Kinetic and Potential Energy Partitioning for Antibonding Molecular Orbitals

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Expectation values of kinetic and potential energy are calculated for some lower antibonding orbital states of simple diatomic molecules using H_2^+ and HeH^{2+} as test cases. Common LCAO-MO theory and a scaling procedure are applied which allow an analysis of atomic orbital interactions in terms of RUEDENBERG's [1] promotion and interference effect at various internuclear distances. Contributions to the total energy at different regions of interatomic separations are discussed in detail. A characteristic increase of the kinetic energy is observed for antibonding linear combinations at distances where chemical bonding occurs.

I. Introduction

In his review on "The Physical Nature of the Chemical Bond" RUEDENBERG concludes that chemical bonding in terms of potential and kinetic energy change is not correctly understood unless the validity of the virial theorem is preserved [1]. The seemingly incompatibility of the opinions that bonding is either due to a decrease of the kinetic energy (HELLMANN [2]) or is originated from a drop of potential energy (see e. g. PITZER [3]) could be clarified by a closer analysis of various energy contributions upon molecule formation. The fallacy in the previous arguments was found in the omission of "energy promotion effects" which were introduced in order to satisfy the virial theorem [1]. Energy promotions for bonding states of simple molecules are obtained by increased orbital exponents which lead to a contracted electron density close to the nuclei compared to corresponding charge distributions in the free atoms. Another accumulation of charge is due to the atomic overlap in the bond region (interference effect) yielding a large decrease of kinetic energy which is crucial for covalent bond formation.

Approximate wave functions which fulfill the virial theorem are obtained e. g. by scaling the coordinate system and varying the scaling parameter η such that the energy is minimized [4]. These functions at optimal scale, in general, may still be far from the exact solution, however, if the molecular functions are in particular linear combinations of correct atomic functions the scaling procedure leads to a substantial improvement of the wave functions which for small molecules are close to the exact solution [5]. For the present problem the approximate solution is preferred to the exact one in order to discuss the energy contributions in terms of atomic promotion and interference effects. In bond orbitals at internuclear distances close to the molecular equilibrium the scaling parameter is $\eta > 1$ which produces a promotion effect showing all features discussed by RUEDENERG. However, at intermediate internuclear distances (5 to 15 Bohr radii for the hydrogen molecular ion) the situation is different: The bonding orbital not withstanding the virial theorem is expanded compared to the atomic constituents [6]. This type of interaction which is essentially different from chemical bonding perhaps indicates some sort of LONDON forces. Corresponding results are obtained if the η-parameter is determined by maximizing the overlap integral of the scaled and the exact wave function [7].

In this context a closer investigation of corresponding antibonding orbitals is interesting. Because of larger corrections due to the differential term in the molecular virial theorem entirely different results may be obtained compared to bond orbital states. The energy destabilization of anibonding liniear combinations is generally considered as being due to the necessary introduction of node planes: those orbitals having the greatest number of nodes are expected to be highest in energy. From

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RUEDENBERG's results obtained for bonding orbitals it has been concluded [8] that in antibonding orbitals the increased energy is almost entirely due to a raise of kinetic energy. If this is true various consequences would result: e. g. orbital transitions which are important in optical spectroscopy are then explained essentially by a change of kinetic energy of the valence electrons (Leuchtelektronen). However, these arguments are only correct if the energy partitioning is strictly reversed in bonding and antibonding orbital states. In addition would molecules with hetero atoms further complicate the problem because of internal charge transfer processes.

We want to investigate this question by calculating two very simple diatomic molecules which are used as a model for more complicated systems. Expectation values of the kinetic and potential energy for antibonding states of H_2^+ and of the smallest heteroatomic molecule, i. e. HeH^{2+}, are calculated. The latter molecule has only antibonding states and is therefore of particular interest for the present problem. The promotion and interference effect and its dependence on the internuclear distance are discussed in detail.

