Potential Energy Surfaces for the Na(3p)N_2, Na(3p)HCN and Na(3p)C_2H_2 Complexes: *Ab Initio* Calculations and Model Considerations

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Dedicated to Prof. *Edgar Heilbronner* on the occasion of his 80th birthday

Motto: '*Hier kocht der Chef, kommen Sie dennoch!*'

Highly correlated *ab initio* calculations for the potential-energy surfaces of the systems Na–N_2, Na–HCN, and Na–C_2H_2 have been performed, where the Na atom is in the 3s ground state or in the 3p excited state, and the molecules are kept fixed in their equilibrium configurations. The purpose of these calculations was to enable computer simulation of optical-scattering experiments. In this paper, model considerations are presented that allow easy qualitative understanding of the shapes of the calculated surfaces.

Introduction. – Modern quantum chemistry is a field of both physics and chemistry. No need to discuss its chemical merits in this journal. But surprisingly often also for the interpretation of physical experiments on systems more complex than an atom and less complex than a crystal, quantum chemistry can also make significant contributions. Various kinds of results based on precise numerical calculation of molecular wave functions are required. A few recent examples from my own work, where transition probabilities [1], quantum-defect surfaces [2], or spectroscopic assignments [3] were needed, may illustrate the situation. However, with increasing precision of quantum-chemical results their transparency is lost, and while the results must be accepted, physical understanding can often not account for every numerical detail. The present study was carried out to support the interpretation of optical-collision experiments with molecules [4], providing high-precision interaction potentials for intermolecular forces in electronically excited states, and a physical interpretation of the results is attempted.

One great advantage of quantum chemistry is the use of 'atomic units' (a.u.) throughout, quantities are given in a.u. Conversion factors: length: 1 $a_o = 5.2918 \cdot 10^{-11}$ m; energies: 1 a.u. $= 4.3598 \cdot 10^{-18}$ J; dipole moments: 1 a.u. $= 8.4783 \cdot 10^{-30}$ Cm; quadrupole moments: 1 a.u. $= 4.4865 \cdot 10^{-40}$ Cm^2.

Optical Collisions. – A classical technique is to study the interaction of particles by means of scattering experiments. Theoretically, the interaction is described by a potential or, in more complicated cases, by a potential 'surface', depending on the distance and mutual orientation of the collison pair. At infinite separation, these potential surfaces are reduced to the sum of the energy levels of the unperturbed collision partners; repulsion or attraction during the encounter will shift the energy away from its asymptotic value. On the surfaces, trajectories can be defined that, for given initial conditions, represent the evolution of a binary encounter of the colliding partners. The shape of the potential together with the initial momentum controls the trajectory.

With electronically excited particles, excited-state interaction potentials can likewise be tested. In particular, the scattering process is called an 'optical collision' when optical excitation takes place during the encounter. The processes to be discussed here are optical collisions of Na atoms with molecules M [5]:

$$\mathrm{Na(3s)} + \mathrm{M} + h\nu \rightarrow \mathrm{Na(3p)} + \mathrm{M} \tag{1}$$

where, for the present study, M will be N_2, HCN, or C_2H_2. As the photon energy $h\nu$ is detuned from the free $\mathrm{Na(3s \rightarrow 3p)}$ resonance, the excitation can take place only during the collision at positions where the photon energy exactly matches the separation of the two potential surfaces involved. The experiments are carried out with polarized laser light and, therefore, probe not only the energy difference as a function of the mutual arrangement of the colliding complex but also the orientation of the transition dipole of the optical excitation. In this way, a spatial picture of the collisional process and the alignment of the 3p orbital in the final state can be obtained [6]. Let us note that the transition may take place before or after the closest encounter of the colliding particles. For optical collisions of Na with noble gas atoms, even quantum-mechanical interferences of trajectories that change the surface at the first or second resonance ('*Condon* points') have been detected [7]. This effect is even more probable for scattering with molecules, but could not yet be observed due to reduced resolution and poorer statistics.

