Radiative transitions between Rydberg states of molecules

E. M. Balashov, G. V. Golubkov, and G. K. Ivanov

Institute of Chemical Physics, Adademy of Sciences of the USSR, Moscow

(Submitted 23 November 1983)
Zh. Eksp. Teor. Fiz. **86**, 2044–2055 (June 1984)

The multichannel quantum defect method is used in the quasiclassical approximation for the radial motion of the electron to calculate the oscillator strengths for transitions between the highly excited Rydberg states of diatomic molecules and transitions from Rydberg states to the continuum. It is shown that, because of the nonadiabatic coupling between electron and nuclear motion, the photoabsorption spectrum (position of peaks, their intensity, and shape) depends significantly on the initial state of the molecule. The effect of the electron-rotational and electron-vibrational interactions on the shape of the spectrum is analyzed. It is shown that, in the photoionization process, the evolution of the line profiles depends in an important way on interference between direct and resonance mechanisms. The result of this is that the final profile may differ appreciably from the Fano-Feshbach profile. Numerical calculations have been performed for the hydrogen molecule and a number of features in the photoionization and photoabsorption spectra of this molecule are predicted.

1. INTRODUCTION

Highly excited atoms and molecules are important and extensively investigated quantum-mechanical objects. Extensive literature has now accumulated on the Rydberg states of atoms and their interaction with other particles and the electromagnetic field. We note, above all, the classical results reported in a number of books and monographs[1–4] and original papers,[5–10] in which the quasiclassical methods of calculating radiative transitions between highly-excited states are developed. This has provided the necessary foundation for investigations of processes occurring in high excited states of molecules for which the analogy with atomic objects is complemented by essentially new features. The Rydberg states of molecules are, as a rule, states that are mixed by interference, i.e., they are superpositions of states corresponding to different channels of vibrational and rotational excitation of the core. The possibility of energy exchange between electrons and nuclear degrees of freedom leads to the appearance in the optical spectra of the molecules of a number of interesting features that are not seen in atomic spectra. These features are, in fact, the subject of the present paper.1)

The motion of weakly bound electron in a highly-excited Rydberg state of a molecule can be imagined as the motion of a particle in a Coulomb field that is disturbed at short distances by scattering by the ion core. This shifts its phase and mixes different trajectories. When processes involving a Rydberg electron are considered, it is therefore natural to employ concepts, methods, and results from the quantum theory of scattering of slow electrons by molecular ions. This is the basic idea of the multichannel quantum defect method (MQD),[12–14] which is an intergral procedure in which the complete continuous wave functions of the electron + molecular ion system are directly expressed in terms of the Coulomb functions and the elements of the T-operator for the collision between the electron and the ion core, and discrete states are described by the τ-matrix (level shift operator) that is the analog of the T-operator for finite motion, is used to describe discrete states.

The integral MQD method enables us to obtain sufficiently simple analytic expressions for the amplitude for bound-free and bound-bound dipole transitions (see Secs. 2 and 5), which predict the appearance of interference anomalies in the photo-ionization spectra of molecules, and a sharp dependence of the intensity and line shape on the level number of the initial highly-excited molecule (see Secs. 3 and 4). They also show that the intensities in spectral-line series due to bound-bound transitions have an irregular pattern (see Sec. 5). We note that optical transitions between Rydberg states of molecules have not been examined theoretically before.

2. TRANSITIONS FROM THE RYDBERG STATES OF DIATOMIC MOLECULES TO THE CONTINUUM

Radiative transitions are described with the aid of the matrix elements

$$\mathbf{D}_{if}=\langle\psi_i|\mathbf{D}|\psi_f\rangle, \tag{1}$$

where $\psi_{i(f)}$ are the total wave functions of the initial (final) state of the system and D is the dipole moment operator. The initial states of the system are characterized by the total angular momentum J_i and its component M_i along a given axis.[2] As usual in MQD theory, it must also be assigned a classification index $q_i=\{v_i,N_i\}$ (the set of vibrational v_i and rotational N_i quantum numbers) indicate that a given energy level belongs to a particular Rydberg series (we use the atomic system of units in which $\hbar=m_e=e=1$). The total wave function of the initial state can be represented by a superposition of functions corresponding to different channels of vibrational and rotational excitation of the core, i.e.,

$$\psi^{J_iM_i}_{q_iE_i}(\mathbf{r},\mathbf{R})=\sum_{lq}(-1)^l\frac{\tau^{(l)}_{q_iq}(E_i)}{\sin\pi\nu_q(E_i)}\,\nu_q^{3/2}Q_{lqE_i}(r)\,\chi_{v}(R)\,\Phi^{J_iM_i}_{lN}, \tag{2}$$

0038-5646/84/061188-07$04.00

where the radial electron wave functions are determined outside the ion core and are given by[14]

$$Q_{lqE}=[\Gamma(\nu_q-l)\Gamma(\nu_q+l+1)]^{-1/2}\frac{1}{r\nu_q}W_{\nu_q,\,l+1/2}\left(\frac{2r}{\nu_q}\right), \tag{3}$$

where $\Gamma(x)$ is the complete gamma-function, $W_{\mu\nu}(x)$ is the Whittaker function, r is the coordinate of the electron, R is the interatomic distance in the ion XY^+, E_i is the total energy of the initial bound Rydberg state of the system ($E_i<0$), ν_q is the effective principal quantum number of the Rydberg level, given by

$$\nu_q(E_i)=[2(E_q-E_i)]^{-1/2}, \tag{4}$$

which is related to the corresponding quantum shift μ_q by $\nu_q=n-\mu_q$, E_q is the excitation energy of the ion core, $\chi_v(R)$ measured from the ground state of the ion, $\Phi_{lN}^{J_iM_i}(\hat{r},\hat{R})$ is the total angular function of the compound system consisting of the electron and the freely rotating rotator, i.e.,

$$\Phi_{lN}^{JM}(\hat{r},\hat{R})=\sum_m(lN,mM-m|JM)Y_{lm}(\vartheta\varphi)Y_{NM-m}(\Omega), \tag{5}$$

$(lN,mM-m|JM)$ are the vector composition coefficients,[15] $Y_{lm}(x)$ are the spherical harmonics, ϑ and φ are angles defining the position of a particular electron in the laboratory frame, and Ω is the set of angles specifying the orientation of the molecular ion.

