dealt with in the literature. A special section deals with possible applications of studies of radiative parameters (above all the Franck-Condon factors with allowance for molecular rotations) in the effective solution of many applied and theoretical problems in different branches of science, engineering, and technology, which are concerned with molecular transitions between EVR levels.

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1. INTRODUCTION

Quantitative description of the intensity distribution in the electronic-vibrational-rotational (EVR) spectra of molecules and ions in the gaseous phase is essential for many of the theoretical and applied problems that arise in astrophysics, plasma physics, plasma chemistry, molecular spectroscopy, laser chemistry, and the photochemistry of planetary atmospheres, as well as in many other branches of science, engineering, and technology that come into contact with molecular transitions between EVR levels. Such calculations rely on the availability of a variety of molecular parameters such as the electronic, vibrational, and rotational level energies, which determine the transition wavenumbers, and also the EVR transition probabilities. They include the transition strengths S_e^{mn} , the Franck-Condon factors $q_{v',v''}$, and the Hönl-London factors $S_{J',J''}$ (the last of these and the electronic oscillator strengths f_e^{mn} , the electronic transition dipole elements R_e^{mn} , and the lifetimes of the electronic excited states τ_m , are usually collectively referred to as the *radiative parameters*).

The aim of the present paper is to review the con-

temporary state of research on the radiative parameters of diatomic molecules, to discuss the problems that arise in the description of intensity distributions in molecular spectra, to examine possible ways of solving these problems, and to survey progress already achieved in the solution of such problems. Our review is a natural development of our previous publications¹⁻³ in this field. Important changes have taken place in this area in the course of the last decade.

Firstly, experimental methods for investigating electronic transition probabilities (such as different methods of measuring electronic excited-state lifetimes, and so on) have undergone intensive development and are now widely used with the result that many measurements have been performed on electronic transition probabilities in a large number of molecular systems. These questions have been examined in detail in our previous publications^{2,3} and will be touched upon here only briefly for the sake of completeness. Secondly, recent experimental studies have served as a basis for further progress in the theory of EVR transition probabilities. Here, it is important to emphasize above all the fact that it has now been convincingly shown that the

EVR interaction must be taken into account in the theoretical description of the intensity distribution in molecular spectra. The associated problems are examined in this paper, and particular attention is devoted to the contemporary state of research into the effect of the vibrational-rotational (VR) interaction on the Franck-Condon factors, and to possible ways of taking it into account, since these topics have not been adequately dealt with in the literature.

The need for this review has arisen above all for essentially practical reasons such as the fact that not only the traditional radiative parameters, but even the dependence of the electronic transition dipole moments on the nuclear separation and the Franck-Condon factors corrected for rotation are now being taken into account in different applications in engineering and technology. A simple survey of the applications of radiative parameters would therefore be inappropriate, and we have had to provide a special section in which we discuss in detail possible applications of these parameters (above all the Franck-Condon factors with and without the VR interaction) to the effective solution of many applied and theoretical problems.

2. INTENSITY DISTRIBUTION IN ELECTRONIC-VIBRATIONAL-ROTATIONAL SPECTRA

(a) Born-Oppenheimer adiabatic approximation

In accordance with the Born-Oppenheimer (BO) approximation,⁴ the intensity distribution in the rotational structure of the EVR spectrum is determined by the Hönl-London (HL) factors $S_{J'J''}$, whereas in the vibrational structure it is determined by the Franck-Condon factors (FCF) $q_{v'v''}$, where the electronic transition dipole moment matrix element R_e^{mn} (or the strength of the electronic transition S_e^{mn} which is uniquely related to it) is independent of the nuclear separation:

$$S_{J'J''} = \sum_{M'M''} \left| \int \psi_{J'M'} f(\theta, \varphi) \psi_{J''M''} \sin \theta d\theta d\varphi \right|^2, \quad (1)$$

$$q_{v'v''} = \left| \int \psi_{nv'}(r) \psi_{mv''}(r) dr \right|^2, \quad (2)$$

$$|R_e^{mn}|^2 = \left| \int \psi_{ne} \hat{P} \psi_{me} d\tau_e \right|^2, \quad (3)$$

$$S_e^{mn} = \sum_{\Sigma'} \sum_{\Lambda'} |R_e^{mn}|^2 = K |R_e^{mn}|^2 \quad (4)$$

where ψ_{JM} , ψ_v , ψ_e represent the rotational, vibrational, and electronic wavefunctions, respectively.

The sum in (1) is evaluated over all the Zeeman components (M is the magnetic quantum number) and the function $f(\theta, \varphi)$ describes the dependence of the dipole moment on the angular coordinates θ and φ . In equation (3), \hat{P} is the dipole moment operator for the particular electronic transition, the symbols Σ and Λ in (4) define the components of the spin and Λ doublet, K is determined by the normalization of the HL factors, and v , J are the vibrational and rotational quantum numbers. Parameters with a single prime refer to the upper level n and those with a double prime to the lower level m .

The intensity of an individual rotational line can then be described as follows:

$$\int I(\tilde{\nu}) d\tilde{\nu} = \frac{16\pi^3 c}{3} \frac{\tilde{\nu}_{nv'J'}}{\tilde{\nu}_{mv''J''}} N_{nv'J'} \frac{S_e^{mn}}{K} q_{v'v''} \frac{S_{J'J''}}{2J''-1}, \quad (5)$$

$$\int k(\tilde{\nu}) d\tilde{\nu} = \frac{8\pi^3}{3hc} \frac{\tilde{\nu}_{nv'J'}}{\tilde{\nu}_{mv''J''}} N_{nv'J'} \frac{S_e^{mn}}{K} q_{v'v''} \frac{S_{J'J''}}{2J''-1}, \quad (6)$$

where $j(\tilde{\nu})$ and $k(\tilde{\nu})$ are the emission and absorption coefficients, respectively, $\tilde{\nu}_{n(m)vJ}$ is the wavenumber of the rotational line, and $N_{n(m)vJ}$ is the population of the corresponding level.

As a rule, the wavenumbers $\tilde{\nu}_{n(m)vJ}$ can be readily calculated from the molecular constants of the states connected by the transitions, which can be found in widely available tabulations⁵⁻⁷. For example, the relevant formulas can be found in Refs. 3, 8, and 9. It is important to draw attention to the fact that the concept of a "rotational line" is treated in the literature in different ways. The necessity for a clear definition of this concept becomes particularly obvious when the dipole moment matrix elements of electronic transitions are examined (see Chapter II in Ref. 3, and also Ref. 10).

