Quantum effects in the Rydberg spectra of polar molecules

D. L. Dorofeev and B. A. Zon

Voronezh State University, 394693 Voronezh, Russia

(Submitted 5 March 1996)
Zh. Éksp. Teor. Fiz. **110**, 882–890 (September 1996)

We examine the irregularities in the spectra of the Rydberg states of polar molecules of the symmetric-top type. These irregularities are associated with the degeneracy of the molecular-core wave functions with respect to the sign of the projection of the total angular momentum on the symmetry axis. © *1996 American Institute of Physics.* [S1063-7761(96)00809-8]

1. INTRODUCTION

During recent years extensive research has been in progress in the field of Rydberg spectra of molecules, in particular, by ZEKE spectroscopy methods (see, e.g., the reviews by Müller-Dethlefs and Schlag[1] and Merkt and Softley).[2] The principal quantum number n of the electron states resolved in such studies reaches a value of roughly 200, with the fine features of the molecular core manifesting themselves in the structure of such states. This calls for a theory of highly excited Rydberg states in complex molecules.

For a long time the effect of the core's dipole moment on the spectrum of a Rydberg electron has widely been discussed in the literature. The topic of discussion was, of course, the "penetrating" states, i.e., states with a fairly low value of orbital angular momentum, since states with large angular momenta can be considered hydrogenlike with high accuracy. The penetrating states are excited by a fairly small number of photons and are therefore interesting from the standpoint of ZEKE spectroscopy.

A solution of the Schrödinger equation for a Rydberg electron in the field of a rapidly rotating symmetric molecular core with a dipole moment was found in Ref. 3. The fact that the rotation is rapid means that the Born–Oppenheimer (adiabatic) approximation is inapplicable and that one must use a nonadiabatic approximation, which became known as the inverse Born–Oppenheimer approximation.

However, the discussion in Ref. 3 did not take into account the presence in the rotational spectra of the core of a ω-doublet related to the degeneracy of the rotational levels with respect to the sign of the projection of the core's total angular momentum on the symmetry axis.[1)] As is known,[4] when spatial parity is conserved, stationary states of quantum mechanical systems cannot have nonzero dipole moments. For this reason the dipole moment of polar molecules (measured, for instance, by the Stark effect) is caused by the superposition of neighboring (on the energy scale) stationary states of different parities. A classical example of such a situation is the inverse splitting of levels of the ammonia molecule.[5]

In the absence of inverse degeneracy, the components of the ω-doublet act as the neighboring states in forming the nonzero dipole moment of the molecule. Below we show that this leads to important consequences for the spectroscopy of Rydberg states. Hence the widespread notion that highly excited Rydberg states are essentially classical states is not always true for penetrating Rydberg orbits.

2. A QUALITATIVE TREATMENT

In the inverse Born–Oppenheimer approximation the distance between the levels of a Rydberg electron with different principal quantum numbers $n(\sim Z^2\,\mathrm{Re}/n^3$, where Z is the charge of the molecular core) is assumed much smaller than the distance between different rotational levels of the core ($\sim 2Bj$, where B is the rotational constant, and j is the core's total angular momentum). It is known that the splitting of the ω-doublet (we denote this quantity by δ) is also much smaller than Bj. Hence the results of Ref. 3 are valid if

$$\delta \ll Z^2\mathrm{Ry}/n^3 \ll 2Bj. \tag{1}$$

In this case ω-splitting can be ignored and we can think of the molecular core as a system that has a constant dipole moment, in addition to having an electric charge. The presence of a dipole moment lifts the degeneracy of the spectrum of a Rydberg electron with respect to the orbital angular momentum and leads to the emergence of quantum defects determined by the size of the dipole moment.

But if

$$Z^2\mathrm{Ry}/n^3 \ll \delta, \tag{2}$$

a Rydberg electron has only a small effect on the core's stationary states, which are the components of the ω-doublet, i.e., the symmetric and antisymmetric combinations of the core's wave functions with different signs of ω. In these stationary states the dipole moment is zero, so that in the limit (2) a Rydberg electron moves in a purely Coulomb field, provided of course that we have ignored the higher multipole moments and the short-range part of the core potential.