II. Calculation

The method applied is the common MO-LCAO procedure with scaled 1s hydrogen-like atomic functions with charges α and β on the two nuclei

$$\varphi_\alpha(\eta) = \eta^{3/2}(\alpha/\pi)^{1/2}\, e^{-\alpha\eta r_a};$$
$$\varphi_\beta(\eta) = \eta^{3/2}(\beta/\pi)^{1/2}\, e^{-\beta\eta r_b}. \qquad (1)$$

In this problem all overlap, coulomb and resonance integrals can be expressed analytically. The coefficients c_{ij} of the atomic orbitals are then determined by solving a 2×2 secular equation yielding two electronic energies E_a and E_b for the antibonding and bonding states, respectively. For a given set of nuclei α and β these energies are functions of the scaling parameter η and the internuclear distance R. The η's are then varied at each R in such a way that the energy becomes a minimum:

$$\left[\frac{\partial E_{a,b}(\eta, R)}{\partial \eta}\right]_{R=\text{const}} = 0. \qquad (2)$$

This procedure, of course, does not yield the "best LCAO-approximation for the optimal basis set" since the coefficients c_{ij} and the orbital exponent η are not varied simultaneously. However, the functions obtained by successive variation of c_{ij} and η fulfill the virial theorem, too, which is of main importance for the present problem. Expectation values for kinetic and potential energies of the electrons as function of R are obtained from the calculated molecular orbital ψ_i ($i=$ a or b for the antibonding and bonding orbital, respectively) by

$$\overline{V}_i(R) = \int \psi_i(r)\, V\, \psi_i(R)\, d\tau,$$
$$\overline{T}_i(R) = \text{correspondingly}. \qquad (3)$$

Numerical calculations were performed on a Honeywell 120 electronic computer. The program was written in Fortran IV language.

III. Results and Discussion

The results of the computations are presented in Table 1 and 2. Scaling parameters, coefficients, energies and expectation values are listed as function of the internuclear distance R, given in Bohr units. Also, the differential term in the molecular virial theorem

$$E_i + \frac{\alpha\beta}{R} = -\overline{T}_i + R\,\frac{d(E_i+\alpha\beta/R)}{dR} \qquad (4)$$

is presented in which the nuclear repulsion $\alpha\beta/R$ is included. One notices that for almost all distances this corection term is larger for the antibonding linear combination than for the bonding one. This relation is reversed only for HeH^{2+} at intermediate distances. For bonding states at equilibrium separation the molecular theorem Eq. (4) simplifies to

$$E_b + \alpha\beta/R = -\overline{T}_b \qquad (5)$$

which is apart from the term $\alpha\beta/R$ identical with the atomic theorem. Deviations from the latter theorem are certainly large for strongly antibonding states. In the tables potential energies without internuclear repulsions, i. e. electronic potential energies, are also listed. They are always negative for all states and distances because of a general gain of potential energy due to the addition of another nucleus on molecule formation.

Now, considering the scaling parameter (Fig. 1) we observe similar behaviour for η in H_2^+ and HeH^{2+}. For small nuclear distances the bonding orbitals ψ_b are contracted ($\eta>1$) and the antibonding orbitals ψ_a are expanded ($\eta<1$) compared to the separated atom limit. However, the promotion effect in general is smaller for HeH^{2+} than it is for

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$R(a_0)$	η	$E+\frac{1}{R}$	$\overline{T}$	$\overline{V}+\frac{1}{R}$	$R\frac{d(E+1/R)}{dR}$	$\overline{V}$
(1) bonding orbital $\psi_b(c_{b\alpha}=c_{b\beta})$						
0.2623	1.9062	1.9221	1.7231	0.1990	− 3.6452	− 3.6134
0.5750	1.7392	0.0565	1.3128	− 1.2563	− 1.3693	− 2.9954
0.9664	1.5521	− 0.4230	0.9708	− 1.3938	− 0.5478	− 2.4286
1.4546	1.3750	− 0.5623	0.7303	− 1.2926	− 0.1680	− 1.9801
2.0393	1.2308	− 0.5864	0.5799	− 1.1663	0.0065	− 1.6567
2.6447	1.1344	− 0.5749	0.5009	− 1.0758	0.0740	− 1.4539
3.8676	1.0342	− 0.5405	0.4469	− 0.9874	0.0936	− 1.2460
4.9891	1.0022	− 0.5194	0.4507	− 0.9701	0.0687	− 1.1705
6.0299	0.9950	− 0.5089	0.4669	− 0.9758	0.0420	− 1.1425
10.0085	0.9950	− 0.5003	0.4976	− 0.9979	0.0027	− 1.0978
(2) antibonding orbital $\psi_a(c_{a\alpha}=-c_{a\beta})$						
0.4890	0.5112	1.5759	0.5417	1.0342	− 2.1176	− 1.0108
1.0934	0.6859	0.3517	0.7267	− 0.3750	− 1.0784	− 1.2896
1.5449	0.8091	0.0238	0.8012	− 0.7774	− 0.8250	− 1.4247
1.9584	0.8936	− 0.1521	0.8102	− 0.9623	− 0.6581	− 1.4729
2.3701	0.9493	− 0.2646	0.7848	− 1.0494	− 0.5202	− 1.4713
3.0141	0.9953	− 0.3692	0.7224	− 1.0916	− 0.3532	− 1.4234
3.9391	1.0155	− 0.4420	0.6399	− 1.0819	− 0.1979	− 1.3358
4.9232	1.0156	− 0.4751	0.5798	− 1.0549	− 0.1047	− 1.2580
9.9912	1.0009	− 0.4997	0.5024	− 1.0021	− 0.0027	− 1.1022

