Structure and vibrations of the phenolammonia cluster

A. Schiefke, C. Deusen, C. Jacoby, M. Gerhards, M. Schmitt et al.

Additional information on J. Chem. Phys.
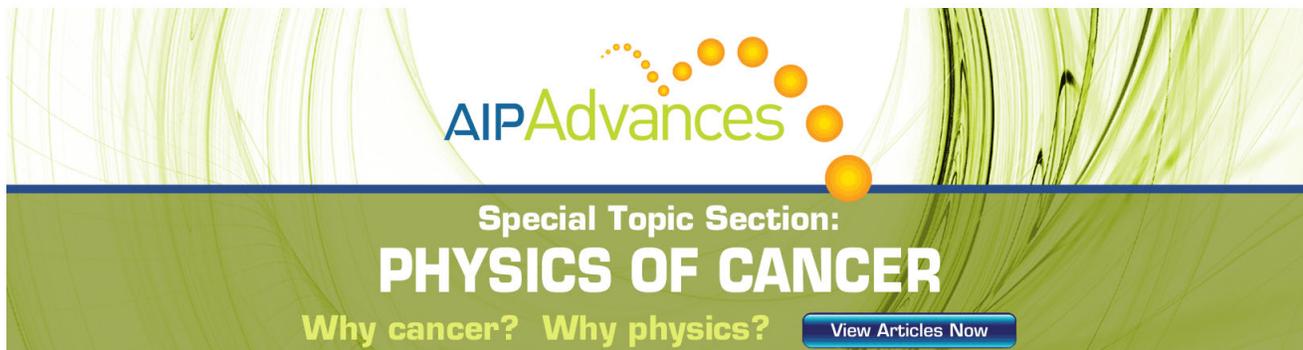
Structure and vibrations of the phenol-ammonia cluster

A. Schiefke, C. Deusen, C. Jacoby, M. Gerhards, M. Schmitt, and K. Kleinermanns[a)]

Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie und Elektrochemie I, D-40225 Düsseldorf, Germany

P. Hering

Max-Planck-Institut für Quantenoptik, D-85748 Garching, Germany

The phenol-ammonia 1:1 complex has been investigated by mass resolved hole burning spectroscopy and *ab initio* methods at the HF/6-31G(d,p) and HF/6-31++G(d,p) levels of theory. By means of spectral hole burning four bands in the region of intermolecular vibrations could be assigned to the 1:1 complex. The *ab initio* computed cluster structure and its normal vibrations are reported and compared to the experimental results. Anharmonic calculations were carried out for the ammonia torsion. The results are compared to structurally related complexes. © *1995 American Institute of Physics.*

I. INTRODUCTION

Clusters of the phenol-water type have gained much interest in the last years. They are easily accessible by laser spectroscopical methods—in contrast to pure solvent clusters, e.g., the water dimer—and they are of fundamental interest to solvent chemistry as well as molecular biology, where hydrogen bonding determines structure and function of proteins and nucleic acids. But whereas the OH···O interaction in clusters was investigated in numerous experimental[1-34] and theoretical works[35-49] and the NH···N potential was extensively explored in the case of the ammonia dimer,[50-64] there is mainly experimental work on the mixed hydrogen bonds NH···O and N···HO.[8,29,65-75] Only few *ab initio* studies for this cluster type are available.[57,62,76-78] However, a quick view in any biochemical textbook shows that the majority of biological relevant hydrogen bonding is due to mixed interaction of the NHO type.[79,80]

What possibilities do exist to investigate these important structures? The water–ammonia cluster itself is probably not accessible to highly sensitive methods like resonance enhanced multiphoton ionization (REMPI) or laser induced fluorescence (LIF) due to the absence of stable low lying electronic states. Results of ir studies in a matrix in the region of OH- and NH-stretch vibrations have been published by Engdahl, Nelander, and Nord[65,71] for the ammonia–water system. In a microwave study[67] Herbine and Dyke conclude that this system is essentially linear bonded with an N–O distance of 2.98 Å. Some high-level *ab initio* studies on this system are also available.[76-78] While the ammonia–water system is a fine example for the study of solvent chemistry and acid-base reactions, it is more realistic to connect the active groups to a carbon backbone when considering the cluster as a biological model system. There are two spectroscopically predestinate complexes to start with aniline–water and phenol-ammonia. This paper deals with the latter complex.