Thus, within the $n\sim n_\delta$ range of principal quantum numbers, where

$$n_\delta = (Z^2\mathrm{Ry}/\delta)^{1/3}, \tag{3}$$

the Rydberg electron spectrum undergoes a transformation: the fraction of the quantum defect associated with the dipole moment vanishes.

1063-7761/96/090485-05$10.00

3. THE BASIC EQUATIONS

We introduce the following notation: **J** is the total angular momentum of a molecule, M is its projection on an axis fixed in space, **j** is the angular momentum of the core, and m and ω are the projections of **j** onto the fixed axis and the core's symmetry axis, respectively; the effects associated with the spin of a Rydberg electron are not taken into account.

The Hamiltonian of a Rydberg molecule can be written as follows (throughout this paper we use the atomic system of units):

$$H=H^{+}+T+V, \tag{4}$$

where H^{+} is the rotational part of the core Hamiltonian that allows for the splitting of the ω- doublet, T is the kinetic energy of the Rydberg electron, and

$$V=-\frac{Z}{r}+\frac{\mathbf{dr}}{r^{3}} \tag{5}$$

is the electron–core interaction potential, with Z the core's charge, **d** the core's dipole moment, and **r** the radius vector of the Rydberg electron. The dipole moment is assumed directed along the core's symmetry axis.

We also introduce the wave functions of a symmetric top,[6]

$$\phi^{j}_{\omega m}(\Omega)=\sqrt{\frac{2j+1}{8\pi^{2}}}\,D^{j*}_{m\omega}(\Omega), \tag{6}$$

which depend on the Euler angles. Then the core wave functions, characterized by a definite parity[2] $g=\pm 1$, are linear combinations of the functions (6) (see Refs. 7 and 8):

$$\begin{gathered}\varphi^{gj}_{\omega m}(\Omega)=\frac{1}{\sqrt{2}}\left[\phi^{j}_{\omega m}(\Omega)+(-1)^{j+\omega}g\,\phi^{j}_{-\omega m}(\Omega)\right],\\ H^{+}\varphi^{gj}_{\omega m}=\left[E_{r}(j)+\frac{\delta}{2}g\right]\varphi^{gj}_{\omega m}.\end{gathered} \tag{7}$$

Here $E_r(j)$ is the rotational energy, which depends on the type of coupling of the angular momenta in the molecular core.

We seek the complete wave function of the molecule in the form

$$\psi^{JM}_{j\omega}(\Omega,\mathbf{r})=\sum_{gl}R^{Jj\omega}_{gl}(r)\sum_{ml_z}C^{JM}_{jmll_z}\varphi^{gj}_{\omega m}(\Omega)Y_{ll_z}\left(\frac{\mathbf{r}}{r}\right). \tag{8}$$

Plugging (8) into the Schrödinger equation, we arrive at an equation for the radial function, and since J and M are always good quantum numbers and j and ω are such in the inverse Born–Oppenheimer approximation, we drop these labels in $R(r)$:

$$\begin{gathered}\left[\frac{\delta}{2}g-\frac{1}{2r^{2}}\frac{d}{dr}\left(r^{2}\frac{d}{dr}\right)+\frac{l(l+1)}{2r^{2}}-\frac{Z}{r}-\varepsilon\right]R_{gl}(r)\\ =\frac{d\omega}{r^{2}}\sum_{l'=l\pm 1}Q^{Jj}_{ll'}R_{-gl'}(r),\\ Q^{Jj}_{ll'}=\sqrt{\frac{(2l+1)(2j+1)}{j(j+1)}}\,C^{l'0}_{l010}W(j1Jl';jl).\end{gathered} \tag{9}$$

The total energy of the molecule in this approximation is

$$E=E_{r}(j)+\varepsilon. \tag{10}$$

As Eq. (9) implies, the dipole interaction mixes only core states with different parities. And since the states that are mixed are those of the Rydberg electron that differ in the values of orbital angular momentum by ±1, the complete molecular functions on the whole is one with definite parity. This fact can be taken into account explicitly if we introduce the parity of the molecular function,

$$G=(-1)^{l}g, \tag{11}$$

and replace g by G in Eqs. (7)–(9):

$$\Phi^{Gjl}_{\omega m}(\Omega)=\frac{1}{\sqrt{2}}\left[\phi^{j}_{\omega m}(\Omega)+(-1)^{j+l+\omega}G\,\phi^{j}_{-\omega m}(\Omega)\right], \tag{12}$$