Table 1. H_2^+ ($\alpha=\beta=1$) internuclear distances R are in Bohr units. Energies are given in atomic units (1 a. u. = 27.21 eV).

$R(a_0)$	$c_{b\alpha}$	$c_{b\beta}$	η	$E+\frac{2}{R}$	$\overline{T}$	$\overline{V}+\frac{2}{R}$	$R\frac{d(E+2/R)}{dR}$	$\overline{V}$
(1) positive linear combination $\psi_b(c_{b\alpha}/c_{b\beta}>0)$								
0.2	0.9714	0.2373	2.0688	5.8364	3.7370	2.0994	− 9.5734	− 7.9006
0.6	0.8524	0.5228	1.3917	− 0.0769	2.5433	− 2.6202	− 2.4664	− 5.9535
1.0	0.7099	0.7042	1.1537	− 0.9719	2.1543	− 3.1262	− 1.1824	− 5.1262
1.2	0.6403	0.7681	1.1002	− 1.1615	2.0728	− 3.2343	− 0.9113	− 4.9010
1.5	0.5373	0.8433	1.0534	− 1.3371	2.0155	− 3.3526	− 0.6784	− 4.6859
2.0	0.3804	0.9247	1.0186	− 1.5028	1.9936	− 3.4964	− 0.4908	− 4.4964
2.5	0.2559	0.9666	1.0064	− 1.6010	1.9953	− 3.5963	− 0.3943	− 4.3963
3.5	0.1065	0.9943	1.0007	− 1.7143	1.9994	− 3.7137	− 0.2851	− 4.2851
5.0	0.0262	0.9996	1.0000	− 1.8000	1.9998	− 3.7998	− 0.1998	− 4.1998
10.0	0.0002	0.9999	1.0000	− 1.8999	2.0001	− 3.9001	− 0.1001	− 4.1001
(2) negative linear combination $\psi_a(c_{a\alpha}/c_{a\beta}<0)$								
0.2	− 0.7380	0.6747	0.9443	8.9571	0.9678	7.9893	− 9.9249	− 2.0107
0.6	− 0.7303	0.6830	0.8959	2.3000	1.1181	1.1819	− 3.4819	− 2.2152
1.0	− 0.7472	0.6645	0.9965	0.8288	1.5287	− 0.6999	− 2.3575	− 2.6999
1.2	− 0.7783	0.6278	1.0485	0.4321	1.5568	− 1.1247	− 1.9889	− 2.7914
1.5	− 0.8378	0.5459	1.1081	0.0438	1.4373	− 1.3935	− 1.4811	− 2.7268
2.0	− 0.9246	0.3809	1.1482	− 0.2829	1.0835	− 1.3664	− 0.8006	− 2.3664
2.5	− 0.9700	0.2429	1.1243	− 0.4126	0.8040	− 1.2166	− 0.3914	− 2.0166
3.5	− 0.9950	0.0991	1.0485	− 0.4850	0.5775	− 1.0625	− 0.0925	− 1.6339
5.0	− 0.9996	0.0257	1.0062	− 0.4990	0.5081	− 1.0071	− 0.0091	− 1.4071
10.0	− 0.9999	0.0001	1.0000	− 0.4999	0.5000	− 0.9999	0.0000	− 1.1999

Table 2. HeH^{2+} ($\alpha=1$; $\beta=2$) units are given in Table 1.