The coefficients $\tau_{q_iq}^{(l)}(E_i)$ in (2) characterize the weight of the different states of the ion core for given energy E_i, and are normalized by

$$\sum_{lq}\left|\frac{\tau_{q_iq}^{(l)}(E_i)}{\sin\pi\nu_q}\nu_q^{3/2}\right|^2=1. \tag{6}$$

The final state wave function ψ_f must, in general, correspond to states in the continuum, in which the released electron moves at large distances from the ions in a particular direction. It is well known that this function must take the asymptotic form of a plane or a converging spherical wave.[16] However, if we leave on one side the question of the angular distribution of the emitted electron, the final wave functions ψ_f of the system can be taken to be the wave functions describing the scattering of a slow electron with angular momentum l_f by a molecular ion with a given set of quantum numbers g_f, J_f, M_f. These functions have the form[14]

$$\psi_{l_fq_fE_f}^{J_fM_f}(\mathbf{r},\mathbf{R})=F_{l_fq_fE_f}^{J_fM_f}(\mathbf{r},\mathbf{R})-\sum_{l'q'}(-1)^{l'}\frac{T_{l'q'l_fq_f}^{(J_f)}}{\sin\pi\nu_{q'}}\nu_{q'}^{3/2}Q_{l'q'E_f}(r)\chi_{v'}(R)\Phi_{l'N'}^{J_fM_f}(\hat{r},\hat{R}), \tag{7}$$

where $F_{lqE}^{JM}(\mathbf{r},\mathbf{R})$ is the wave function in the exit channel, i.e.,

$$F_{lqE}^{JM}(\mathbf{r},\mathbf{R})=R_{lE}(r)\chi_v(R)\Phi_{lN}^{JM}(\hat{r},\hat{R}), \tag{8}$$

$R_{lE}(r)$ is the Coulomb radial wave function for the continuous spectrum, which is regular at the origin and is normalized to the energy δ-function. The elements of the T and τ matrices in (2) and (7) are given by

$$T=t+taT, \tag{9}$$

$$\tau=ta\tau, \tag{10}$$

where a is the diagonal matrix

$$a_{lqlq}=\begin{cases}\operatorname{ctg}\pi\nu_q, & E<E_q\\ -i, & E>E_q\end{cases}. \tag{11}$$

The elements of the t-matrix

$$t_{lql'q'}^{(J)}=\langle\chi_v\Phi_{lN}^{JM}|t|\Phi_{l'N'}^{JM}\chi_{v'}\rangle \tag{12}$$

are linear functions of the elements of the adiabatic scattering matrix $t_\Lambda^{ll'}$ (Ref. 12) ($\Lambda=|m|$ is the absolute magnitude of the component of the angular momentum of the electron along the molecular axis). They are defined by

$$t_\Lambda^{ll'}=\langle Y_{lm}(\vartheta'\varphi')\varphi_l|t|\varphi_{l'}Y_{l'm}(\vartheta'\varphi')\rangle, \tag{13}$$
$$\varphi_l=(2\pi/r)^{1/2}J_{2l+1}(\sqrt{8r}),$$

where $J(x)$ is a Bessel function and ϑ' and φ' are the angles defining the position of the electron in the coordinate frame attached to the molecule. We shall look upon them as the parameters of the problem.

We note that the range of validity of (9) and (10), and of the formulas reproduced below, is restricted by the condition $r_0|E|\ll 1$ is the effective range of the interaction between the electron and the ion core (r_0 is of the order of the elliptic dimensions of the ion core[14]).

For distances

$$(l+1/2)^2\ll r\ll|\varepsilon_q|^{-1}\quad(\varepsilon_q=E_q-E) \tag{14}$$

the wave functions given by (2) and (7) can be written in the quasiclassical approximation, i.e.,

$$\psi_{qE}^{JM}=\left(\frac{2}{\pi^2r^3}\right)^{1/4}\times\sum_{l'q'}\frac{\tau_{qq'}^{(l')}}{\sin\pi\nu_{q'}}\sin\left[\sigma_{q'}(r)-\pi l'-\pi\nu_{q'}-\frac{\pi}{4}\right]\chi_{v'}\Phi_{l'N'}^{JM} \tag{15}$$

for the discrete spectrum ($E<0$), and

$$\psi_{lqE}^{JM}=\left(\frac{2}{\pi^2r^3}\right)^{1/4}\left\{\sin\left[\sigma_q(r)-\pi l-\frac{\pi}{4}\right]\chi_v\Phi_{lN}^{JM}+\sum_{l'q'}\frac{T_{lql'q'}^{(J)}}{\sin\pi\nu_{q'}}\sin\left[\sigma_{q'}(r)-\pi l'-\pi\nu_{q'}-\frac{\pi}{4}\right]\chi_{v'}\Phi_{l'N'}^{JM}\right\} \tag{16}$$