$$\Psi^{JM}_{Gj\omega}(\Omega,\mathbf{r})=\sum_{l}R_{Gl}(r)\sum_{ml_z}C^{JM}_{jmll_z}\Phi^{Gjl}_{\omega m}(\Omega)Y_{ll_z}\left(\frac{\mathbf{r}}{r}\right), \tag{13}$$

$$\begin{gathered}\left[\frac{1}{r^{2}}\frac{d}{dr}\left(r^{2}\frac{d}{dr}\right)-\frac{l(l+1)}{r^{2}}+2\left(\frac{Z}{r}+\varepsilon\right)-(-1)^{l}G\delta\right]R_{Gl}(r)\\ =-\frac{2d\omega}{r^{2}}\sum_{l'=l\pm 1}Q^{Jj}_{ll'}R_{Gl'}(r).\end{gathered} \tag{14}$$

Here the functions (12) acquire a dependence on the label l, which makes it impossible to interpret these functions as core functions. This should come as no surprise since in the presence of a Rydberg electron-core interaction the respective variables separate.

We also note the disappearance of dipole coupling between a Rydberg electron and the core at $\omega=0$, which is possible if j is an integer. The classical interpretation of this fact is straightforward: at $\omega=0$ the core rotates about an axis perpendicular to the dipole; in the inverse Born–Oppenheimer approximation such rotation is assumed very rapid, which means that all projections of the dipole moment disappear after averaging. According to quantum mechanics,[8] when $\omega=0$, there can be no linear Stark effect.

4. LIMITING CASES

At $\delta=0$ the dependence of the radial functions on the label G disappears. In this case, which corresponds to the inequality (1) being valid, Eq. (14) admits of an analytic solution (see Ref. 3).[3] The radial function differ only by constant factors,

$$R_{Gl}(r)=a_{l}R(r), \tag{15}$$

and formally $R(r)$ coincides with the Coulomb radial function:

$$R^{\rho}_{n_r}(r) = \frac{1}{\nu r}\left(\frac{Z n_r!}{\Gamma(\nu+\rho+1/2)}\right)^{1/2}\left(\frac{2Zr}{\nu}\right)^{\rho+1/2} \times \exp\left(-\frac{Zr}{\nu}\right) L^{2\rho}_{n_r}\left(\frac{2Zr}{\nu}\right). \qquad (16)$$

Here L stands for Laguerre polynomials, $n_r = 0,1,\ldots$ is the radial quantum number,

$$\nu = n_r + \rho + 1/2 \qquad (17)$$

is the nonintegral analog of the principal quantum number, and the values of

$$\rho = \sqrt{\Lambda + 1/4} \qquad (18)$$

are determined by the eigenvalues Λ of the following system of homogeneous linear equations:

$$l(l+1)a_l - 2d\omega \sum_{l'=l\pm1} Q^{Jj}_{ll'} a_{l'} = \Lambda a_l. \qquad (19)$$

Here the molecule's energy is given by Eq. (10) with

$$\varepsilon = -Z^2/2\nu^2. \qquad (20)$$

Now we can examine the limit (2). Since δ is large, we can ignore the off-diagonal term (the right-hand side) in Eqs. (14), which makes the orbital angular momentum l a good quantum number. Here

$$\Lambda \to l(l+1), \quad \rho \to l + 1/2, \quad \nu \to n, \qquad (21)$$

where n is an integer. In this limit only one coefficient a_l in Eq. (15) is nonzero, with (16) being the wave function of a hydrogen-like atom, provided that the limiting relations (21) hold.

The similarity of the analytical formulas for the solutions of Eqs. (14) in the two limiting cases (1) and (2) suggests that the solution in the intermediate case has a similar form.