(b) Deviations from the Born-Oppenheimer approximation. Allowance for the electronic-vibrational-rotational interactions

Most calculations of the intensity distribution in EVR spectra have been confined, until recently, to within the framework of the model represented by equations (1)–(6). However, it is now well-known that the adiabatic BO approximation (various types of this approximation are discussed in detail in the review paper given in Ref. 14) is often too crude, so that the EVR interaction in the molecule must then be taken into account. It turns out that, for most molecular systems, the most important effect is that due to the electronic-vibrational (EV) interaction in the corresponding electronic states connected by the transitions, which ensures that the electronic transition strength S_e^{mn} becomes a function of the nuclear separation. The computational model can be improved by replacing the constant S_e^{mn} in equations (5)–(6) with a function of the nuclear separation, $S_e^{mn}(\tau)$. So far, quantum-mechanical calculations of this function have been rather difficult, so that, in practice, the function $S_e^{mn}(\tau)$ has been determined by using various semiempirical approximations for S_e^{mn} as a function of τ . The approximations used over the years are summarized in Refs. 2 and 3 (some of the details can also be found in the recently published Refs. 11–13). The most popular procedure has been that based on the method of τ -centroids.

It turns out that this semiempirical procedure can be used to obtain the function $S_e^{mn}(\tau_{v'v''})$ where $\tau_{v'v''}$ is the τ -centroid that defines a certain "mean nuclear separation" for the $v' - v''$ vibrational band associated with a given electronic transition, where $\tau_{v'v''} = q_{v'v''}^{-1/2} \int \psi_{v'}(\tau) \times \tau \psi_{v''}(\tau) d\tau$. We have critically reviewed all published work on $S_e^{mn}(\tau_{v'v''})$ up to 1979 inclusive, in order to identify the most reliable among them. The resulting recommendations for approximately 50 electronic transitions are given in Table 4.7 of Ref. 3 (see also Ref. 2). We then used the recommended functions $S_e^{mn}(\tau_{v'v''})$ for 35 molecular systems to transform the $S_e^{mn}(\tau_{v'v''})$ into simple and, physically, readily interpreted S_e^{mn} as functions of wavelength λ , which are also very convenient in machine computations of intensity distributions¹⁵. The

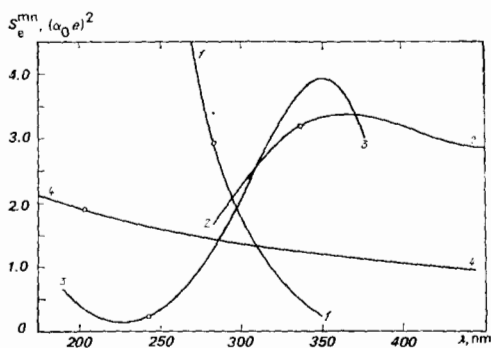


FIG. 1. Transition strengths S_e^{mn} for the electronic band systems of diatomic molecules as functions of wavelength. The symbol \circ marks on each line the value of S_e^{mn} for the (0, 0) band: 1—CO ($b^3\Sigma - a^3\Pi$) ($3+$), 2—N₂ ($C^3\Pi_u - B^3\Pi_g$) ($2+$), 3—SO ($B^3\Sigma_u - X^3\Sigma_g$), 4—O₂ ($B^3\Sigma_g - X^3\Sigma_g$)—Schuman-Runge system.

data on the functions $S_e^{mn}(\lambda)$ are shown in Figs. 1–7 which clearly illustrate possible variations in S_e^{mn} and the extent to which these variations are unpredictable *a priori* (see, for example, the Vigar-Kaplan system of N₂, the $B^2\Sigma - X^2\Sigma$ system of LaO, or the $B^1\Sigma - X^1\Sigma$ system of BeO).

Let us now consider the accuracy of the functions $S_e^{mn}(\lambda)$ in Figs. 1–7. Without going into details, which can be found in Ref. 15, we note that the approximate expressions for $S_e^{mn}(\lambda)$, upon which Figs. 1–7 are based, were obtained on the basis of the following criterion: the maximum differences between S_e^{mn} given by these expressions and the “accurate” initially specified values of this quantity (obtained from the functions $S_e^{mn}(r_{v,v'})$ in Table 4.7 of Ref. 3) must not exceed 10%. This numerical condition was forced on us by the fact that the true accuracy of the initial functions $S_e^{mn}(r_{v,v'})$ determined from experimental data (on the relative intensities of different EV bands, or from the lifetimes of different EV levels) usually amounts to a few percent (see Refs. 2, 16, and 17).

Thus, for example, the graph of $S_e^{mn}(\lambda)$ for the second positive system of N₂ (the $C^3\Pi - B^3\Pi$ transition; see curve 2 in Fig. 1) was plotted by using the expression

$$S_e^{mn}(\lambda) = (457 \pm 36.6) [1 - 8.046 \cdot 10^{-3}\lambda + 19.65 \cdot 10^{-6}\lambda^2 - 15.76 \cdot 10^{-9}\lambda^3]^2, \quad (7)$$

where S_e^{mn} is in units of $(a_0 \cdot e)^2$ and λ is in nanometers.

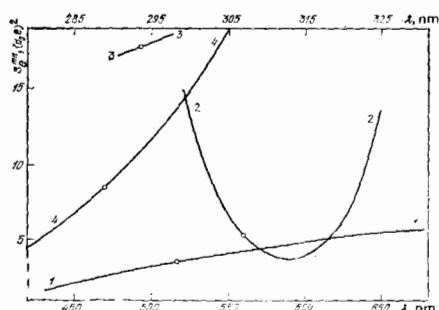


FIG. 2. Same as in Fig. 1: 1—C₂ ($d^3\Pi - a^3\Pi$) Swann system, 2—LaO ($B^2\Sigma - X^2\Sigma$), 3—Na₂ ($B^1\Pi - X^1\Sigma$), 4—SiF ($B^2\Sigma - X^2\Pi$) (upper wavelength scale runs from 285 to 325 nm).

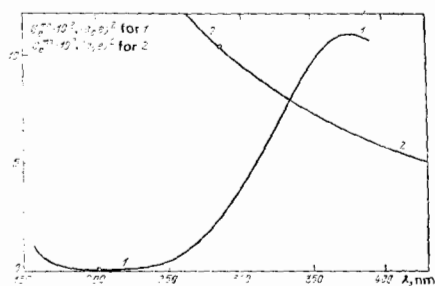


FIG. 3. Same as in Fig. 1: 1—N₂ ($A^3\Sigma_u - X^1\Sigma_g^+$)—Vigar-Kaplan system, 2—O₂ ($A^3\Sigma_u^+ - X^3\Sigma_g^-$)—forbidden Herzberg system I.

When the S_e^{mn} were calculated from this expression, the deviation from the initially specified “accurate” values of S_e^{mn} was found to be less than 8% (see Table 3 in Ref. 15; we note, by the way, that the expression for the ($2+$)-system of N₂ must now be augmented with recent independent measurements^{18,19} of $S_e^{mn}(r_{v,v'})$).