for the continuous spectrum ($E>0$). For low values of orbital angular momentum of the electron, $l\ll|\varepsilon_q|^{-1/3}$, the quasiclassical phase $\sigma_q(r)$ in the highest-order approximation in the small parameter $r|\varepsilon_q|$ is given by

$$\sigma_q(r)\approx\sqrt{8r}+\frac{\sqrt{2}}{3}r^{2/3}\varepsilon_q. \tag{17}$$

Since, in photoprocesses, possible values of l are restricted by selection rules, it is precisely this case that is of particular interest to us. We must now consider the dipole matrix elements (1) with wave functions (15) and (16). We start with the radial parts which contain integrals of the form

$$r_{if}^{qq'}=\int\limits_0^\infty r^{3/2}\sin(\sigma_q{}^i-\eta_q{}^i)\sin(\sigma_{q'}{}^f-\eta_{q'}{}^f)\,dr,$$

$$\eta_q^{i(f)}=\pi l+\pi\nu_q(E_{i(f)})+\frac{\pi}{4}. \tag{18}$$

The main contribution to (18) is provided by the region $r\sim|\Delta\varepsilon_{if}^{qq'}|^{-2/3}$. Hence, the requirement that this region must lie at a large distance from the turning point $r_{\max}\approx 2\nu^2$ leads to the additional restriction

$$\Delta\nu\gg 1, \tag{19}$$

which we shall adopt below. Clearly, this restriction is not essential from the physical point of view, but it enables us to ensure that the final results are simple and compact in form. Evaluating the integrals, we obtain

$$r_{if}^{qq'}=\frac{1}{\pi}\Gamma\left(\frac{2}{3}\right)\left(\frac{4}{3}\right)^{1/3}(\Delta\varepsilon_{if}^{qq'})^{-5/3}\cos\left(\Delta\eta_{qq'}^{if}-\frac{\pi}{6}\right). \tag{20}$$

where $\Delta\eta_{qq'}^{if}$ is the phase difference between the final and initial states and $\Delta\varepsilon_{if}^{qq'}=(E_q-E_i)-(E_{q'}-E_f)$ is the difference between the electron energies. Subsequent integration with respect to the nuclear variables in the sum over q and q' leaves only the term corresponding to $q=q'$. Hence, $\Delta\varepsilon_{if}^{qq}$ is independent of q and is equal to the energy of the incident photon, i.e., $\Delta\varepsilon_{if}^{qq}=E_f-E_i=\Delta\varepsilon_{if}$. For the purely Coulomb interaction (for which the phase difference is a multiple of π), expression (20) leads to the result given in Ref. 10.

We must now consider the angular parts of the dipole matrix elements (1). It will be convenient to introduce the operator[15]

$$\hat{\mathrm{S}}=\left(\frac{4\pi}{3}\right)^{1/2}\sum_p Y_{1p}{}^*(\vartheta\varphi)\mathbf{e}_p,\quad \mathbf{r}=\mathrm{r}\hat{\mathrm{S}}$$

with a polarization unit vector $\mathbf{e}_p (p=0,\ \pm 1)$. The angular part of the p-th spherical component of the dipole moment operator is then given by

$$S_{lNl'N'}^{JMJ'M'}(p)=\left(\frac{4\pi}{3}\right)^{1/2}\langle\Phi_{lN}^{JM}|Y_{1p}{}^*|\Phi_{l'N'}^{J'M'}\rangle$$

$$=[(2l+1)(2J+1)]^{1/2}$$

$$\times(l100|l'0)(1JpM|J'M')W(1lJ'N;l'J)\delta_{NN'}, \tag{21}$$

where $W(1lJ'N;l'J)$ are the Racah coefficients. Combining the radial and angular parts, we finally have

$$D_{if}^{(p)}=\frac{1}{\pi}\Gamma\left(\frac{2}{3}\right)\left(\frac{4}{3}\right)^{1/3}(\Delta\varepsilon_{if})^{-5/3}\sum_{ll'q'}[(2l+1)(2J_i+1)]^{1/2}$$

$$\times(1J_ipM_i\,|\,J_fM_f)\frac{\tau_{q_iq'}^{(l)}(E_i)}{\sin\pi\mu_{q'}(E_i)}W(1lJ_fN';l'J_i)(l100\,|\,l'0)$$

$$\times\left\{\cos\pi\left(\mu_{q'}(E_i)+\frac{1}{6}\right)\delta_{l'l_f}\delta_{q'q_f}\right.$$

$$\left.+\frac{T_{l'q'l_fq_f}^{(J_f)}}{\sin\pi\nu_{q'}(E_f)}\cos\pi\left(\mu_{q'}(E_i)+\nu_{q'}(E_f)+\frac{1}{6}\right)\right\}. \tag{22}$$

This formula has a clear physical interpretation and describes photoionization as a superposition of direct and two-stage processes. The latter are characterized by the instantaneous transition of the molecule to an intermediate state when the photon is absorbed, followed by rescattering of the released electron by the ion core, which leads to the final state of the system. Of all the possible intermediate states, the only important ones are those that are genetically related to the given configuration of the system through the collision T-operator.

Formula (22) describes two types of nonadiabatic interaction, namely, electron-vibrational and electron-rotational. The former is characterized by weak coupling in a large group of interacting states and the latter is usually distinguished by strong coupling between a small number of kinematically allowed channels. In the ensuing analysis, we shall consider situations in which vibrational and rotational coupling can be analyzed independently. If, in the final state, the energy of the system is $E_f\ll\omega$, where ω is the vibrational quantum of the ion, we may neglect electron-vibrational transitions. If must, however, be remembered that this is valid when the above energy range does not contain levels (random resonances) belonging to the autoionizing Rydberg series corresponding to vibrationally excited states of the ion. We shall now consider in detail each of these types of coupling separately, and will analyze different limiting and special cases.