H_2^+. At larger internuclear separations the parameters η_a and η_b for the functions ψ_a and ψ_b, respectively, of HeH^{2+} are both $\eta>1$ with $\eta_a>\eta_b$. Again we observe at intermediate distances an effect

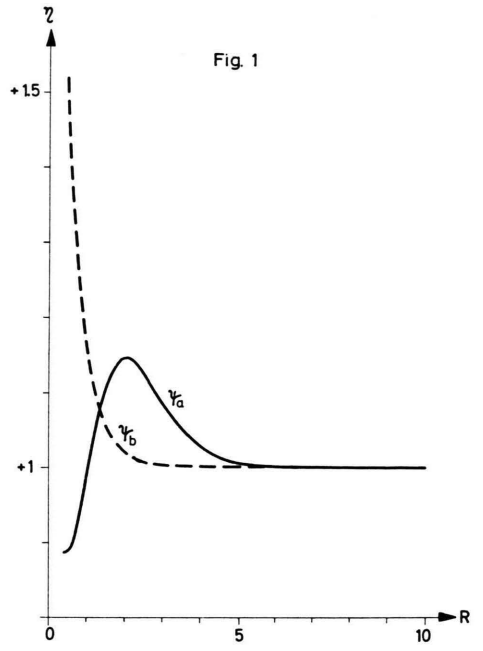

Fig. 1. Dependence of the scaling parameter η from the internuclear distance R for the positive ψ_b and negative ψ_a atomic linear combination in HeH^{2+}.

which is similar to that in H_2^+; it is, however, more distinct; the η_a-values are increased in HeH^{2+} up to 1.15. This probably simulates an interaction (VAN DER WAALS or LONDON forces?) which is non-bonding or weakly bonding in character and which is different from interactions obtained for usual chemical bonding because of reversed promotion effects. It is larger for molecules with hetero atoms.

More interesting than looking at the scaling parameter is an investigation of the R-dependence of the kinetic and potential energy contributions due to molecular bond formation. These energies are obtained by substracting from the kinetic and potential energies in Table 1 and 2 the respective values for the separated atoms. For H_2^+ this limit at infinite internuclear separations is identical with the ground state energy of the hydrogen atom, i. e. the kinetic energy is $\bar{T}_\infty = 0.5$, and the potential energy is $\bar{V}_\infty = -1.0$ atomic units. The lower state of HeH^{2+} changes for infinite distances into the ground state of He^+, i. e. $\bar{T}_{b\infty} = 2$ and $\bar{V}_{b\infty} = -4$, and the excited state of HeH^{2+} goes into the ground state energy of the hydrogen atom. Kinetic and potential energies due to the interaction of the atomic components, i. e. $\bar{T} - \bar{T}_\infty$ and $\bar{V} + \alpha\beta/R - \bar{V}_\infty$, respectively, are plotted in Fig. 2 and 3.

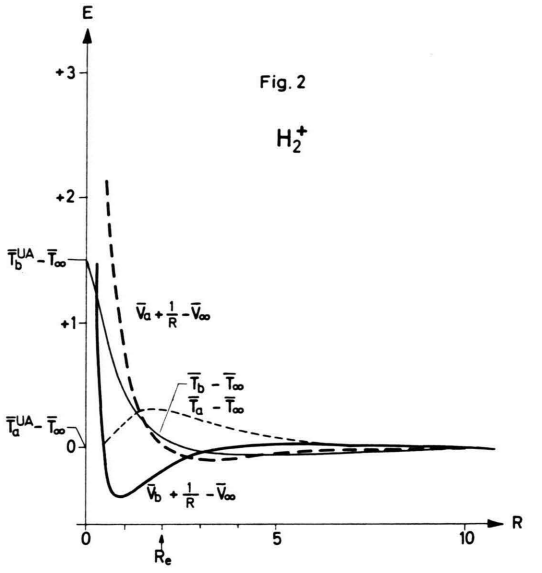

Fig. 2. Kinetic $(\bar{T} - \bar{T}_\infty)$ and potential $(\bar{V} - \bar{V}_\infty)$ energy contributions to the bond energy for bonding (b) and antibonding (a) molecular orbital states of H_2^+.