In contrast to scattering experiments with atomic targets [8], the interpretation of experiments with even linear molecules is a rather difficult task because only an average over possible orientations of the molecular axis with respect to the direction of the incident Na-atom as well as over different rotational states (or rotation velocities, for a classical approach) can be observed. The interpretation can be attempted by computer simulation of the scattering experiments by classical kinematics on the interaction surfaces. Only when the simulated scattering cross sections agree with experiment can we hope to understand mathematically the intermolecular interactions. Our situation is simplified insofar as, hitherto in the experiments, solely positive detunings between 120 and 480 $\mathrm{cm^{-1}}$ have been applied. As a consequence, by optical excitation of these complexes, only the highest potential surfaces could be attained and, thus, are needed for the interpretation of the scattering data.

Quantum-Chemical Calculations. – To enable numerical simulation of optical-collision experiments of Na atoms with N_2, HCN, and C_2H_2 targets, we have calculated the relevant potential-energy surfaces as well as the transition-dipole-moment functions for transitions from the ground state to all Na(3p) components. Transition moments were evaluated within the *Hartree-Fock* approximation, whereas, for energies, the CEPA-0 ('coupled-electron-pairs approximation') program of *Fink* and *Staemmler* [9] has been used. The wave functions are expanded in a slightly modified aug-cc-pVTZ basis set as published by *Dunning* and co-workers [10][11] where self-made basis functions for the orbitals of ground state and excited Na had been added.

Care was taken to allow for both the polarizability of the target molecule and the 3s → 3p excitation of Na. For isolated Na-atoms, we obtain an excitation energy of 16899 cm^{-1} (spin-orbit averaged experimental value 16968 cm^{-1} [12]) and an oscillator strength of 1.05 (1.00 [13]); our total energy for the Na(3s) ground state is -161.11212 a.u. The *Hartree-Fock* quadrupole moments are -0.93 a.u. for N_2 (experimental value -1.0 a.u. [14]) and $+5.44$ a.u. for C_2H_2 ($+6.2$ a.u. [15]); for the dipole moment of HCN we find 1.29 a.u. (1.17 a.u. [16]) and 2.06 a.u. for the quadrupole. Thus, the *Hartree-Fock* error caused by incorrect multipole moments, relevant for the spatial orientation of the transition dipoles, is below 10%. (Of course, correlated wave functions yield more precise multipole moments, but these values, intrinsic to the energy calculations, have not been evaluated.) The molecules were kept fixed in their equilibrium geometries; thus, we deal with a planar arrangement of C_s symmetry. To enable smooth interpolation of the surfaces, a dense equidistant grid for both remaining internal coordinates (center-of-mass distance and angle with the molecular axis) was used.

Our results comprise several thousand numbers (both energies and transition-vector components are not suited to publication in a journal, but they can be obtained from the author on request). Here, a pictorial presentation of the transition-dipole functions is given in *Fig. 1.* According to the needs of the experimentalists, this figure shows the calculated transition dipoles of the $Na-N_2$, Na−HCN and $Na-C_2H_2$ complexes for transitions from 3s to the uppermost 3p surface as a function of the mutual arrangement of the Na-atom and the target molecule (whose position is indicated in the center of the figures). The circular lines indicate the positions where the detuned optical transitions can take place. The magnitude of the transition moments (the lengths of the bars) is everywhere practically the same as for isolated Na-atoms, the sign of the vectors cannot unambiguously be defined, and their orientation is indicated by the direction of the bars. For not too close separation of Na and M, the orientation of the transition dipole coincides with the alignment of the (real) Na(3p) orbital in the final state. The three pictures show characteristic similarities and differences, and it is obvious that the alignment obeys some underlying rules. Therefore, in the next section, we shall try to present a semiquantitative description of the physics controlling these optical collisions.

Theory. – If the target is a linear molecule assumed to be rigid, and if the *Born-Oppenheimer* approximation is used, the colliding complex is planar and belongs to the point group C_s except for some special $C_{\infty v}$ or C_{2v} arrangements. The symmetry of the total wave function is characterized by the atomic orbital of the outer Na electron. Due to the presence of the target, the degeneracy of the three Na(3p) components is removed. Four different potential surfaces evolve: $1^2A'$ for the 3s ground state, $2^2A'$ and $3^2A'$ for the two in-plane components of 3p and $1^2A''$ for the perpendicular component. Removal of the degeneracy of the excited Na states means also loss of the spherically symmetric charge distribution: in the complex, the 3p orbitals are real functions oriented according to the interaction with the target.