3. ELECTRON-ROTATIONAL COUPLING IN OPTICAL TRANSITIONS FROM RYDBERG STATES TO THE CONTINUUM

To be specific, consider transitions from Rydberg states fo the molecule X_2 that belong to the optical series R (0), assuming that these states are formed as a result of single-quantum excitation of the σ-electron from the ground state of the molecule. The initial quantum numbers are then $J_i=l_i=1$ and, in accordance with the rules for the composition of angular momenta, N_i is either 0 or 2. Moreover, we shall neglect the coupling to vibrational motion, and substitute $v_i=v_f=0$. This means that the subscript q in (22) will be replaced with N.

In the final state of the molecule (after absorption of the photon), the total angular momentum J_f assumes the values 0, 1, 2 (which corresponds to the P, Q, and R branches), and the orbital angular momentum l_f, which has the values 0 and 2, is no longer a quantum number. Highly-excited states are now classified in accordance with the type of adiabatic molecular orbital that describes them for small n (n is the principal quantum number). For the molecules X_2, these can be the S-, D_σ-, D_π-, and D_δ-orbitals, where the S- and D_σ-orbitals mix, forming the $p\sigma$–doublet, and D_π and D_δ describe noninteracting states. The subscript ρ characterizes the type of molecular orbital and assumes the values 0 and 2. As the principal quantum number n is reduced, the adiabatic conditions are no longer satisfied, and coupling between electron and rotational motions comes into play and mixes these states, forming four series of Rydberg levels that converge to three different ionization limits $I_N=BN(N+1)$ where B is

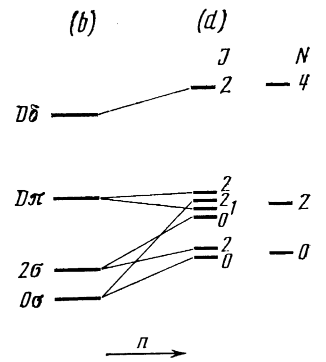

FIG. 1. Correlation diagram showing the transition from Hund b-coupling to d-coupling as the principal quantum number n increases in the Rydberg series of the molecule X_2.

the rotational constant of the ion and $N = 0, 2, 4$ (these limits are measured from the limit of the continuum). The corresponding correlation diagram illustrating the transition from the Hund b-coupling (low n) to d-coupling (large n) is shown in Fig. 1.

We note that the series $D\,4R\,(1)$, which correlates with the adiabatic D_δ-states, is populated only as a result of the rescattering of the electron by the ion core. This is a consequence of the kinematic selection rule, i.e., the vanishing of the corresponding Racah coefficient in (22).

Let us first analyze photoionization for the optical transitions $R\,(0)\rightarrow P\,(1)$ (this is the case where $J_f = 0$). In accordance with the diagram shown in Fig. 1, this involves the mixing of two configurations, namely, $l = N = 0$ and $l = N = 2$, the ionization limits of which differ by the amount $6B$. The Beutler part of the spectrum

$$0<E_f<6B, \tag{23}$$

is of particular interest. The second channel, which corresponds to the first configuration, is open in this region (i.e., $\tan \pi\nu_0 = i$), whereas the second channel is closed. The coupling between them determines the resonance and interference structure of the photoionization spectra, which is conveniently characterized by the oscillator strength of the transition.[2] The expression for the oscillator strength, given by

$$F_{if}=\frac{2\Delta\varepsilon_{if}}{2J_i+1}\sum_{M_iM_f}|D_{if}^{(p)}|^2, \tag{24}$$

does not depend on the photon polarization and can be written in the form

$$F_{if}=\frac{2g_{if}^2(2J_f+1)}{9\varkappa(E_i)}W^2(E_i)\left|\frac{\operatorname{tg}\pi\nu_2(E_f)-\alpha(E_i)}{\operatorname{tg}\pi\nu_2(E_f)-\delta+i\gamma}\right|^2, \tag{25}$$

where[30]

$$g_{if}=\frac{1}{\pi}\Gamma\left(\frac{2}{3}\right)\left(\frac{4}{3}\right)^{1/3}(\Delta\varepsilon_{if})^{-7/6},\quad \varkappa(E_i)=\nu_0^3+\left(\frac{\partial\mu_0}{\partial\nu_2}\right)\nu_2^3,$$

$$W(E_i)=\cos\pi(x_0-\Delta_\sigma^{00})+\beta\sin\pi x_2,\quad \beta=\left[\frac{2}{5}\gamma\left(\frac{\partial\mu_0}{\partial\nu_2}\right)_{E_i}\right]^{1/2}, \tag{26}$$

where

$$x_N=\mu_N(E_i)+{}^1/_6,\qquad \Delta_\Lambda{}^{ll}=-\pi^{-1}\operatorname{arctg}t_\Lambda{}^{ll}, \tag{27}$$

and t_Δ^{ll} are the elements of the adiabtic scattering matrix (13). The quantities (α, δ and γ) in (25) are strictly real and are given by

$$\delta=t_\sigma{}^{22}-\gamma t_\sigma{}^{00},\quad \gamma=\frac{(t_\sigma{}^{02})^2}{1+(t_\sigma{}^{00})^2},\quad d_l=[1+(t_\sigma{}^{ll})^2]^{1/2}. \tag{28}$$