It should be clear from the foregoing that when the EV interaction is taken into account by introducing the functions $S_e^{mn}(r)$ (with S_e^{mn} determined by the r -centroid procedure, or S_e^{mn} as a function of the wavelength λ , or S_e^{mn} as a function of the wavenumber $\bar{\nu}$), this substantially improves the final calculated intensity distributions. However, the numerous experimental data that have now accumulated on the individual rotational lines in EVR spectra¹ show that the inclusion of only the EV interaction (through the functions $S_e^{mn}(r)$) is often inadequate for an accurate description of the intensity distribution. When this is so, we have to face the problem of taking into account the effect of the VR interaction on Franck-Condon factors.

Although all this must now be fairly obvious, there is some point in emphasizing that the present authors hold the view that a reliable quantitative description of the intensity distribution in the EVR spectra of diatomic molecules can be achieved on the basis of the adiabatic model (5)–(6) with “corrections” for the EV and VR interactions.² Corrections for the EV interaction (functions $S_e^{mn}(r)$) have now been discussed in sufficient detail. We must now concentrate on the present state of research on the effect of the VR interaction on Franck-Condon factors, and ways of taking this into account, since this has not as yet been adequately discussed in the literature. It then becomes necessary to analyze carefully the numerous questions relating to the validity of the various potentials $U(r)$ for the computation of classical Franck-Condon factors (without taking rotation into account, i.e., with $J=0$), which are also being used to compute the Franck-Condon factors with allowance for rotation (i.e., with $J \neq 0$), the development of computational methods for the Franck-Condon factors, and a number of other questions.

¹Modern experimental methods for the investigation of the EVR spectra of molecules and possible future developments are reviewed, for example, in the excellent review of Macpherson and Barrow.²⁰

²In other words, actually remaining with the “framework” of the BO approximation.

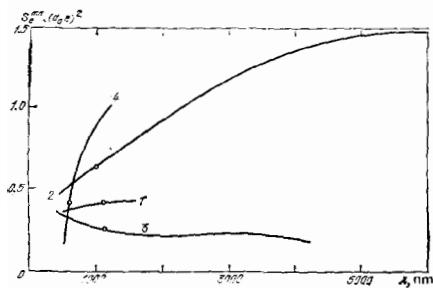


FIG. 4. Same as in Fig. 1: 1—CN ($A^2\Pi - X^2\Sigma$)—red system, 2— N_2 ($B^3\Pi - A^3\Sigma$)—(1+)—system, 3— Nb_2^+ ($A^2\Pi - X^2\Sigma$)—Meinel system, 4— O_2^+ ($b^4\Sigma - a^4\Pi$)—(1-)—system.

3. THEORETICAL METHODS FOR DETERMINING FRANCK-CONDON FACTORS

(a) Current state of the problem

The Franck-Condon principle^{21,22} is very widely used in qualitative explanations of various cases of intensity distributions in EVR spectra. The Franck-Condon factors are used within the framework of the BO approximation in the quantitative interpretation of intensities.

Effective methods of computing Franck-Condon factors have now been developed^{1,23}. The most complete and systematic account of the majority of the more important methods was given in Ref. 3. However, since that time, several new papers have been published that are devoted, on the one hand, to the improvement of traditional methods of calculating Franck-Condon factors and, on the other hand, to the development of new approaches to the computation of Franck-Condon factors with allowance for rotation. We shall therefore proceed in the following order: we shall first discuss new aspects of traditional methods for the determination of Franck-Condon factors, and then go on to consider the effect of the VR interaction of these factors. Finally, we shall conclude with a discussion of different areas of application of Franck-Condon factors.

(b) Calculations of Franck-Condon factors in the harmonic approximation

It is well-known that the harmonic approximation is relatively crude even for low-quantum numbers (see for example, Refs. 3 and 24). However, there are both theoretical and applied problems that do not require

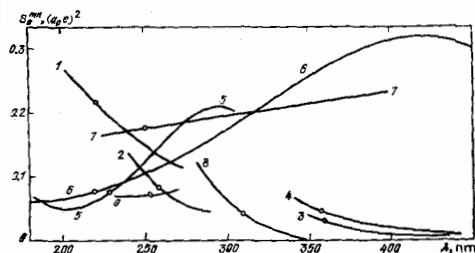


FIG. 5. Same as in Fig. 1: 1— CO^+ ($B^2\Sigma - X^2\Sigma$) (1-), 2—CS ($A^1\Pi - X^1\Sigma$), 3— HBr^+ ($A^2\Sigma - X^2\Pi$), 4— HCl^+ ($A^2\Sigma - X^2\Pi$), 5—NO ($A^2\Sigma - X^2\Pi$) γ , 6—NO ($B^2\Pi - X^2\Pi$) β , 7— O_2^+ ($A^2\Pi - X^2\Pi$) (2-), 8—OH ($A^2\Sigma - X^2\Pi$), 9—PN ($A^1\Pi - X^1\Sigma$).

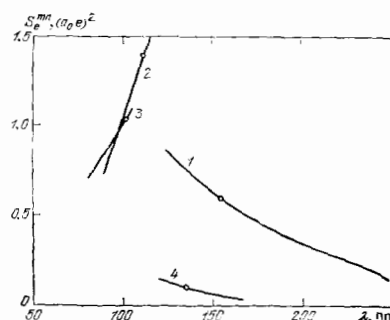


FIG. 6. Same as in Fig. 1: 1—CO ($A^1\Pi - X^1\Sigma$)—fourth positive system, 2— H_2 ($B^1\Sigma - X^1\Sigma$)—Lyman system, 3— H_2 ($C^1\Pi - X^1\Sigma$)—Werner system, 4— NO^+ ($A^1\Pi - X^1\Sigma$).

highly precise Franck-Condon factors and, in such cases, even the harmonic approximation is quite acceptable²⁵⁻²⁸.

The first analytic expressions for the Franck-Condon factors were obtained in the classical paper of Hutchinson²⁹ who used harmonic oscillator wavefunctions. Many attempts were subsequently made to obtain these expressions in a simpler or more general form (the formulas given in Ref. 29 are valid only for $v', v'' \leq 4$). It will be sufficient to mention the papers of Manneback³⁰, Wagner³¹, Mnatsakanyan²⁶, Lin³², and Nicholls^{33,34}. Frequent attempts were also made to improve on the harmonic approximation by introducing different "perturbations" into the harmonic wavefunction. Here again, we mention only the most important papers, namely, those in Refs. 35-37, since a complete critical survey of all this work is given in the review literature^{1,38}. We also particularly mention the two very recent and very perceptive analytic reviews by Terasaka and Matsushita³⁹ and by Waldenström and Razi Nagvi,⁴⁰ which give detailed comparative analyses of the physical and mathematical properties of different models involving the harmonic approximation. Papers not covered by these reviews but deserving attention are those given in Refs. 26, 32 and 33, which put forward the idea of the average α -parameter of the harmonic wavefunction and report two-parametric formulas for the Franck-Condon factors. However, the very simple algebraic relationships reported in a recent paper by Nicholls³⁴ are the most convenient. The working formulas contain only one molecular transition parameter,

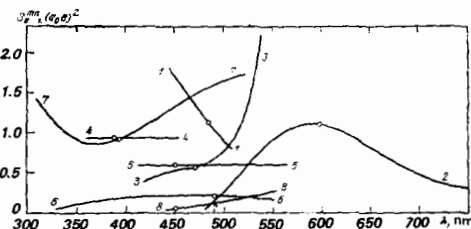


FIG. 7. Same as in Fig. 1: 1—AlO ($B^2\Sigma - X^2\Sigma$), 2—BaO ($A^1\Sigma - X^1\Sigma$), 3—BeO ($B^1\Sigma - X^1\Sigma$), 4—CN ($B^2\Sigma - X^2\Sigma$)—violet system, 5—CO ($B^1\Sigma - A^1\Pi$)—Angstrom system, 6— CO^+ ($A^2\Pi - X^2\Sigma$)—comet-like system, 7— N_2^+ ($B^2\Sigma - X^2\Sigma$)—first negative system, 8—PbO ($B1 - X^1\Sigma$).