At intermediate distances, the interaction of the Na-atom and the target molecule is essentially determined by the longest-range permanent electric moment of the target. In the case of the three isoelectronic molecules discussed here, this is a positive quadrupole for C_2H_2, a negative quadrupole for N_2, and a combination of dipole and

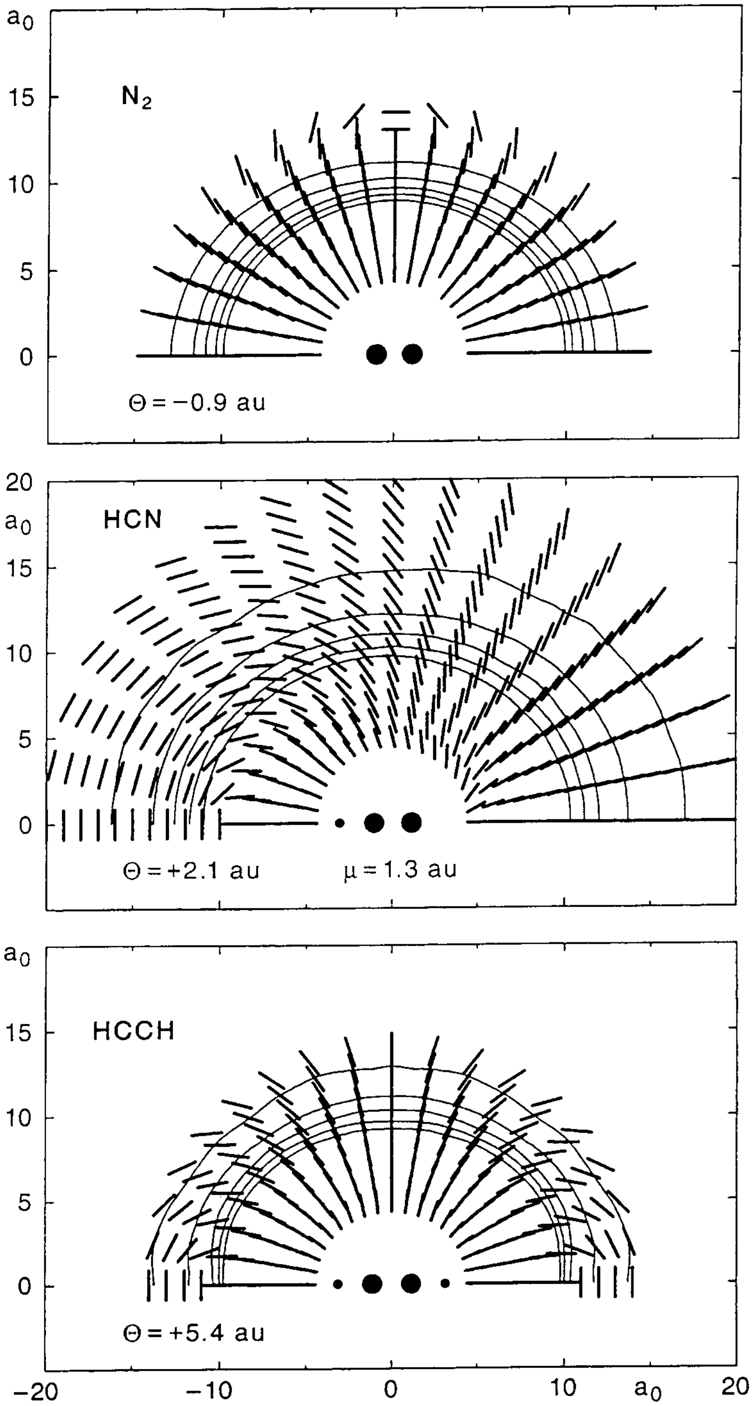

Fig. 1. *Transition dipoles to the uppermost 3p surface of the Na–N_2, Na–HCN, and Na–C_2H_2 complexes.* The calculated transition moments are shown as bars. The position of the Na-atom is varied, it is located at the center of the bars; the target molecule is indicated in the center by circles representing atoms. μ and Θ are calculated values for the dipole and quadrupole moments of the target molecules. The curves are the *Condon* lines for the detunings of 120, 240, 360, and 480 cm^{-1} used in the experiments.