Formula (25) describes the Fano profile with well-defined dependence of the line shape on the initial energy E_i of the system. If the off-diagonal matrix element t_σ^{02} is small in comparison with t_σ^{00} the nonresonance and resonance parts of the spectrum may be considered independently of one another. In fact, substituting $t_\sigma^{02} = 0$ we have

$$F_{if}^{(0)}={}^2/_9\,g_{if}^2K(E_i), \tag{29}$$

for the first region, where

$$K(E_i)=\varkappa^{-1}(E_i)\cos^2\pi(x_0-\Delta_\sigma{}^{00}). \tag{30}$$

For the second region, we expand (25) in powers of the reduced energy $\xi = 2(E - E_{2n})/\Gamma_{2n}$ around the point of resonance, the energy E_{2n} and width Γ_{2n} of which are given by

$$\operatorname{tg}\pi\nu_2(E_{2n}-i\Gamma_{2n}/2)=\delta-i\gamma,$$

and this gives us the expression

$$F_{if}=F_{if}^{(0)}(q+\xi)^2/(1+\xi^2) \tag{31}$$

with the profile index

$$q=-\frac{\beta}{\gamma}\left[\frac{1+(t_\sigma{}^{22})^2}{1+(t_\sigma{}^{00})^2}\right]^{1/2}\frac{\cos\pi(x_2-\Delta_\sigma{}^{22})}{\cos\pi(x_0-\Delta_\sigma{}^{00})}. \tag{32}$$

The dependence on the initial energy of the system E_i in (30) and (31) can be illustrated by the special case of the hydrogen molecule. The table lists the values of the quantities given by (30) and (32) for different E_i. They were calculated with the aid of published data on quantum shifts[17] and scattering phases[18,19] for the singlet para-states of H_2 that belong to the optical Rydberg series $nPNR\,(0)$ ($v = 0$). It is clear that the coefficients K and q are irregular functions of the initial energy E_i, which is a consequence of the strong nonadiabatic coupling between electron and rotational motion in the initial Rydberg state of the molecule.

When $J_f = 1$, it is clear from the correlation diagram that photoabsorption produces an isolated ($l = N = 2$) series $D\,2Q\,(1)$ with ionization limit I_2 (for low n it corresponds to the adiabatic nD_π states). The oscillator strengths of the transitions are determined in this case by Eqs. (29) and (30), in which x_0 and Δ_σ^{00} must be replaced with x_2 and Δ_π^{22}. The irregular dependence on the initial energy of the molecule, described by the factor (30), is thus found to remain intact.

Let us now consider photoionization in relation to the $R\,(0)\rightarrow R\,(1)$ transitions ($J_f = 2$). From the point of view of the resonance structure of the spectrum, the most interesting regions ar the Beutler region, given by (23), and the region

$$6B<E_f<20B. \tag{33}$$

In the Beutler region, we have the situation where one chan-

TABLE I.

nPN	μ_0	μ_2	$K(E_i)\cdot 10^5$	$qt_{\sigma}^{02}\cdot 10$	$\mathrm{Im}(\alpha/\gamma)$
10*P*0	−0.013	−0,302	32.38	2.413	−1,003
10*P*2	−0,690	0.163	2.522	−4,8862	−10,287
11*P*0	−0,592	−0.122	29.90	3,124	−1,638
12*P*0	0,122	−0.739	1,958	3,666	3.911
11*P*2	−0,185	0.036	20,95	9.669	−2,804
13*P*0	0,030	−0,525	9,851	−6,507	−0,163
12*P*2	−0,482	0,119	6.233	18,01	−5,000
14*P*0	−0,025	−0,247	13,00	−2,394	−1,180
15*P*0	0.164	−0,776	0,172	−8,602	10.760
13*P*2	−0.159	0,019	12,37	−8,114	−2,600
16*P*0	0,021	−0,484	5,982	4,872	−0,360
14*P*2	−0,609	0.144	1,892	−12.33	−6,931
17*P*0	−0,062	−0.116	8.706	3.204	−1,666
18*P*0	0,052	−0.606	2,886	102.99	0,402
15*P*2	−0,470	0,117	3,130	18.28	−4,909
19*P*0	−0,042	−0,174	5.914	−2.658	−1,429
20*P*0	0.057	−0.622	1.950	−22,91	0,563
16*P*2	−0.487	0,120	1.608	−17,88	−5.084
21*P*0	−0.053	−0.139	1,765	2,942	−1,567
22*P*0	0,034	−0,539	2,060	−9.461	−0,083

nel ($l=2$, $N=0$) is open and the other three interacting channels are closed (Fig. 2). If we confine our attention to the part of the spectrum (23) in which there is no overlap with resonances corresponding to the series $D\,4(R_1)$, the expression for the oscillator strengths given by (24) can be reduced to the form

$$F_{if}=\frac{4g_{if}{}^2W^2(E_i)}{9\varkappa(E_i)}\left|\prod_{s=0,\,2}\frac{\mathrm{tg}\,\pi\nu_2(E_f)-\alpha_s(E_i,E_f)}{\mathrm{tg}\,\pi\nu_2(E_f)-\delta_s(E_f)+i\gamma_s}\right|^2, \tag{34}$$

where g_{if} and $\varkappa(E_i)$ are defined by (26) and

$$W(E_i)=\cos\pi x_0+\beta\sin\pi x_2,\quad \beta=\left[{}^1/{}_2\gamma_0\left(\frac{\partial\mu_0}{\partial\nu_2}\right)_{E_i}\right]^{1/2}. \tag{35}$$