5. THE VARIATIONAL METHOD

We seek the solution of Eqs. (14) in the form of (15) and (16) with a value of ρ that has yet to be found. According to the Ritz variational principle,[8] after averaging (14) over the functions (15) and (16), with ε taken as a Lagrange multiplier for normalizing the vectors $\{a_l\}$, we find that

$$\sum_l \left[\varepsilon(\rho) + \frac{Z^2}{2\nu^2}\right] a_l^2 = G\frac{\delta}{2}\sum_l (-1)^l a_l^2 + \frac{Z^2}{2\nu^3\rho}\left\{\sum_l \left[\left(l + \frac{1}{2}\right)^2 - \rho^2\right] a_l^2 - 2d\omega \sum_{l'l} Q^{Jj}_{ll'} a_l a_{l'}\right\}. \qquad (22)$$

In deriving Eq. (22) we used the value of the matrix element of r^{-2} between the wave functions (16) (see Ref. 8; for nonintegral values of ν we used the semiclassical approximation in calculations[9]):

$$\langle n_r\rho | r^{-2} | n_r\rho \rangle = Z^2/\nu^3\rho. \qquad (23)$$

Varying (22) in a_l, we arrive at the following system of linear equations:

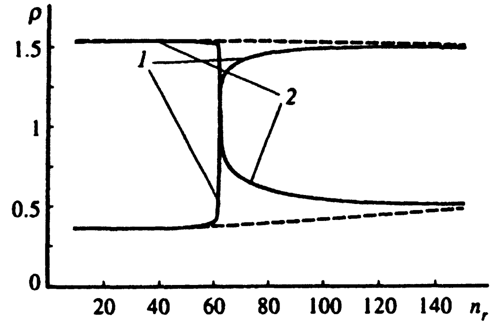

FIG. 1. Optimized values of ρ as functions of the radial quantum number n_r in states with $j=J=1/2$. The solid curves correspond to $G=1$ and the dashed curves to $G=-1$. Curve *1* represents the function that in the limit of small values of n_r corresponds to the state with $\rho \simeq 1/2$ and in the limit of large values of n_r to the state with $\rho = 3/2$. Curve *2* represents the function that in the limit of small values of n_r corresponds to the state with $\rho \simeq 3/2$ and in the limit of large values of n_r to the state with $\rho = 1/2$.

$$(-1)^l G\frac{\delta}{2} a_l + \frac{Z^2}{2\nu^3\rho}\left[\left(l + \frac{1}{2}\right)^2 - \rho^2\right] a_l - \frac{Z^2 d\omega}{\nu^3\rho}\sum_{l'} Q^{jJ}_{ll'} a_{l'} = \left[\varepsilon(\rho) + \frac{Z^2}{2\nu^2}\right] a_l, \qquad (24)$$

where $\varepsilon(\rho)$ can be found from the condition that this system has a nontrivial solution.

In the simplest cases where $J = j = \frac{1}{2}$to each value of G there correspond two energy eigenvalues:

$$\varepsilon(\rho) = -\frac{Z^2}{2\nu^2} + \frac{Z^2(5-4\rho^2)}{8\nu^3\rho} \pm \frac{Z^2}{2\nu^3\rho} \times \left[(1 - G\delta\nu^3\rho)^2 + \frac{4}{2}d^2\right]^{1/2}. \qquad (25)$$

Varying in ρ the smallest value of ε, which in (25) corresponds to the lower sign in front of the third term on the right-hand side, we get the optimum value of ρ. The corresponding eigenvectors are given by the following expressions:

$$a_0(\rho) = \frac{2Z^2 d}{3N}, \qquad a_1(\rho) = \frac{1}{N}(Z^2\Lambda - G\nu^3\rho\delta),$$

$$N = \left[(Z^2\Lambda - G\nu^3\rho\delta)^2 + \left(\frac{2Z^2 d}{3}\right)^2\right]^{1/2}, \qquad (26)$$

$$\Lambda = 1 - \left[\left(1 - G\nu^3\frac{\rho\delta}{Z^2}\right)^2 + \left(\frac{2Z^2 d}{3}\right)^2\right]^{1/2}.$$

The energy of the upper level can be found by reasoning along similar lines and allowing for orthogonalization of the eigenvectors.

Figure 1 depicts the values of ρ optimized in this manner as functions of the radial quantum number n_r for $G=-1$ (dashed curves) and $G=1$ (solid curves). In the limit of small n_r these values of ρ coincide with the result of Ref. 3, while in the limit of large n_r they assume the hydrogen-like values $\frac{1}{2}$ and $\frac{3}{2}$. The transition from one asymptotic value to the other takes place in the region where $\nu \simeq n_\delta$ ($n_\delta \simeq 60$ for the data of Fig. 1), which agrees with the qualitative discussion in Sec. 2. Note that the difference between n_r and the principal quantum number n of a hydrogen-like state, mentioned in Sec. 3, is small for penetrating Rydberg orbits.