U , which is calculated from the molecular constants ω_e , r_e , μ_A as follows:

$$U = \frac{S^2}{2}, \quad (8)$$

where

$$S = \frac{\sqrt{\mu_A \omega_e \Delta r_e}}{5.807}, \quad (9)$$

$$\tilde{\omega}_e = \frac{2\sqrt{\omega_e^2 \omega_e^*}}{\sqrt{\omega_e^*} + \sqrt{\omega_e}}. \quad (10)$$

It is important to emphasize that, unfortunately, Nicholls' paper³⁴ suffers from an error which has crept into equation (2e) for the parameter S , so that *this parameter must be calculated from equation (9) given above*.

The idea that has enabled Nicholls³⁴ to obtain one-parameter formulas is simple and involves taking the average of the half-widths $W = 5.807/\sqrt{\mu_A \omega_e}$ of the potentials for $v = 0$ in the rigorous expressions for the vibrational wavefunctions for the combining states, i.e., $\bar{W} = (W' + W'')/2$.

The overlap integral (2) then leads to the general expression for $q_{v'v}$ ($0 \leq v \leq 3$ and $0 \leq V \leq 6$; $v = v'$, $V = v''$):

$$q_{v'v} = \frac{U^{V-v} e^{-U}}{v!V!} \{ (U-V)^v - F(v-2)V[v(U-V)+2]^{v-2} \}; \quad (11)$$

where F is the Heaviside function. By exploiting the properties of this function we can readily show that

$$q_{0,v} = \frac{U^V e^{-U}}{V!}, \quad V \geq 0, \quad (12)$$

$$q_{1,v} = \frac{U^{V-1} e^{-U}}{V!} (U-V)^2, \quad V \geq 1, \quad (13)$$

$$q_{2,v} = \frac{U^{V-2} e^{-U}}{2!V!} [(U-V)^2 - V]^2, \quad V \geq 2, \quad (14)$$

$$q_{3,v} = \frac{U^{V-3} e^{-U}}{3!V!} \{ (U-V)^2 - V[3(U-V)+2] \}^2, \quad V \geq 3. \quad (15)$$

The satisfactory validity of these computational formulas can be illustrated by comparing the calculated values of the Franck-Condon factors with values obtained by the most accurate RKR approximation for the CN red band system.

In conclusion of this discussion of harmonic approximations, it is, in our view, essential to emphasize once again that *the use of these approximations is a compromise*. The great attraction of harmonic approximations is that they enable us to obtain analytic solutions for many problems, but their undesirable feature is that the accuracy of the Franck-Condon factors and, frequently, of the final result, is low. This dilemma must be examined in each particular case in the light of the fact that there exists the basically more accurate anharmonic approximation that can be used to evaluate the Franck-Condon factors.

(c) Anharmonic potentials

The most accurate values of Franck-Condon factors are obtained by using the RKR method, or one of its modifications³. However, the use of the RKR potentials gives rise to its own important complications. Firstly, the Schrodinger equation incorporating this potential does not have an exact analytic solution, so that approximate methods of integration have to be employed. There is practically no published information on uncer-

tainties in the values of ψ_v due to the approximate nature of the solution of the Schrodinger equation. Most programs for the computation of Franck-Condon factors by the RKR method use the Numerov-Cooley⁴¹ method (see, for example, Refs. 42 and 43) in which the wave equation is replaced by a finite-difference equation that is then solved by iteration.³⁾ We have used the example of the $A^1\Sigma$ state of BaO to estimate⁴³ the uncertainties in the wavefunctions that arise when the exact Schrodinger equation is replaced with the approximate Numerov equation, and have shown that the uncertainty does not exceed 2%. Secondly—and this is much more important—a sufficient volume of reliably determined spectroscopic data for the determination of the true RKR potentials is not always available, especially near the dissociation limit.

It is precisely for this reason that various analytic potentials are widely used in addition to true potentials. The three-parameter Morse potential is undoubtedly the most popular among them. Blinkova and Popova⁴⁴ have analyzed the usefulness of certain other three-parameter potentials (those of Levin, Varshney, and Lippincott). Other analytic potentials that are being used include those of Hulburt and Hirschfelder,^{45,46} Lennard-Jones⁴⁷, and Poschl and Teller.^{48,50} There have also been attempts to use effective vibrational potentials in the form of power functions, obtained by expanding the function $U(r)$ into a series. For example, Huffaker⁵¹ has derived formulas for the coefficients in series such as those of Dunham, Simons, Parr and Finlan, and others in terms of spectroscopic data, and has discussed the validity and reliability of such potentials. Other analytic potentials could be mentioned here (see, for example, Refs. 54–57), but it is probably better to refer the reader to recent reviews^{58,59} dealing with potentials for diatomic molecules.

Finally, it is important to note that the last decade has seen the development of *ab initio* quantum-mechanical calculations of potential functions not only for the ground states but also the excited electronic states which, in turn, has led to *ab initio* calculations of Franck-Condon factors (see, for example, Refs. 60–62). To obtain reliable data, one must then use either the configuration interaction or the multiconfigurational self-consistent field method. The latter method is reviewed, for example, in Ref. 63, and a complete examination of problems arising in quantum-mechanical calculations is given in the monograph by Rambidi *et al.*⁶⁴

Thus, it will be clear from the foregoing survey that a great variety of different molecular potentials is available for the computation of Franck-Condon factors. However, it is important to emphasize that the great

³⁾ In addition to the difference methods, other techniques are being developed for the solution of the vibrational problem for numerically specified potentials.⁵² Searches are also continuing for rational ways of computing the integrals $f(\psi)$ and $g(\psi)$ which are known to determine the turning points on the RKR potentials. Thus, Telle and Telle⁵³ have proposed a new promising method for eliminating the singularity in the integrals.