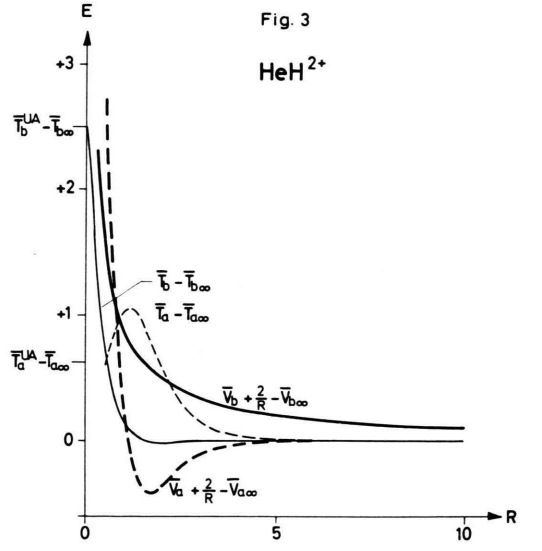

Fig. 3. Corresponding energy curves for HeH^{2+}. Notice that the separated atom limits are different for positive and negative linear combinations.

Kinetic and potential energy curves for the bond orbital of H_2^+ calculated from the exact solution have been discussed earlier [5]. Corresponding curves obtained from scaled approximate functions are very close to the exact solution [5]. In the following we want to discuss the behaviour of these curves in terms of the promotion effect for which the scaling parameter η is an indication. At first, as R decreases from in-

finity to intermediate distances, it is the "inference effect" due to the orbital overlap which is the important factor for the kinetic and potential energy change. The "promotion effect" at these distances is very small ($\eta \approx 1$) since the atomic virial theorem is still well obeyed. A piling up of charge in the overlap region for the bonding orbital leads to an increase of potential energy and to a more than compensating drop of kinetic energy. On the other hand a removal of charge due to the node plane in the antibonding orbital correspondingly has the opposite effect on the energy distribution. The reversed promotion effect discussed in the preceding paragraph also causes energy changes in the same sense as obtained for the interference effect. These are, however, of minor importance as is seen by inspecting the energy curves at points without promotion effect where the scaling parameter has exactly the value $\eta = 1$. At smaller internuclear distances the promotion effect becomes more and more important and changes the situation completely. Energy contributions in bonding and antibonding orbital states in general do not have opposite signs. While in the bonding linear combination both kinetic and potential energy change sign due to promotion effects, the kinetic energy in the antibonding state remains always positive and goes through a maximum close to the equilibrium distance at $R_e = 2.0$ at. u. The potential energy at smaller R-values becomes also positive because of the increased internuclear repulsion. For distances between $R = 0$ and R_e all energy contributions for the antisymmetric linear combination are positive. The virial theorem is fulfilled due to the large negative differential term by which the atomic virial theorem is corrected. The potential and kinetic contributions to bond energy at equilibrium distance is therefore primarily determined by the virial theorem which causes large promotion effects. An understanding of chemical bonding in terms of kinetic and potential energy is therefore only possible if the validity of the virial theorem is accounted for. Although promotion effects are predominant in the two energy contributions they are of minor importance to the total energy since they operate in opposite direction: the decrease in potential energy due to promotion is compensated by an increase in kinetic energy. The drop in total energy on molecular formation is caused by atomic interference. At very small interatomic distances the potential energy goes to infinity because of the increased internuclear repulsion. The kinetic energies, however, assume fixed values determined by the united atom. It should be pointed out that for antibonding states these limits are not correctly obtained from the present method. Therefore respective curves for these states cannot be drawn up to the united atom limit in Fig. 2 and 3.

The shapes of energy curves for the heteroatomic molecule HeH^{2+} (see Fig. 3) are largely similar to corresponding H_2^+ curves. Only the potential curve of the positive linear combination behaves entirely different. Due to the strong nuclear repulsion this curve is positive for all interatomic separations. In the negative linear combination the nuclear repulsion term in the potential curve is compensated by a charge transfer process within the molecule. Since the separated atom limit for this state consists of a hydrogen atom H and a helium nucleus He^{2+}, a transfer of electronic charge from H to He^{2+} by molecule formation is accompanied by a gain of potential energy due to the higher coulomb attraction. The total energy, however, is repulsive because of the large increase of kinetic energy which results from a combined interference and promotion effect in the higher orbital state. Since these effects operate in the $\bar{T}_b$-curve in opposite direction, a slight decrease in energy is observed. The promotion energy is increased for relatively small internuclear distances. In this region the $\bar{T}_a$-curve drops because of a continuous decrease of the η-parameter (see Fig. 1). Close to the united atom the curve becomes more and more incorrect since the present procedure is not able to reproduce the correct state for this limit. This error is obviously larger for HeH^{2+} than for H_2^+.