We draw the reader's attention to the qualitatively different behavior of levels with positive and negative parity. Negative-parity levels vary smoothly, while positive-parity levels change even the shells to which they belong. Such asymmetric behavior of the spectra for states of different parity is due to the choice of the sign of the value of the ω-splitting $\delta > 0$ and to the fact that the parity of the complete molecular wave function depends on the parity of the orbital angular momentum of the Rydberg electron. For instance, the state with angular momentum $l=0$ (in the hydrogenlike approximation) from a lower shell is in resonance with the states with $l=1$ from the adjacent upper shell. At the same time, the similar states with the angular momentum $l=0$ from the upper shell and the state with $l=1$ from the lower shell are not in resonance: the ω-splitting moves these states apart rather than together, so that their perturbation is fairly weak. Note that the signs of δ for the neighboring values of j are different.[8]

The above reasoning suggests that the smooth variation of negative-parity levels for the case $J=j=\frac{1}{2}$ considered here will be replaced by a more rapid variation if we take into account the mixing of states with different values of n_r, which was not done when Eqs. (14) were replaced by the approximate equations (22). And although in view of the semiclassical nature of Rydberg states the off-diagonal matrix elements (in n_r) of the type (23) are generally smaller than the diagonal matrix elements, the presence of a resonance leads to a dramatic change in the behavior of levels with $G=-1$ depicted in Fig. 1. More precisely, if we incorporate the resonant interaction of levels with different n_r into the picture, the dashed curves in Fig. 1 change and become to resemble in shape the solid curves, which correspond to $G=1$.

6. PERTURBATION THEORY

The perturbation theory in the dipole interaction of a Rydberg electron and the core provides a correct description of the behavior of the levels, with the exception of the immediate vicinity of the crossing point. For an unperturbed base we can take the hydrogenlike one, which meets the conditions (21). The off-diagonal term (in l) in (24) can be taken as the perturbation. Since the values of ρ are not varied here, the wave functions with different values of n_r are automatically mutually orthogonal.

Without going into the details of calculations, we list the corrections to the energy levels in second-order perturbation theory for the simplest cases. By introducing the notation

$$x \equiv \frac{G\delta n^3}{Z^2}, \qquad y^{(\pm)} \equiv -\frac{Z^2}{2n^2} \pm G\frac{\delta}{2}$$

we can easily arrive at the following formulas:

(1) For $J=j=\frac{1}{2}$,

$$\varepsilon_{n0}^{(G)} = y^{(+)} + \frac{4Z^2d^2}{9n^3(x-2)}, \qquad \varepsilon_{n1}^{(G)} = y^{(-)} - \frac{4Z^2d^2}{27n^3(3x-2)}.$$

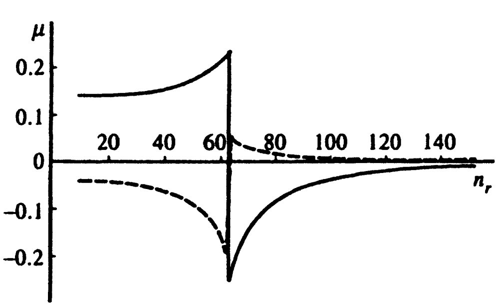

FIG. 2. Quantum defects μ_{nl}^G as functions of the radial quantum number n_r in states with $j=J=1/2$ and $G=1$. The solid curve corresponds to $l=0$ and the dashed curve to $l=1$.

Here the second subscript on ε stands for the orbital angular momentum of the hydrogenlike state "generating" the given excited states. We see that the above expressions become meaningless for $G=1$ at $n \simeq n_\delta$ because of the resonances mentioned in Sec. 5. But at the same time they make it possible to obtain more precisely the resonant values of n.