majority of calculations of these factors have been performed with the RKR or Morse potentials. It was therefore interesting to compare the values obtained for the Franck-Condon factors by using all these potentials in turn. It was natural to expect that, when the shapes of the true and the Morse potential curves were in agreement, there should be an adequate correlation between the corresponding values of the Franck-Condon factors. Franck-Condon factors are now available for more than 400 molecular systems, so it was possible to compare the factors calculated from the Morse and RKR potentials for 80 systems. It was confirmed that there was in fact good correlation between the Franck-Condon factors when the RKR and Morse potentials were close to one another.⁴⁾

It is important to note that, so far, we have been concerned with Franck-Condon factors obtained for the Morse potential (and other analytic potentials) by numerical integration of the wavefunctions. The advantages of traditional methods of numerical integration, and difficulties encountered in such calculations, are well known.³ On the other hand, the development of accurate methods of numerical integration of wavefunctions for anharmonic potentials has been paralleled by the development of approximate methods for their evaluation. For example, Doktorov *et al.*⁷¹⁻⁷³ have reported a further development of the α -averaging method for the Morse potential. The recurrence formulas that they have proposed for the evaluation of the Franck-Condon factors are valid for arbitrary relationships between the parameters α' and α'' .

The α -averaging method gives rise to a considerable simplification, but reliable results are obtained by this method only for small values of v . WKB methods³ have therefore continued to be used, since it is precisely for large values of v that they enable us to replace the Laguerre polynomials, which have alternating signs, with their asymptotic integral expressions. Modifications of the WKB method have recently been put forward.⁷⁴⁻⁷⁶ The WKB integrals were evaluated in Ref. 74 by the method of steepest descents, which reduces numerical difficulties and leads to relatively simple analytic expressions for Franck-Condon factors. Another approach to the estimation of WKB integrals is developed in Refs. 75 and 76. The algorithm put forward in Ref. 76, and based on the use of an accurate representation for the inverse Vandermonde matrix, deserves particular attention. This algorithm results in a considerable saving in machine time without loss of precision. However, as far as the WKB approximation is concerned, we must

⁴⁾As an example illustrating this situation, we mention the good agreement obtained for the Franck-Condon factors for the $B^3\Pi_{g^-} - X^1\Sigma_g^+$ system of I_2 , calculated by the Morse method by Halmann *et al.*⁶⁵ and subsequently by Bugrim and Makrenko⁶⁶, and by the RKR method by Zare⁶⁷ and subsequently by Tellinghuisen.⁶⁸ The differences do not exceed a few percent for Franck-Condon factors with $v' \leq 26$ and $v'' \leq 20$. It is also quite clear that, when there is a discrepancy between the Morse and RKR potentials (for example, for the $B^2\Sigma$ state of CH^{69} or the $B^2\Sigma$ state of AlO^{70}), the Franck-Condon factors for the corresponding molecular systems may turn out to be very different.

make the following general observation. In our view, the use of this approximation is a compromise because, although it successfully overcomes computational difficulties for high v , it is not founded on a detailed physical model that in some way "guarantees" the reliability of the final results. It is, therefore, essential to ensure that WKB methods are subjected to suitable control criteria capable of confirming the reliability of the resulting Franck-Condon factors [see subsection 4(b)].

In conclusion of our discussion of methods based on the use of the Morse potential, we simply cannot ignore the series of striking papers by Huffaker and Dwivedi^{51,77-83,158} who have successfully implemented the idea of the perturbed Morse potential. They have calculated Franck-Condon factors for a large number of EV bands of diatomic molecules, and have compared the results with RKR data, showing excellent agreement between them (see for example, the comparison⁷⁹ of the $B^1\Pi - X^1\Sigma_g^+$ data for Na_2 , the $B^3\Pi - X^1\Sigma_g^+$ and $(2+)$ data for N_2 , and the $A^1\Sigma^+ - X^1\Sigma_g^+$ data for Ca_2).

It is particularly important to note that the authors of the above papers have also applied their method of calculating Franck-Condon factors to the case of the rotating perturbed Morse oscillator,⁷⁹⁻⁹³ and have carried out an extensive series of computations of $q_{v'v''}^{j'j''}$ for TiO , ZrO , MgO , LaO , and SiO in Ref. 84 and for CN , C_2 , CO , and CH in Ref. 85. These results will be considered in greater detail in the section devoted to the effect of vibration-rotation interactions on Franck-Condon factors.

4. FRANCK-CONDON FACTORS WITH ALLOWANCE FOR ROTATION

(a) Current methods of computation

To find the Franck-Condon factors with allowance for the VR interaction, we must determine the vibrational wavefunctions with allowance for rotation, $\psi_{v,j}(r)$, and find

$$q_{v'v''}^{j'j''} = \left| \int \psi_{v',j'}(r) \psi_{v'',j''}(r) dr \right|^2. \quad (16)$$

To do this, the Schroedinger equation is solved for some effective potential $U_{eff}(r)$ that takes into account the centrifugal distortion of the molecules during rotation:

$$\frac{d^2\psi_{v,j}(r)}{dr^2} + \frac{2\mu}{\hbar^2} [E_{v,j} - U_{eff}(r)] \psi_{v,j}(r) = 0. \quad (17)$$

The effective potential $U_{eff}(r)$ can be approximated in two ways. Firstly, it can be assigned an analytic form in which the potential for the "nonrotating" molecule is augmented with a term representing rotation. Secondly, $U_{eff}(r)$ can be specified in tabular form as a vibration-rotation RKR potential (see, for example, Refs. 67, 68, 86, and 87). Calculations of wavefunctions for tabulated potentials involve numerical integration of (17), which is complicated [see subsection 3(c)]. The result can be reached much more simply with an analytically specified potential. The Morse-Pekeris potential⁸⁸

$$U_{eff}(r) = U(r)_{Morse} + \frac{\hbar}{8\pi^2c\mu} \frac{J(J+1)}{r^2}, \quad (18)$$

is particularly widely used, and equation (17) can be

solved exactly for this potential.⁸⁹ The wavefunctions given by Lerner⁸⁹ are convenient in practical calculations of Franck-Condon factors, and are widely used (see Ref. 90). Shumaker⁹¹ has given a somewhat simplified Morse-Pekeris model, and has obtained the following solution of (17):

$$\psi_{v,J}(r) = N_{v,J} \exp\left(-\frac{z}{\alpha}\right) z^{\beta/2} L_{v,J}^{\beta}(z), \quad (19)$$

where

$$z = K_1 \exp[-\alpha(r - r_0)], \quad \beta = K_2 - 2v - 1.$$

We must now write down all the remaining parameters defining the wavefunction (19), since we shall use them below:

$$\left. \begin{aligned} r_0 &= r_e(1 + \alpha_e), \\ K_1 &= 2\sqrt{\frac{D_2 + C_2}{\omega_e x_e}}, \quad K_2 = 2(2D_1 - C_1) \omega_e x_e K_1, \\ D_1 &= D_e \exp(-\alpha r_e \alpha_e), \quad D_2 = D_e \exp(-2\alpha r_e \alpha_e), \\ C_1 &= \frac{A}{\alpha r_0 (1 + \alpha_e)^2} \left[4 - \frac{6}{\alpha r_0} \right], \\ C_2 &= \frac{A}{\alpha r_0 (1 + \alpha_e)^2} \left(\frac{3}{\alpha r_0} - 1 \right), \\ \alpha_e &= \frac{4AB_e}{\omega_e^2}, \quad A = B_e J(J + 1) \end{aligned} \right\} \quad (20)$$

where v and J are the vibrational and rotational quantum numbers, D_e , α , and r_e are the parameters of the Morse potential, ω_e , $\omega_e x_e$, and B_e are the usual spectroscopic constants in cm^{-1} , $N_{v,J}$ is the normalizing factor, and $L_{v,J}^{\beta}$ is the generalized Laguerre polynomial.