By analogy with (28), the parameters γ_s, α_s and δ_s are strictly real and given by

$$\begin{gathered}\gamma_0=(t_{0220}^{(2)})^2,\quad \gamma_2=(t_{0202}^{(2)}t_{2220}^{(2)}-t_{0222}^{(2)}t_{0220}^{(2)})^2(t_{0202}^{(2)})^{-2};\\ \alpha_s=\delta_s+\beta\lambda_s,\quad s=0,\ 2;\\ \delta_0=t_{0202}^{(2)}-\frac{(t_{0224}^{(2)})^2}{t_{2424}^{(2)}-\mathrm{tg}\,\pi\nu_4(E_f)},\quad \delta_2=t_{2222}^{(2)}-\frac{(t_{0222}^{(2)})^2}{t_{0202}^{(2)}}.\end{gathered} \tag{36}$$

For convenience, we have also substituted

$$\begin{gathered}\lambda_0=W^{-1}(E_i)\,(\cos\pi x_2-t_{0202}^{(2)}\sin\pi x_2),\\ \lambda_2=-\left(\frac{7\gamma_2}{10\gamma_0}\right)^{1/2}\frac{\cos\pi x_2}{\cos\pi x_0}t_{0202}^{(2)}.\end{gathered} \tag{37}$$

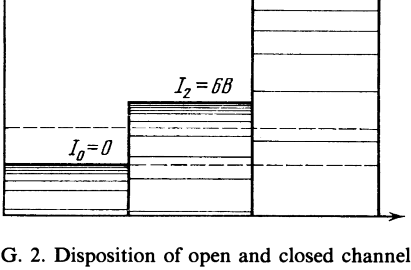

FIG. 2. Disposition of open and closed channels for the motion of the electron with χ_0 and $0<E_f<6B$.

Expression (34) is written with allowance for the fact that the absolute value of the matrix elements $t_{lNl'N'}^{(J)}$ falls rapidly with increasing $l+l'$. It is clear from (34) that there are certain definite values of the photon energy at which the photoionization cross section rapidly falls to zero. Moreover, each of the resonances separately exhibits the Fano-Feshbach structure which has the property that the line-shape parameters depend on the energy of the initial and final states of the system. We also note that, in this case, $|\alpha_s-\delta_s|\gg\gamma_s$, so that the profile indices of the corresponding profiles are high. However, the intensities of these series are appreciably different from one another because $\gamma_0\gg\gamma_2$. Physically, this is due to the fact that the $l=0$, $N=2$ series interacts much more strongly with the ionic core than the series $l=N=2$.

Above the Beutler region (when $\mathrm{tg}\pi\nu_0=\mathrm{tg}\pi\nu_2=i$), formula (34) is replaced by the simpler expression

$$F_{if}\sim\frac{[\mathrm{tg}\,\pi\nu_4(E_f)-\mathrm{Re}\,\alpha]^2+(\mathrm{Im}\,\alpha)^2}{[\mathrm{tg}\,\pi\nu_4(E_f)-\delta]^2+\gamma^2}. \tag{38}$$

We shall not reproduce the explicit form of the coefficients α, δ and γ, which can readily be deduced from the general formula (22), and merely note the most general properties of (38). Thus, for example, because of interaction in the open channels, the profile index becomes complex above the Beutler region, and the photoionization process is not suppressed by interference, i.e., strictly speaking, the line profile is not of the Fano-Feshbach type. At the same time, the parameter α in (38) depends on both the initial and final states of the system, and this means that the idea of the compound state is not valid in this case since, in contrast to the Lorentz line, which is common to all the channels (and is predicted by the compound state model), each channel now has its own individual spectrum shape. Physically, this is explained by the fact that, in addition to resonant photoionization, there is also an essential contribution due to direct photoionization, and interference between these two mechanisms produces an appreciable distortion of the resonance line shape. Clearly, the result must depend on the angular momentum l_f carried off by the optical electron. In fact, for the $l_f=2$

channels, we have typically

$$\left|\mathrm{Re}\,\frac{\alpha-\delta}{\gamma}\right| \sim |t_\sigma{}^{02}| \ll 1, \quad \mathrm{Im}\,\frac{\alpha}{\gamma} \approx -1, \tag{39}$$

so that the spectrum is described by a smooth curve (corresponding to the direct photoionization mechanism) accompanied by slight distortions of its shape near the corresponding resonance. On the other hand, for the $l = 0$, $N = 2$ channel,

$$\mathrm{Re}\,\frac{\alpha-\delta}{\gamma} \approx t_\sigma{}^{00}, \quad \mathrm{Im}\,\frac{\alpha}{\gamma} = -\left[1+\mathrm{tg}\,\pi\left(x_2+\frac{1}{\pi}\,\mathrm{arctg}\,t_\sigma{}^{00}\right)\right], \tag{40}$$

i.e., there is a well-defined resonance structure, the specific form of which is determined by the magnitude of the adiabatic matrix element t_σ^{00}. All this is illustrated in Fig. 3, which shows the oscillator strength (38) as a function of the energy of the system for different values of the shape parameters.

Examination of the picture as a whole shows that the dominant contribution to the resonance structure of the photo-ionization spectrum is provided by the series with $l_f = 0$, for which the electron has the strongest interaction with the ion core. In accordance with the diagram of Fig. 1, these series correlate with the adiabatic states 0σ, and region (33) contains only one well-defined resonance $R(1)$ series with total angular momentum $J_f = 2$. On the other hand, in the Beutler region defined by (23), there are two series of resonance lines, namely, $P(1)$ and $R(1)$, respectively. Since, however, the positions of these lines are very different, they can be investigated independently by modern optical methods.