Compared to its water analogue there are relatively few publications on the phenol-ammonia system.[29,69,70,73,74] Mi-

kami *et al.*[69] studied the photodissociation properties of phenol-ammonia. A (1+1)-REMPI spectrum with low spectral and without mass resolution and two dispersed fluorescence spectra were also reported. They identified the electronic origin at 35 717±2 cm^{-1}. A band at 182 cm^{-1} relative to the origin was assigned to the H bond stretching vibration in the S_1 state. The corresponding vibration in the S_0 state has a frequency of 164 cm^{-1} and exhibits a distinct anharmonic behavior. A series of papers from Tramer and co-workers[70,73,74] deals mainly with the proton transfer properties of phenol-ammonia clusters. Mass resolved REMPI spectra of low spectral resolution are reported for the $n=1-3$ clusters. While the $n=1,2$ traces show distinct vibrational structure, the spectrum at the $n=3$ mass exhibits only a broad featureless absorption. Hartland *et al.*[29] performed an ionization detected stimulated Raman spectroscopy (IDSRS) study of a series of 1:1 clusters of the phenol-water type including the phenol-ammonia cluster. They recorded Raman spectra in the region of 1000–1300 cm^{-1}. No spectra in the region of the NH/OH-stretch vibrations were reported. No *ab initio* work on the phenol-ammonia cluster has been published to our knowledge up to now.

In this paper we present two-color REMPI spectra as well as mass resolved hole burning spectra of the phenol-ammonia system. Our aim is to clarify which bands in the intermolecular spectral region do belong to the 1:1 complex. We will compare our results to those of previous investigations. Furthermore, we apply *ab initio* methods for structure determination and normal mode analysis of phenol-ammonia to get additional information for the assignment of the observed intermolecular bands. A comparison with structurally related clusters will complete this study.

II. METHODS

A. Computational procedure

Minimum energy structure and normal mode calculations were performed for phenol, ammonia and the phenol-ammonia cluster with the GAUSSIAN 92 program.[81] The structure was fully optimized at the HF/6-31G(d,p) and HF/6-31++G(d,p) levels. As various authors have shown[42,46,48]

[a)]To whom correspondence should be addressed.

these levels of theory are quite suitable for the determination of structural parameters and harmonic frequencies of hydrogen bonded clusters of the phenol-water type. For the minimum energy structure and for the transition state of internal rotation of phenol-ammonia, normal modes were calculated using force constants from analytical second derivatives of the SCF potential energy surface. The intramolecular vibrations of the cluster were scaled with an empirical scaling factor[42] derived from free phenol. Intermolecular vibrations remained unscaled.

The HF stabilization energy of the cluster was calculated as the difference between the total SCF energy of the fully optimized phenol-ammonia cluster and the energies of the phenol and ammonia moieties. Corrections were made for zero point energy (ZPE), basis set superposition error (BSSE) and correlation contributions (at the MP2 level).

B. Experimental setup

Two color REMPI measurements were carried out using two Nd:YAG pumped frequency doubled dye laser systems (two LDL 205 dye lasers from LAS Inc., pumped by GCR-3 and GCR-170 Nd:YAG lasers from Spectra Physics) using Fluorescein 27 or DCM dyes. Hole burning spectra have been obtained using the first laser system as the (tunable) burn laser, while the second one probes the origin of the 1:1 complex. For the two color REMPI spectra pulse energies below 100 μJ were used for electronic excitation and 2 mJ for ionization (weakly focused). For the hole burning experiment the burn laser delivered uv pulses of 0.5 mJ, but the hole burning signal was strongly enhanced by adding the laser fundamental to the process.[17]

The molecular beam was produced by expanding an appropriate mixture of phenol, ammonia and a seed gas (helium or neon) through a pulsed valve (General Valve) with a 500 μm orifice into a vacuum chamber. The skimmed expansion was introduced into a second chamber where the laser beams interact with the molecular beam at right angles between the first two plates of a Wiley–McLaren type time-of-flight (TOF) mass spectrometer.[82] The vacuum in the two chambers was maintained by a 1000 l/s oil diffusion pump (Alcatel) and a 150 l/s turbo pump (Leybold) at 10^{-4} mbar (nozzle chamber) and 10^{-6} mbar (TOF chamber), respectively. Under these conditions a maximum stagnation pressure of 3000 mbar at a gas pulse length of 300 μs could be used.

The TOF arrangement showed a mass resolution of 92 at $m/e = 111$. This was sufficient for resolving masses 111 and 112 (phenol-ammonia and phenol-water, respectively) at least qualitatively by observing the oscilloscope traces. All spectra were recorded with relatively wide gates (2–3 mass units) but occasionally additional narrow gates were used to discriminate bands from water clusters or isotopomers against the interesting complexes. The TOF signal was digitized by a 500 MHz digitizing oscilloscope (TDS 520A, Tektronix) and transferred to a computer where the TOF mass spectrum was displayed by means of a program written in Labview (National Instruments). The program is able to simulate several boxcar integrators to store and display the
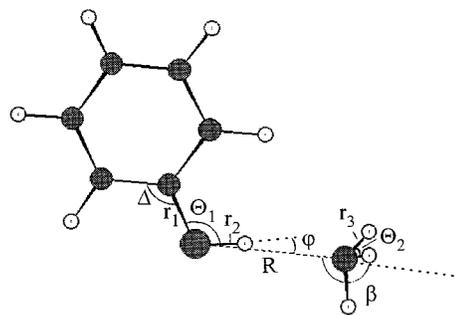

FIG. 1. Geometry of phenol–ammonia and definition of the structural parameters (β is the angle between the O–N axis and the C_3 axis of the ammonia moiety).

integrated ion and background signals as a function of laser wavelength.