quadrupole for HCN. (Positive quadrupole moment means that, in HCCH, the H-atoms have a positive excess charge, and negative charge is accumulated in the C≡C bond, in contrast to N_2 where the lone-pair electrons cause negative-charge excess at the ends of the molecule and a positive center. Accordingly, the HCN dipole has its positive pole at the H end and the negative pole near the N atom.)

It is these multipole moments that determine the orientation of the 3p orbitals of excited Na-atoms flying by. The orientation is energetically favorable when the atomic p orbital is directed towards a positive pole of the target, and also when the positive Na^+ core is attracted by the negative pole of the target; accordingly, reversed polarity gives rise to repulsion. In fact, the charge distribution of Na excited to a real 3p orbital can be viewed as a negative quadrupole consisting of the Na^+ center between an elongated electron cloud. With *ab initio* calculations, we find the rather large value of -16.76 a.u. for this $Na(3p_o)$ quadrupole moment. Thus, the interaction of the collision partners can qualitatively be understood as a quadrupole-quadrupole interaction and, in the case of HCN targets, as dipole-quadrupole interaction. It is obvious that interaction of the target with the spherically symmetrical Na(3s) ground state is much weaker. Thus, in most optical scattering events, only interaction after excitation will be important.

The situation sketched here is visualized in *Fig. 2*. The interaction potential of HCCH with Na(3p) is shown for the T-shaped C_{2v} and collinear $C_{\infty v}$ symmetries of the colliding pair together with the orientation of the 3p orbital. In addition to what has been discussed already, the figure shows also cuts through the potential surface of a second Na(3p) state with higher energy (the third component, 3pa″, is omitted). The wave functions of the higher electronic states must be orthogonal to the lower ones; in the present case, this means that the higher 3p functions are rotated by right angles. The interaction of the electric moments of the target molecule with excited Na defines three orthogonal axes for the three 3p components of Na and the lowest 3p state has the energetically most favorable orientation, as shown in *Fig. 2*. The radiation that gives rise to excitation of the highest state, also shown, is polarized parallel to the corresponding final 3p orbital, directed to the target for the T-shaped arrangement, and perpendicular to the connecting line in the linear case. This picture will be inverted for target molecules such as N_2 that have a negative quadrupole moment (the orientation of the lower and higher 3p functions should be exchanged on both sides of *Fig. 2*, and the polarization arrows should be rotated by right angles).

This discussion is valid for longer and intermediate separations of the colliding particles. At shorter distances, we should also consider polarization effects and the interactions of higher multipoles and, most important, the repulsion that arises when the electronic wave functions penetrate each other. It is obvious qualitatively that this *Pauli* repulsion is particularly efficient and may operate already at intermediate distances when the 3p orbital is directed towards the target molecule.

Now we are in the position to discuss the results pictured in *Fig. 1*. Remember that this figure shows the orientation of the transition dipole for optical excitation of the Na(3s) electron to the highest component of 3p as a function of the mutual arrangement of the colliding partners. Compare first the HCCH target (bottom) with *Fig. 2:* for separations larger than *ca.* 10 *Bohr* radii and for the $C_{\infty v}$ and C_{2v} geometries, our qualitative model agrees exactly with the calculated results. Note that, for a linear arrangement, the 3p states are split into a σ component with a wave function directed to