4. ELECTRON-VIBRATIONAL TRANSITIONS

Let us now consider electron-vibrational transitions that take place during the photoionization of highly-excited molecules when rotational motion is adiabatic, i.e.,

$$B|\varepsilon_q|^{-3/2} \ll 1, \quad E_f > I_4.$$

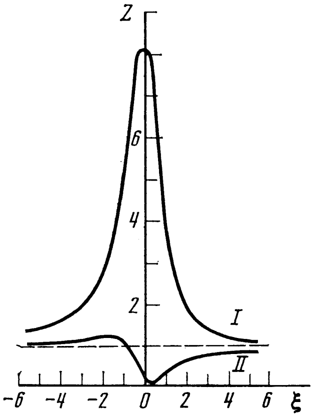

FIG. 3. Energy dependence of the transition oscillator strengths (38), $Z(\xi) = [(\xi - q)^2 + p^2]/(1 + \xi^2)$ expressed in units of $\xi = \gamma^{-1}[\mathrm{tg}\pi\nu_4(E_f) - \delta)]$ with parameters $(q = \mathrm{Re}[\alpha - \delta)/\gamma]$ and $p = \mathrm{Im}(\alpha/\gamma)$. Curves I and II were calculated for the hydrogen molecule, using the data tabulated in Ref. 19, and correspond to neighboring initial Rydberg levels (respectively, $11P2$ and $13P0$).

This means that the angular variables can be omitted from the general expression (22), and the orientation of the molecule can be regarded as fixed. Since the matrix element t_σ^{02} it is responsible for the nonadiabatic coupling to rotation) is small in comparison with t_σ^{00}, we may set t_σ^{02} equal to zero when we analyze the case $l_f = 0$ to which we shall confine our attention here. In the simplest two-channel variant ($v = 0$ and 1), we then find that the transition oscillator strength for the Λ-component is given by an expression analogous to (25) with the parameters (26)–(28), in which β and x_N are replaced with

$$\beta = -\left[\gamma\left(\frac{\partial\mu_0}{\partial\nu_1}\right)_{E_i}\right]^{1/2},$$
$$x_v = \frac{1}{\pi}\,\mathrm{arctg}\,(\langle\chi_v|\mathrm{tg}\,\pi\mu_\Lambda(R)\,|\chi_v\rangle) + \frac{1}{6}, \tag{41}$$

and $t_\Lambda^{ll'}$ are the matrix elements

$$t_{vv'}^{(\Lambda)} = \langle\chi_v|t_\sigma{}^{00}|\chi_{v'}\rangle. \tag{42}$$

Since the nonadiabatic coupling to vibrational motion is weak, one of the states in the wave function can be looked upon as a small admixture, and the quantum defects turn out to be practically independent of energy. At the same time, the dependence on the initial energy E_i in the normalizing coefficients $\tau_{\nu\nu'}^{(\Lambda)}$ is very strong. In fact, if the initial state with energy E_i belongs to the $v = 0$ Rydberg series, we have $(\partial\mu_0/\partial\nu_1)_{E_i}^{1/2} \ll 1$ and, in the highest-order approximation in the small parameter $(t_{01}^{(\Lambda)})^2$, we obtain

$$F_{00}^{(\Lambda)}(i\to f) \sim g_{if}{}^2\nu_{\Lambda 0}{}^{-3}(E_i)\cos^2\pi(x_0-\Delta_{00}^{(\Lambda)}),$$
$$\Delta_{00}^{(\Lambda)} = -\frac{1}{\pi}\,\mathrm{arctg}\,t_{00}^{(\Lambda)}. \tag{43}$$

This corresponds to the direct (single-channel) mechanism of photoionization, the properties of which are investigated in Ref. 10 in the case of purely Coulomb interaction. On the other hand, for a level corresponding to a vibrationally excited state of the core (which may lie near the corresponding $v = 0$ level), the relation between the coefficients $\tau_{\nu\nu'}^{(\Lambda)}$ is reversed, i.e., $(\partial\mu_0/\partial\nu_1)_{E_i}^{1/2} \ll 1$. In this case,

$$F_{10}^{(\Lambda)}(i\to f) \sim g_{if}{}^2\nu_{\Lambda 1}{}^{-3}(E_i)\sin^2\pi x_1\gamma\left|\frac{\mathrm{tg}\,\pi\nu_1(E_f)-\mathrm{ctg}\,\pi x_1}{\mathrm{tg}\,\pi\nu_1(E_f)-\delta+i\gamma}\right|^2, \tag{44}$$

which corresponds to the resonance mechanism occurring as a result of the population of intermediate autoionizing Rydberg states with $v = 1$, and their subsequent decay as a result of interaction with the continuum, the amplitude for which is $\gamma^{1/2}$. Thus, here we have only two alternative situations which strictly alternate as we pass from one optical series in the initial state to the other.

5. BOUND-BOUND ELECTRON-ROTATIONAL TRANSITIONS

Let us now examine the main features of bound-bound transitions. Since the resonantly-excited Rydberg state with $l_i = 1$ is considered to be the initial state of the molecule, the final state produced as a result of photoabsorption is characterized by weak coupling between electron channels. The general expression describing transitions between discrete Rydberg states is obtained from (22) by discarding the free term (the first expression in braces) and replacing the matrix elements of the T-operator with the elements of the τ-matrix that describes the final states of the system. Analysis of the general expression is outside the scope of this paper, so that we shall confine our attention to the special case $J_f = 0$, for which the problem becomes methodologically equivalent to that examined above. In the final state, we then have two weakly interacting series $l = N = 0$ and $l = N = 2$ and, for the corresponding transitions, we have

$$F_{if} \sim g_{if}{}^2 \nu_f{}^{-3} \cos^2 \pi [x_{N_f}(E_i) - \Delta^{(0)}_{l_f N_f l_f N_f}],$$
$$\Delta^{(J)}_{l_f N_f l_f N_f} = -\frac{1}{\pi} \operatorname{arctg} t^{(J)}_{l_f N_f l_f N_f}. \tag{45}$$

It is clear that the absorption spectrum is also characterized by an irregular dependence on the level number n when the transition energy is altered by a small amount. The situation as a whole is analogous to that described by (29). Since the channels for some transitions are suppressed by interference, the oscillator strengths may turn out to be anomalously low. For example, for the hydrogen molecule (according to tabulated data), transitions from the 15POR(0) level to the n00P(1) levels are of this kind. The existence of such phenomena (not observed in atomic spectra) is one of the most characteristic features of photoprocesses occurring in the Rydberg states of molecules.