The striking similarity of the two kinetic energy curves $\bar{T}_a - \bar{T}_{a\infty}$ for HeH^{2+} and H_2^+ deserves special interest. They both go through a maximum at interatomic distances where chemical bonding occurs. Corresponding potential curves on the other hand deviate only very little from their separated atom limits: with other words, potential energy contributes very little to the total (anti)-bonding energy. This may be an indication that negative linear combinations are destabilized primarily by an increase of kinetic energy. The result favours the opinion [8] that the destabilization of antibonding orbitals is almost entirely due to the presence of nodes in negative linear combinations of molecular orbitals. This is certainly true for homonuclear molecules like H_2^+

where the increase in kinetic energy is entirely due to the interference effect which raises the energy in the antisymmetric linear combination. However, for heteronuclear molecules this increase is also due to promotion energy which enhances the maximum of the antibonding kinetic energy curve at normal bond distances.

A generalization of the present results, of course, cannot be made without strong reservations. However, they may be taken as basis for a discussion of more complicated molecules which should include electronic repulsions. Such investigations would also have special interest in electronic spectroscopy. Since electronic transitions in particular occur between the highest occupied and the lowest empty orbital states which are essentially antibonding in character it is important for an understanding of these transitions if these are mainly due to a change in kinetic energy of the electrons. Moreover, if destabilization due to nodes in the electronic density is the main contribution to the total energy, it would be the kinetic energy which determines the order of antibonding orbitals in the orbital energy scheme. These questions, however, can only be settled if further results on more complex molecules are available.

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Der Rotations-Zeeman-Effekt der *l*-Typ-Übergänge linearer Molekeln. OCS und HCN

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The high-field rotational Zeeman effect has been observed in several rotational transitions of the (010) vibrational state in OCS and HCN. The magnetic-field splittings are in agreement with a simple first-order energy expression which is derived to hold for the Zeeman energies of rotation-vibrational states of a linear polyatomic molecule showing rotational *l*-type-doubling. In this way, the presence of intrinsic magnetic moments in the π-vibrational states has been shown experimentally. The *g*-values along the molecular axis are $g_{\parallel}^{(010)} = +0.061 \pm 0.002$ for OCS and $g_{\parallel}^{(010)} = \pm 0.38 \pm 0.06$ for HCN. No magnetic anisotropies could be detected within the plane perpendicular to the molecular axis. The other parameters measured are $g_{\perp}^{(010)} = -0.0285 \pm 0.0006$ and $(\chi_{\perp} - \chi_{\parallel})^{(010)} = (8.0 \pm 1.0) \times 10^{-6}$ erg/G^{2}mole for OCS and $g_{\perp}^{(010)} = \mp 0.100 \pm 0.001$ for HCN which can be considered an approximate value for the vibrational ground-state. Either the upper or the lower signs hold for the *g*-values of HCN. The intrinsic *g*-values, $g_{\parallel}^{(010)}$, are discussed in terms of nuclear and electronic contributions. A quantity measuring the slip of a rotating nuclear framework within its electronic environment is defined and also discussed.

I. Einführung

Der Rotations-Zeeman-Effekt in starken Magnetfeldern wurde bisher an einer Vielzahl von Molekülen im Schwingungsgrundzustand untersucht. Die Feldaufspaltungen führen, in Übereinstimmung mit der Theorie [1, 2], zur Bestimmung der molekularen *g*-Faktoren und der Anisotropien der magnetischen Suszeptibilität. Von geringen Abweichungen abgesehen, die in einem Falle, beim Formaldehyd, gefunden wurden und die wahrscheinlich auf Zentrifugaleffekte zurückzuführen sind [3], konnten die gemessenen Aufspaltungen im Rahmen eines starren Molekülmodells beschrieben werden. Das gilt selbst für eine Untersuchung am Acetaldehyd-Molekül, in dem eine mit 1160 cal/mol mittelstark drehgehinderte Methylgruppe vorliegt [4].

Abweichungen sowohl vom starren Molekülmodell als auch vom Aufspaltungsbild der Rotationsüber-

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