Chang and Karplus^{92,93} have used (19) to obtain simple analytic expressions for $q_{v',v''}^{J',J''}$, which are widely used in practical calculations.⁹⁴⁻⁹⁶

We have already noted in subsection 3(c) that the idea of the perturbed Morse oscillator was extended by Hufaker and Dwivedi to calculations of $q_{v',v''}^{J',J''}$. Results obtained by this method are practically identical to the RKR data (see Refs. 84 and 85 for further details).

Finally, we note a very recent paper⁵⁹ that reports accurate analytic expressions for the energies, wavefunctions, and matrix elements for the rotating Morse oscillator.

(b) Precision of calculations

It is important to emphasize that, whatever potential is used, the reliability of the resulting Franck-Condon factors can be satisfactorily controlled only on the basis of special comparison criteria. The most commonly used criterion is the difference between the experimental value of the rotational constant B_v^{exp} and the calculated value B_v^{calc} given by the formula

$$B_v^{\text{calc}} = \frac{\hbar}{8\pi^2 c_{\mu}} \int \left| \frac{\psi_v(r)}{r} \right|^2 dr = \frac{\hbar}{8\pi^2 c_{\mu}} \left\langle \frac{1}{r^2} \right\rangle. \quad (21)$$

The choice of the parameter $\xi = B_v^{\text{exp}} - B_v^{\text{calc}}$ as the indicator of the reliability of the calculated $q_{v',v''}$ and $q_{v',v''}^{J',J''}$ seems the most appropriate, since it is precisely the rotational constants that determine the relative "shift" of the potential curves between which the transitions take place. Wentink and Spindler⁹⁷ have performed a model calculation illustrating the variation in the values of Franck-Condon factors with the nuclear separation in the states connected by the $A^2\Sigma - X^2\Pi$ transition in LiO.

They showed that a difference of 0.01 Å in r_e for even one of the two states (which corresponds to an uncertainty in the third significant place in B_v) produces an appreciable change in the Franck-Condon factors. In practical calculations, therefore, one usually tries to ensure that $\xi \leq 0.005$ Å. The difference ξ is the most frequently used but, for calculations of $q_{v',v''}^{J',J''}$, it is also useful to compare experimental and calculated values of not only B_v but also D_v and H_v . This was done, for example, in Refs. 98 and 99. On the other hand, whenever experiment allows, the Franck-Condon factors calculated with allowance for rotation should be directly compared with precision measurements of the rotational-structure intensities.^{100,101}

Finally, we note the usefulness of estimates of reliability of calculated wavefunctions based on the evaluation of the so-called "noise factor" which is the convolution of the vibrational wavefunctions of a given electronic state:

$$q_m = \left| \int \psi_{m\sigma_i}(r) \psi_{m\sigma_k}(r) dr \right|^2, \quad i \neq k. \quad (22)$$

It is known that, since the wavefunctions are orthogonal, the noise factor should be zero. The difference between the calculated "noise factor" and the "machine zero" can serve as an additional measure of the reliability of the resulting wavefunctions^{43,102}. For example, calculations¹⁰² of Franck-Condon factors for the Asundi systems ($a'^3\Sigma - a^3\Pi$) and the triplet bands ($d^3\Delta - a^3\Pi$) of the CO molecule have shown that, for these states, $q_m \approx 10^{-8}$. Since the absolute values of the Franck-Condon factors for these CO systems are usually $\geq 10^{-4}$, this value of the "noise factor" guarantees the reliability of the calculated Franck-Condon factors.

(c) Analysis of data on Franck-Condon factors calculated with allowance for rotation

We have already frequently emphasized the fact that, until quite recently, most calculations of Franck-Condon factors were performed without taking the VR interaction into account. In this review, we present the first systematic analysis of all work⁵⁾ on the calculation of $q_{v',v''}^{J',J''}$. It is important to note, however, that most published calculations involve models, and are not very suitable for practical purposes. This is why the calculations of $q_{v',v''}^{J',J''}$ performed by Dwivedi *et al.*^{94,95} for 25 molecular systems that are of importance in practice are so valuable. Each of these calculations was performed for many vibrational bands up to high values of J . For example, for the gamma-system of TiO, data were obtained for $v' \leq 8$, $v'' \leq 7$ and $0 \leq J \leq 180$; for the red system of CN, they were obtained for $v' \leq 13$, $v'' \leq 9$, and $0 \leq J \leq 180$; and so on. A particularly valuable feature of these calculations is that the factors $q_{v',v''}^{J',J''}$ for each vibrational band were approximated by a least-squares procedure, using simple analytic expressions

⁵⁾The $q_{v',v''}^{J',J''}$ have now been calculated for more than 60 molecular systems. Because of the restricted space available to use in a journal article, we cannot reproduce the corresponding references in full here.

of the form

$$q_{v''v'''}^{J''J'''} = A(1 + BX + CX^2), \quad (23)$$

where $X = J'' (J'' + 1)$.

The uncertainty with which (23) represents the accurate calculated values of $q_{v''v'''}^{J''J'''}$ is 0.1% for strong bands and not more than 10% for the very weakest bands.

Analysis of the data on $q_{v''v'''}^{J''J'''}$ confirms that the dependence of Franck-Condon factors on J is complicated and is different for different types of electronic transitions and even for different values of v . As an example, Fig. 8 shows $q_{v''v'''}^{J''J'''}$ as a function of J'' for the R branch $v'' = 0$ of the progression $A^1\Sigma_u^+ - X^1\Sigma_g^+$ of Mg_2 (Based on the data reported in Ref. 86). It clearly illustrates the very substantial differences that can arise between the Franck-Condon factors as J is varied. For low values of J (for example, $J'' = 15$), the strongest is the (12-0) band and the weakest the (20-0) band. The increase in J is accompanied by a sharp variation in intensity: for $J'' = 50$, the strongest band is now the (16-0) band and the weakest the (10-0) band.