(2) For $J=j=\omega=1$,

$$\varepsilon_{n0}^{(G)} = y^{(+)} + \frac{2Z^2d^2}{3n^3(x-2)}, \qquad \varepsilon_{n2}^{(G)} = y^{(+)} + \frac{2Z^2d^2}{15n^3(5x+4)},$$

$$\varepsilon_{n1}^{(G)} = y^{(-)} + \frac{2Z^2d^2}{9n^3}\left[\frac{1}{x-2} + \frac{1}{2(3x+4)}\right].$$

In this case there is a resonance for both $G=1$ and $G=-1$.

7. CONCLUSION

Anomalies in the Rydberg spectra similar to those just described can manifest themselves in atoms when there is resonance between the frequencies of transitions between Rydberg states and the states of the atomic core belonging, say, to different sublevels of the fine structure.[10] However, the absence of a dipole moment in the stationary states of quantum systems is a direct consequence of spatial parity conservation in the interaction of the particles comprising the system. In this sense the described anomalies in the spectra of penetrating molecular Rydberg orbits can be thought of as being of a purely quantum nature.

Figure 2 depicts the variations of the quantum defects μ_{nl}^G in states with $j=J=\frac{1}{2}$at $G=1$. To allow for ω-splitting it is advisable to define quantum defects in the following way:

$$\varepsilon_{nl}^G = (-1)^l G\frac{\delta}{2} - \frac{Z^2}{2(n-\mu_{nl}^G)^2}. \tag{27}$$

We see that at $n \simeq n_\delta$ the quantum defects undergo a considerable change, with the result that the very concept of a quantum defect looses its constructive meaning.

Quantum-defect theory has reached its greatest popularity in atomic physics (see, e.g., Refs. 11 and 12) and in applications to homonuclear diatomic molecules.[13,14] The theory presupposes the possibility of analytic continuation of quantum defects from the bound-states region to the region of continuous states. However, because of the anomalies of the quantum defect in polar molecules described in this paper, extending quantum-defect theory to such molecules constitutes a nontrivial problem.

The authors would like to express their gratitude to Prof. J. Jortner for fruitful discussions of the various aspects of the effect of quantum defects on molecular Rydberg states. The work was supported by a grant from the Russian Fund for Fundamental Research (Grant 95-02-05756).

[1)] A similar effect in diatomic molecules is known by the name of Λ-doubling. In symmetric molecules with Hund coupling of type a the commonly used term is Ω-doublet. In this paper we denote the quantum numbers of the core by lower case letters and those of the entire molecule by upper case letters.

[2)] In molecular spectroscopy, functions with a given parity g and the parity G introduced here are usually known as positive or negative functions.

[3)] We note in passing an error in Ref. 3: the factor $(-1)^{2j+1}$ should be dropped from Eqs. (5) and (6) in Ref. 3.

---

[1] K. Müller-Dethlefs and E. W. Schlag, in *Annual Rev. Phys. Chem.*, Vol. 42, Palo Alto, Calif. (1991), p. 109.

[2] F. Merkt and T. P. Softley, Int. Rev. Phys. Chem. **12**, 205 (1993).

[3] B. A. Zon, Phys. Lett. A **203**, 373 (1995).

[4] A. I. Baz', Ya. B. Zel'dovich, and A. M. Perelomov, *Scattering, Reactions, and Decay in Non-relativistic Quantum Mechanics* [in Russian], Nauka, Moscow (1971); a translation of an earlier Russian edition has been published by NASA, Techn. Transl. F-510 (1969).

[5] A. Vuylsteke, *Elements of Maser Theory,* Van Nostrand, New York (1960).

[6] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskiĭ, *Quantum Theory of Angular Momentum*, World Scientific, Singapore (1987).

[7] P. A. Braun and A. A. Kiselev, *Introduction to the Theory of Molecular Spectra* [in Russian], Leningrad Univ. Press, Leningrad (1983).

[8] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-relativistic Theory,* 3rd ed., Pergamon Press, Oxford (1977).

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

[10] D. L. Dorofeev and B. A. Zon, Phys. Scripta **49**, 553 (1994).

[11] B. A. Zon, N. L. Manakov, and L. P. Rapoport, *The Theory of Multiphoton Processes in Atoms* [in Russian], Atomizdat, Moscow (1978).

[12] D. Moores and E. Saraph, in *Atoms in Astrophysics,* Plenum Press, New York (1983).

[13] U. Fano, Phys. Rev. A **2**, 353 (1970).

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

Translated by Eugene Yankovsky