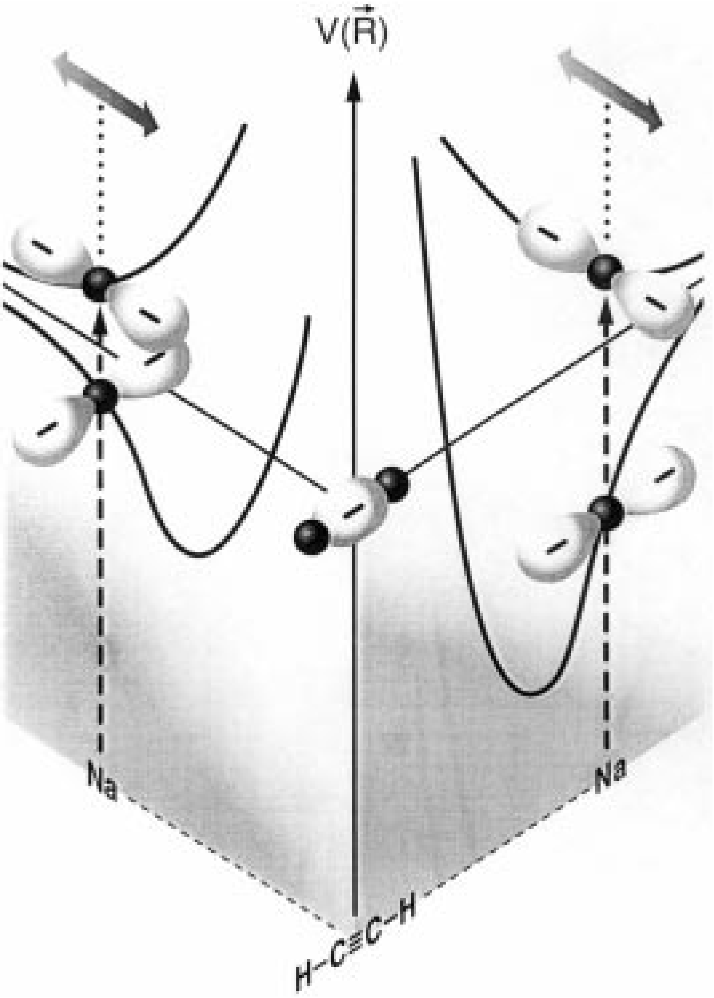

Fig. 2. *Interaction potentials of Na(3p) with C_2H_2 in* C_{2v} *and* $C_{\infty v}$ *symmetry.* The geometric arrangement, charge distribution of C_2H_2, qualitative potential curves of a lower and a higher 3p state, the orientation of the quadrupole of Na(3p), and the polarization vectors for radiation exciting the higher 3s → 3p transition are shown (see text).

the molecule and a doubly degenerate π state with 3p orbitals perpendicular to the connecting axis. In fact, as shown in *Fig. 3*, the short distance repulsion of the σ state leads to a crossing of σ and π near 10.3 a_0. At this conical intersection, the character of the highest 3p surface changes, and so does the orientation of the transition moment. In its surroundings, the change is less abrupt, as in C_s symmetry the $^2A'$ states avoid each other everywhere and the transition between π and σ character occurs continuously. It is remarkable how this change governs the electronic structure even far from the intersection point.