(d) Criteria for estimating the effect of the vibration-rotation interaction on Franck-Condon factors

In view of the foregoing, it is tempting to consider the idea of some quantitative criterion for estimating the possible effect of the VR interaction on Franck-Condon factors. This could then serve as a preliminary indicator of whether or not it is really essential to perform laborious and complicated calculations of $q_{v''v'''}^{J''J'''}$. The first attempt of this kind was reported by James¹⁰³ who showed that, in the first approximation (he used the harmonic oscillator model), the possible influence of the VR interaction is indicated by the value of the ratio $\gamma = 2B_e/\omega_e$ where γ is the average for the two states connected by the transition. It was believed for a long time (see, for example, Ref. 104) that the VR interaction was unimportant for molecules with $\gamma \leq 10^{-3}$, but that special calculations of $q_{v''v'''}^{J''J'''}$ were essential for molecules with $\gamma > 10^{-3}$. However, analysis of published data on $q_{v''v'''}^{J''J'''}$ shows that there are many cases that do not conform to this conclusion. For example, in all three systems of the molecule CH (A-X, B-X, C-X), the ratio γ is high ($\sim 10^{-2}$), but it is only for B-X that the influence of the RV interaction on Franck-Condon factors is considerable, whereas it is negligible in the A-X and C-X systems.⁸⁵ The result obtained for Mg_2 has already been illustrated in Fig. 8 ($\gamma = 2.6 \cdot 10^{-3}$). These examples could be multiplied, but we shall mention only one more molecule I_2 ($\gamma \approx 10^{-4}$) for whose B-X system an appreciable variation in the Franck-Condon factors with J has also been found¹⁰⁵.

It is nevertheless clear that the ratio of the rotational constant B_e to the vibrational frequency ω_e must play an important role in estimates of the possible effect of the VR interaction, though perhaps not in the simple form indicated above. This is demonstrated, in particular, by the work of Kobylyanskiĭ¹⁰⁶ who used the effective harmonic potential with allowance for rotation to investigate the influence of the VR interaction. He obtained a correction factor representing the effect of this inter-

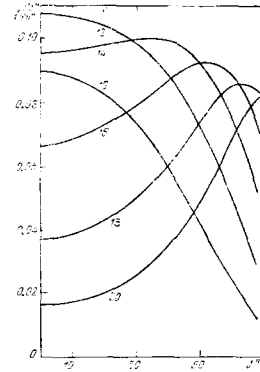


FIG. 8. Franck-Condon factors as functions of the rotational quantum number for the R branch of vibrational bands corresponding to the $v'' = 0$ progression of the $A^1\Sigma - X^1\Sigma$ system of the Mg_2 molecule (according to the data of Ref. 86).

action on Franck-Condon factors, and showed that it was governed by the ratio $(B_e/\omega_e)^{3/2}$.

Theoretical work performed in the anharmonic approximation^{83,89,92-93,107} has, in fact, yielded the most reliable criterion for estimating the effect of the VR interaction on Franck-Condon factors. The well-known fact that the equilibrium nuclear separation increases with increasing quantum number J [see equation (20)] can be used as a basis for deducing that the effect of the VR interaction is best measured by the quantity $|\Delta r_0 - \Delta r_e|$ where Δr_0 and Δr_e are the differences between the equilibrium separations in the two states, with and without allowance for rotation, respectively. It is clear from (20) that, when $J' = J''$, we have

$$\varepsilon = |\Delta r_0 - \Delta r_e| = \left| J(J+1) \left[\left(\frac{2B'_e}{\omega'_e} \right)^2 r'_e - \left(\frac{2B''_e}{\omega''_e} \right)^2 r''_e \right] \right|, \quad (24)$$

and the parameter ε , which increases with J , will increase with increasing relative separation of the minima on the potential curves and with increasing ratio $(2B_e/\omega_e)^2$.

The parameter ε was first used to estimate the effect of the VR interaction on Franck-Condon factors in Ref. 108, and was subsequently applied in Refs. 109 and 110 to several molecular systems of astrophysical interest.

We have calculated the values of ε for all the molecular systems (with $J = 100$) for which ε could be compared with the numerical values of $q_{v''v'''}^{J''J'''}$. As a result, we have shown that small values of ε correspond to small changes in the Franck-Condon factors with J and, conversely, large values of ε correspond to substantial changes in $q_{v''v'''}^{J''J'''}$. Thus, for example, we have already noted that, of the A-X, B-X, and C-X transitions in CH, only the B-X Franck-Condon factors were very sensitive to J . This is readily explained by a simple comparison of the values of ε for these transitions.¹¹¹

We have thus confirmed that ε is sensitive to the effect of the VR interaction on Franck-Condon factors, and that it can be used to explain the behavior of the majority of existing data on $q_{v''v'''}^{J''J'''}$. The most general and important result of our analysis can be formulated as follows: *the effect of the VR interaction on Franck-Condon factors is negligible for molecular systems with*

$\varepsilon < 10^{-2}$ Å; special analyses are essential for systems with $\varepsilon > 10^{-2}$ Å; and Franck-Condon factors of molecular systems with $\varepsilon > 1$ Å vary substantially with increasing J .

The result just given can be used as a basis for the classification of molecular transitions in all diatomic molecules in terms of the degree of probable dependence of their Franck-Condon factors on J . Thus, for examples, it is expected that Franck-Condon factors should be sensitive to J for different systems of H_2 , Mg_2 , the hydrides of alkali metals, the Schumann-Runge system of O_2 , the second negative system of O_2 , and the excimer systems $EHal$ ($E = Ar, Kr, Xe$; $Hal = F, Cl, Br, I$). Conversely, there are many molecular transitions in which the effect of the VR interaction on Franck-Condon factors can be neglected *a priori*. As an example, we mention the fact that these transitions include the Meinel and the first negative system of N_2^+ , which are important in different practical applications.

5. AREAS OF APPLICATION OF RADIATIVE PARAMETERS

The need for the radiative parameters of diatomic molecules arises whenever the emission or absorption properties of gaseous systems in the optical range have to be described quantitatively. In our view, it is important to identify and discuss the main branches of physics and chemistry in which data on the radiative parameters can be used to achieve effective solutions of such problems.

It would seem at first sight that *astrophysics* is precisely the kind of branch of physics that would not require special discussion because, traditionally, astrophysicists have long and successfully exploited all the available data on radiative parameters.¹¹²⁻¹¹⁴ However, recent advances in experimental spectroscopy have revealed a well-resolved rotational structure in the electronic spectra of the interstellar molecules^{20,115}, and the techniques of molecular spectroscopy have become increasingly important in the study of the interstellar medium.^{116,117} It seems useful, therefore, to draw attention to the potential value of data on the rotation-corrected Franck-Condon factors in astrophysical problems.