CONCLUSION

We have derived, for the first time, the formulas providing a detailed description of photoprocesses in the Rydberg states of molecules. Interference mixing of states in the absorption spectra of the molecules was found to be responsible for the irregularity in the disposition of resonance peaks, their intensity, and shape, which has no analog in atomic systems.

For radiative transitions from Rydberg states, the line-profile parameters are expressed in terms of the adiabatic level shifts, i.e., in terms of the same quantities that are used to describe the spectra of highly-excited molecules, the slow-electron scattering cross sections of molecular ions, and near-threshold photoabsorption from the ground electronic state. The fact that the same molecular characteristics are reflected in different physical phenomena suggests that it may be possible to investigate them experimentally in a unified manner.

The properties of photoelectron spectra were analyzed above for the traditional experiment in which the initial Rydberg states were populated as a result of single-photon absorption. On the other hand, there have been recent reports of experimental observations of radiative transitions between Rydberg states of molecules prepared under the conditions of two-photon absorption.[20] When specific calculations, which we propose to carry out in connection with these experiments, are performed, this will require only slight modification of the kinematic scheme of the process because of the increase in the number of optical series populated during two-photon absorption.

---

[1] We shall not consider effects due to the internal shell structure of the ion core, and the entire analysis will be confined to the single-electron approximation with fixed electron configuration of the core. This approximation is widely used in the theory of atomic Rydberg spectra,[11] and is fully justified for molecular systems.

[2] For simplicity, we shall confine our attention to the Russell-Saunders (LS) coupling for which the problem parameters depend only on the total spin of the system, and the spin variables of the electron and the ion core can be ignored.

[3] In the generally accepted notation of MQD theory,[4] we have introduced the derivative $\partial\mu_0/\partial\nu_2$ in (26) and the subsequent formulas. It is readily shown that this derivative is related to the coefficients τ_0 and τ_2 by $\partial\mu_0/\partial\nu_2 = (\tau_2 \sin \pi\mu_0/\tau_0 \sin \pi\mu_2)^2$.

[1] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One and Two Electron Atoms, Springer-Verlag, 1957 [Russian translation, IIL, Moscow, 1960].

[2] I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Fizmatgiz, Moscow, 1963.

[3] N. B. Delone and V. P. Kraĭnov, Atom v sil'nom svetovom pole (The Atom in a Strong Light Field), Atomizdat, Moscow, 1978.

[4] L. P. Rapoport, B. A. Zon, and N. L. Manakov, Teoriya mnogofotonnykh protsessov v atomakh (Theory of Multiphoton Processes in Atoms), Atomizdat, Moscow, 1978.

[5] L. A. Bureeva, Astron. Zh. **45**, 1215 (1968) [Astron. J. **12**, 962 (1969)].

[6] P. F. Naccache, J. Phys. B **52**, 1308 (1972).

[7] I. C. Percival and D. Richards, Adv. Atom. Proc. Phys. **11**, 2 (1975).

[8] A. F. Shestakov, S. V. Khristenko, and S. I. Vetchinkin, Opt. Spektrosk. **33**, 413 (1972) [Opt. Spectrosc. (USSR) **33**, 223 (1972)].

[9] V. A. Davydkin and B. A. Zon, Opt. Spektrosk. **51**, 25 (1981) [Opt. Spectrosc. (USSR) **51**, 13 (1981)].

[10] S. P. Goreslavskiĭ, V. P. Krainov, and N. B. Delone, Zh. Eksp. Teor. Fiz. **82**, 1789 (1982) [Sov. Phys. JETP **55**, 1032 (1982)].

[11] N. B. Delone, V. P. Kraĭnov, and D. L. Shepelyanskiĭ, Usp. Fiz. Nauk **140**, 355 (1983) [Sov. Phys. Usp. **26**, 551 (1983)].

[12] G. V. Golubkov and G. K. Ivanov, Zh. Eksp. Teor. Fiz. **80**, 1321 (1981) [Sov. Phys. JETP **53**, 674 (1981)].

[13] G. V. Golubkov and G. K. Ivanov, Chem. Phys. Lett. **81**, 110 (1981).

[14] G. V. Golubkov and G. K. Ivanov, Khim. Fiz. **6**, 729 (1982).

[15] A. S. Davydov, Teoriya atomnogo yadra (Theory of the Atomic Nucleus), Fizmatgiz, Moscow, 1958.

[16] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhaniki (Quantum Mechanics), Fizmatgiz, Moscow, 1963.

[17] G. Herzberg and Ch. Jungen, J. Mol. Spectrosc. **41**, 425 (1972).

[18] A. Temkin and K. V. Vasadava, Phys. Rev. **160**, 109 (1967).

[19] A. Temkin, K. V. Vasadava *et al.*, Phys. Rev. **186**, 57 (1969).

[20] W. Y. Cheung, W. A. Chupka, *et al.*, J. Chem. Phys. **78**, 3625 (1983).

Translated by S. Chomet