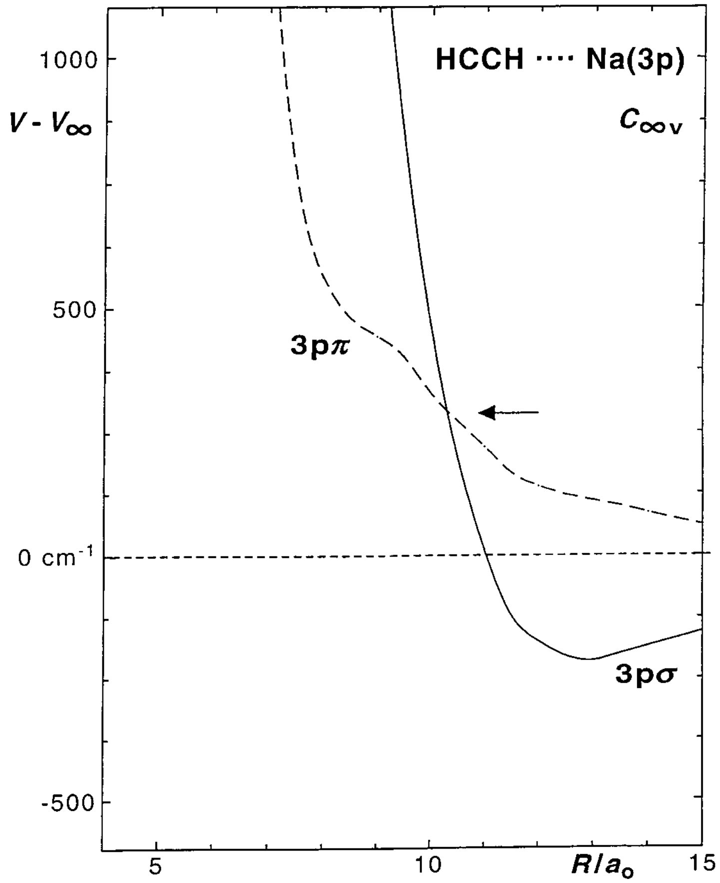

Fig. 3. *Conical intersection of the $2^2A'$ and $3^2A'$ states of Na(3p) · C_2H_2 at* R = *10.3* a_0 (*ab initio* results for the 3pσ and 3pπ potential curves in $C_{\infty v}$ symmetry)

Consider now scattering from N_2 molecules (*Fig. 1*, top panel). The orientation of the 3p atomic orbital in the highest state is just perpendicular to the findings for acetylene at long distances because of the opposite polarity of the molecular quadrupole, and they agree with each other at shorter distances where the interaction is dominated by the repulsion of the electron clouds, always destabilizing the 3p orbital directed to the target. Here, conical intersection of a $^2A_1$ and a $^2B_2$ state occurs in the T-shaped C_{2v} arrangement at a distance of about 14 a_0. This distance is longer than for C_2H_2 because of the smaller magnitude of the molecular quadrupole moment which governs the long-range interaction with Na(3p) atoms. In fact, the intersection occurs on a ring in the sagittal plane of the molecule whereas, in the case of Na$-C_2H_2$, there are only two intersection points.

Most interesting is the case of HCN (*Fig. 1*, central panel). Here, perturbation of the excited Na sets in at longer distances because dipole fields have a longer range than quadrupole fields. For collinear geometries, the picture resembles that for HCCH at the positively charged H end and the interaction with N_2 beyond the N-atom. Again, a short-range region dominated by *Pauli* repulsion and a long-range region characterized by multipole interactions can be distinguished, and we should again keep in mind that only the transition dipoles to the most destabilized surface are shown. As can be seen from the picture, a conical intersection occurs in linear geometry 9.5 a_o away on the H side. The behavior for non-linear geometries can be understood from a discussion of the T-shaped arrangements where the Na-atoms stand perpendicular to the center of the molecule: here, the transition dipoles and thus the 3p orbital is directed under *ca.* 135° to the negative end near the N-atom. This is energetically unfavorable because the orientation of 3p in the lower A' state has the favorable orthogonal orientation of 45° to the positive pole near H. Therefore, the orientation of the transition dipole at longer separations, if followed from left to right, is rotated by 270° like a somersault. In this way, we can also understand the double rotation by 360° of the transition dipole in the more complicated quadrupolar fields of C_2H_2 and N_2.

How reliable are these qualitative arguments? *Fig. 4* shows cross sections through all three 3p surfaces on a half-circle at a constant distance of 15 a_o around the center of mass of HCN. The energies are calculated by means of three different approximations: interaction of the 3p quadrupole Θ with the dipole moment μ of HCN, then including also the quadrupole-quadrupole interaction, and, finally, as interpolated curves connecting *ab initio* results with a spacing of 10°. The model calculations have been carried out by rotating the Na(3p) orbital of $2^2A'$ to the energetically best orientation and for $3^2A'$ as well as $1^2A''$ orthogonal to it, using, for the dipole-quadrupole interaction, $V_{\mu\Theta}$ at a point with coordinates R and α

$$V_{\mu\Theta}\,(R,\,\alpha) = 1.5 \cdot \mu \cdot \Theta \cdot (\cos\alpha\,(3\cos^2\vartheta - 1) - 2 \cdot \sin\alpha\,\sin\vartheta\,\cos\vartheta\,\cos\varphi)/4\pi\varepsilon_o\,R^4 \quad (2)$$