Molecular spectroscopy is a somewhat strange area from the point of view of the problems discussed in this section. Analysis of the data published in leading Soviet and foreign spectroscopy journals⁶⁾ suggests to us that many spectroscopists have not fully appreciated the possibilities that are afforded by the radiative parameters in obtaining reliable information on the structure of molecules. These include data on electronic, vibrational, and rotational states of molecules, the detection of predissociation levels, accurate determinations of the

dissociation limit, and so on. Thus, the utilization of Franck-Condon factors will greatly facilitate the labeling of vibrational levels in the course of vibrational analysis (see, for example, published papers¹²⁰ on CaF^{118} , $CaBr^{119}$ and Sb_2). It is also appropriate to mention Refs. 121 and 122 in which Franck-Condon factors are alone used to reassign bands in the $C^1\Sigma - X^1\Sigma$ system of SrO and the $A^3\Pi_u - X^1\Sigma_g^+$ system of I_2 . An exceedingly promising approach was demonstrated in Refs. 123 and 124 where an analysis of the very complicated vibrational structures of the Br_2 and I_2 molecules (with unresolved rotational structure!) was used to deduce the rotational constants of the states connected by the transitions. This was achieved by varying the required values of B_v until the calculated intensity values coincided with the observed values throughout the entire spectral range under investigation [here again we refer the reader to subsection 4(b)!].

We must conclude our survey of problems that arise in spectroscopy with a general remark of a fundamental nature. In the solution of many problems not only in molecular spectroscopy, but also astrophysics, astrochemistry, geophysics, and so on, the results turn out to be more effective when an effort is made to exploit all the radiative parameters such as Franck-Condon factors, lifetimes of electronic-vibrational-rotational excited states $\tau_{n,v',j'}$, transition strengths $S_{00}^{mn}(\nu)$, and oscillator strengths f_{00}^{mn} . For example, the problem of band assignment, which arises when several electronic systems are found to overlap, can be successfully solved by simultaneously exploiting data on the measured lifetimes of the states under consideration and the calculated Franck-Condon factors for the proposed transitions. A clear illustration of this is the identification of closely-spaced electronic states, for example, those of $BaO^{125,126}$, SnO^{127} , and YF^{128} . The combination of precision measurements of $\tau_{n,v',j'}$ of the individual electronic-vibrational-rotational levels and the factors $q_{v',j'}^{j'',j''}$ enables us to perform a detailed investigation of predissociation processes and various perturbations (see, for example, Refs. 17 and 129).

The impressive advances made in the study of cosmic space present us with the tempting prospect of being able to investigate the *photochemistry of planetary atmospheres* in the solar system, whose composition is very different from that of the terrestrial atmosphere. Experience gained as a result of many years of investigations of the photochemistry of the Earth's atmosphere gives us confidence that it will be possible to develop reliable models of the atmospheres of other planets, but only by exploiting all the available data on the radiative parameters, including Franck-Condon factors. Various aspects of the application of these radiative parameters in the photochemistry of planets are discussed in Okabe's monograph¹³³ (Chapter VIII).

It is well known that the efforts of many research groups are directed toward developing laser systems exploiting molecular electronic transitions (photorecombination, excimer, chemical, etc., etc.). The numerous problems that arise in this connection are discussed in the monographs in Refs. 134-136 and re-

⁶⁾We have analyzed the literature up to the middle of 1982 as published in journals such as "Optika i spektroskopiya", "Zhurnal prikladnoi spektroskopii", "Journal of Molecular Spectroscopy", "Spectroscopy Letters", "Journal of Quantitative Spectroscopy and Radiative Transfer", and other publications.

view papers in Refs. 137–139. One such persistent problem is that of acquiring reliable data on radiative parameters of the corresponding molecular “candidates” (for a typical analysis see Ref. 140 which considers the example of IV A monofluorides).

The traditional use of radiative parameters in *plasma diagnostics* has become increasingly important in recent years, since plasmas of very different molecular composition are being used in both modern physical experiments and in the solution of applied practical problems. There is little point in listing here all the numerous papers in this field. It seems more important to emphasize that, as advances are made in the study of high-temperature and plasma-chemical processes, the use of radiative parameters in analytical chemistry may turn out to be increasingly important.¹⁴¹

Finally, we must particularly emphasize the importance of radiative parameters in the description of *nonequilibrium kinetics of chemical reactions in the gaseous phase*. In the ordinary chemical systems used in traditional chemical technology, the rates of chemical reactions at sufficiently low temperatures and high enough pressures (of the order of atmospheric pressure or higher) are found to be much lower than the probabilities of transitions between EVR states. This is why rapid relaxation usually ensures the establishment of the equilibrium distribution over the levels, which is described by a temperature within the framework of the Arrhenius kinetics. Studies of, say, plasma-chemical systems, on the other hand, which are now encountered in many laboratories and technological installations (plasmotrons, shock waves, gas-dynamic systems, laser excitation, and so on) involve us in the consideration of fundamentally new conditions, e.g., very much higher temperatures which, in turn, lead to much higher chemical reaction rates. In many cases, these rates are then comparable with the rates of transitions between the EVR states, or may even be greater than the transition rates. Classical Arrhenius kinetics is then no longer valid, and nonequilibrium chemical kinetics^{142,143} must be employed. The latter takes into account processes such as excitation and dissociation of molecules by electron impact¹⁴⁴, dissociative electron-ion recombination^{145,146}, and so on. All these processes can only be described by introducing additional data on the energy levels and potential curves of the molecules involved and on the probabilities of radiative EVR transitions, deduced from the function $S_{\nu}^m(\lambda)$ and Franck-Condon factors (it is frequently necessary to have data on Franck-Condon factors corrected for the VR interaction; see, for example, Ref. 145, pages 91–94). The most complete and systematic account of these and other problems encountered in nonequilibrium kinetics can be found in Slovetskii's monograph.¹⁴⁵

6. CONCLUSION

We have given a comprehensive survey of problems that arise in the description of the intensity distribution in the EVR spectra of diatomic molecules, and of progress achieved in overcoming these problems. It seems useful to conclude by mentioning a number of questions

that have not been touched upon in this review, but are closely connected with our main theme and, in our view, demand greater attention.

We note, first, that we have discussed the probabilities of vibrational transitions only for bound-bound electronic transitions (they are specifically referred to as Franck-Condon factors). No less important from the theoretical and applied points of view are the vibrational transition probabilities for bound-free electronic transitions—the so-called Franck-Condon factor densities (these are very important, for example, in the interpretation of photodissociation processes and in the analysis of excimer lasers). In contrast to the situation examined above, theoretical methods for the determination of these quantities are, clearly, still inadequate (see Refs. 56 and 147–149).

This can also be said about calculations of Franck-Condon factors for radiationless electronic transitions, although in this area there has already been some interesting work.^{150–152}

Finally, we emphasize the opportuneness of published work on Franck-Condon factors of polyatomic molecules and, above all, the advances made by Soviet workers in the development of methods for the determination of Franck-Condon factors. Thus, the idea of “mixing” of normal coordinates has been successfully realized^{73,153–156}, and Priyutov¹⁵⁷ has investigated the effect on the Franck-Condon factors of a departure from the adiabatic approximation within the framework of the Herzberg-Teller model.

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