(and a similar formula for the quadrupole-quadrupole interaction [17]), where the orientation of the real 3p orbital with respect to the connecting line is characterized by the angles ϑ (in-plane) and φ (out-of-plane). For $\alpha = 90°$, *e.g.*, *Eqn. 2* predicts vanishing interaction of the dipole with the $3pa''$ component ($\cos\varphi = 0$), whereas, for the $3pa'$ functions, stationary values of the factor $\sin\vartheta \cdot \cos\vartheta$ are found for $\vartheta = 45°$ and 135°. These are the values discussed in the above paragraph. For the two linear arrangements at $\alpha = 0°$ (Na HCN) and 180° (HCN Na), we see the degeneracy of the two π components; the σ state is more stable than π for 0° and less stable for 180°, according to the discussion above. From *Eqn. 2*, the energy separation of the three electronic states can be computed numerically; the figure shows that the agreement of the three calculations is nearly quantitative.

Although not yet important for the experimentalists, we wish to also understand the shape of the potential surfaces at short separations of the collision pair. If the Na-atom comes close to the target molecule M, instead of discussing the electrostatic interaction of the two particles, we must study the structure of the ionic complex MNa^+ and investigate its interaction with the outer electron. For M/Na^+, again electrostatic considerations are relevant: the complex is most stabilized when Na^+ approaches a negative pole of M and destabilized in the opposite case. Thus, at equilibrium, $C_2H_2Na^+$ is T-shaped, N_2Na^+, and $HCN \cdot Na^+$ are linear with Na^+ on the side of the N-atom. At very short distances, of course, *Pauli* and nuclear repulsion keep the particles apart.

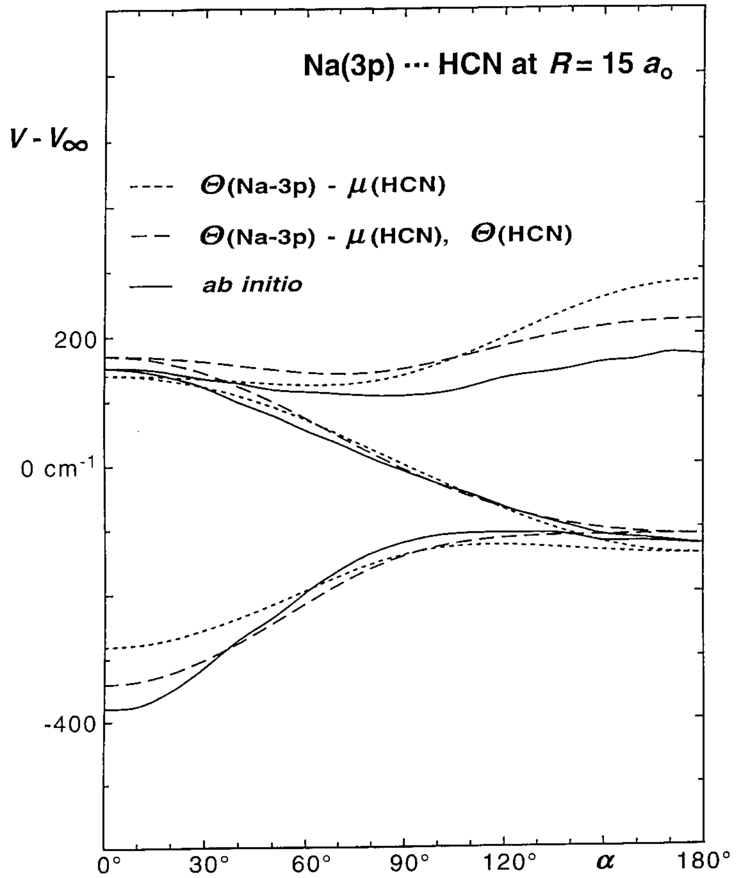

Fig. 4. *Cross section through the three Na(3p)·HCN potential surfaces at $R = 15$* a_0 (comparison of different methods, see text; $\alpha = 0°$ corresponds to linear Na–HCN, 180° to HCN–Na)

Radial cuts through the corresponding ionic potential surfaces are shown in *Fig. 5*; the potential minimum is at a distance of *ca.* 5 a_0 in all three cases. The unpaired electron then occupies one of the *Rydberg* orbitals in the field of the MNa^+ core. The total energies of the electronic states of the neutral complex can be approximated as the sum of the potential energy of MNa^+ and the orbital energy of the occupied orbital. As these orbital energies are determined not only by electrostatic interactions but also by exchange and orthogonality effects with the core electrons, they escape detailed qualitative discussion, but they can easily be estimated by simplified quantum-chemical calculation when the 'frozen core' approximation [18] is used, which can be viewed as the *Koopmans* theorem [19] for *Rydberg* orbitals. But this is not sufficiently transparent for the present purposes and shall not be followed further. Furthermore, in this case, the vibration of the target molecule should no longer be neglected (for NaN_2, see [20]).

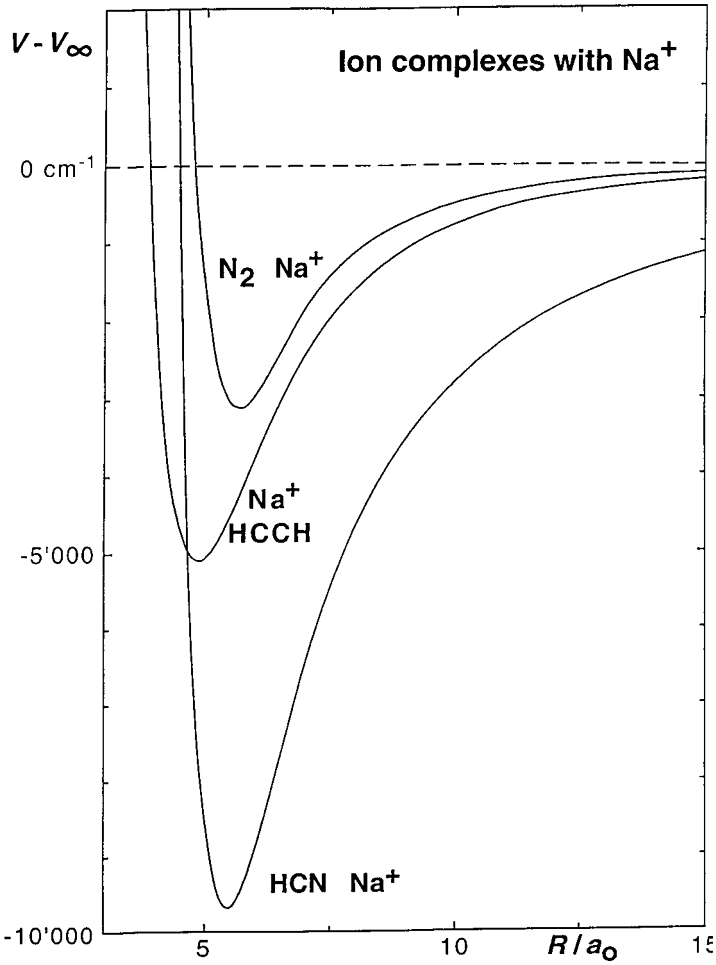

Fig. 5. *Potential-energy curves for the ionic complexes N_2Na^+, $HCN \cdot Na^+$* (both linear), *and $C_2H_2Na^+$* (T-shaped)

Concluding Remark. – This article is a birthday present for Prof. *Heilbronner* who has introduced quantum chemistry at the University of Basel. In his spirit, I tried to demonstrate that the results of complicated quantum-mechanical calculations can be easily understood when an adequately simplified model is used. It may be coincidence that, both in *Hückel* theory and here, atomic p orbitals play a key role. But note the difference: here we deal with intermolecular interactions and, therefore, the charge distributions are important. This leads to a different representation of the orbitals as in *Fig. 2*, where the signs indicate charge distributions rather than the phase of the wave function, in contrast to the pictures found in Prof. *Heilbronner*'s famous book [21].

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