Time delays were managed by two home-built delay generators. The delay between the two laser pulses was fixed to zero in the two color REMPI experiments and to 200 ns for the hole burning experiment. Timing stability was about 2 ns. In the hole burning experiments two traces were recorded for every mass, one for the burn laser and one for the probe laser. All traces could be normalized to the laser power by means of a photodiode.

III. THEORETICAL RESULTS

A. Calculated geometries and binding energies

Due to the much stronger base character of ammonia compared with water and methanol, there is no question that the ammonia moiety is the proton acceptor in this cluster. When choosing a suitable starting geometry for optimization, one should be aware of the possibility of more or less ionic structures, derived from a structure like $(NH_4)^+(C_6H_5O)^-$. However, all calculations (ionic or covalent start geometries) for the electronic ground state of phenol-ammonia finally converged to the structure shown in Fig. 1.

The calculated structure fits well in with the other clusters of the phenol-water type. The important structural parameters are reported in Table I. The optimized structure is of nearly C_s symmetry with one ammonia hydrogen lying in the aromatic plane and the two others placed symmetrically above and below the plane. In contrast to phenol-water the out-of-plane hydrogens reside on the *cis* side of the hydrogen bond axis, probably due to sterical hindrance of the aromatic ring hydrogen.

Analogous geometrical parameters of the phenol-water and phenol-ammonia clusters are quite similar. The OH-bond length r_2 of the phenol moiety is stretched more in the case of phenol-ammonia than in the case of phenol-water. This can be attributed to the stronger proton acceptor character of ammonia compared with water. The length R of the H bond defined by the distance between the heavy atoms (here O and N) is substantially larger in phenol-ammonia compared to phenol-water and phenol-methanol. This result is consistent with microwave data of Herbine and Dyke for ammonia–water, where the ON distance is determined to 2.98 ± 0.05 Å.[67] Rotationally resolved LIF measurements by Plusquellic

TABLE I. Structural parameters (Å and degrees) of bare phenol and phenol complexed with water, methanol and ammonia, computed with the 6-31G(d,p) basis set.

	Phenol[a]	Phenol-water[a]	Phenol-methanol[b]	Phenol-ammonia
r_1	1.352	1.345	1.344	1.341
r_2	0.943	0.949	0.949	0.954
R		2.906	2.891	2.952
r_3		0.944	0.942	1.001
θ_1	110.93	111.58	111.64	112.30
Δ	117.43	117.70	117.71	117.77
φ		3.34	3.50	6.30
β		135.79	143.2	178.30
θ_2		106.83	110.36	107.79
θ_2'[c]				107.60

[a]Schütz *et al.* Refs. 42 and 46.
[b]Gerhards *et al.* (Ref. 48).
[c]θ_2' is the angle between the in-plane and out-of-plane ammonia hydrogens whereas θ_2 is the angle which is intersected by the molecular plane.

et al. show an O–N distance of 2.77 Å in 2-naphthol-ammonia,[75] however. Unfortunately, no *ab initio* calculations have been performed for this large system yet to check whether calculations at the Hartree–Fock level are able to give a reliable description of the O–N distance in aromatic H-bonded systems.

The hydrogen bond in phenol-ammonia is distorted from a linear arrangement by $\varphi = 6.5°$ (cf. Fig. 1). The distortion is larger than in ammonia–water [1.5° at HF/6-31G(d,p)[76]] and phenol-water [3.3° at HF/6-31G(d,p)[46]] which may be explained by stronger sterical interaction of ammonia with the aromatic ring hydrogen. The C_3 symmetry axis of ammonia spans an angle β of 178.3° with the O–N axis. This means that this axis nearly coincides with the O–N axis. Addition of diffuse functions on all atoms in the basis set [6-31++G(d,p)] leads to a similar geometry. The only discernible deviations are the O–N distance R and the angle φ which increase to 2.977 Å and 7.14°, respectively.

The calculated rotational constants are given in Table II. They are compared with those for the free phenol and the corresponding water and methanol clusters. No experimental values for the rotational constants of phenol-ammonia are available yet.

The transition state for the torsional motion of ammonia was calculated as well. Normal coordinate analysis predicts an almost pure rotation about the ammonia C_3 axis. A one-dimensional calculation along this coordinate shows a barrier at $\alpha = 60.0°$, where α is the torsional angle measured from the minimum structure at 0°. The barrier height was calcu-

TABLE II. Rotational constants (MHz) of phenol, phenol-ammonia, phenol-water, and phenol-methanol computed with the 6-31G(d,p) basis set.

	A	B	C
Phenol[a]	5749.7	2659.3	1818.3
Phenol-ammonia	4405.6	1073.0	866.8
Phenol-water[a]	4371.3	1086.2	873.5
Phenol-methanol[b]	3785.7	691.3	605.9

[a]Schütz *et al.* Refs. 42 and 46.
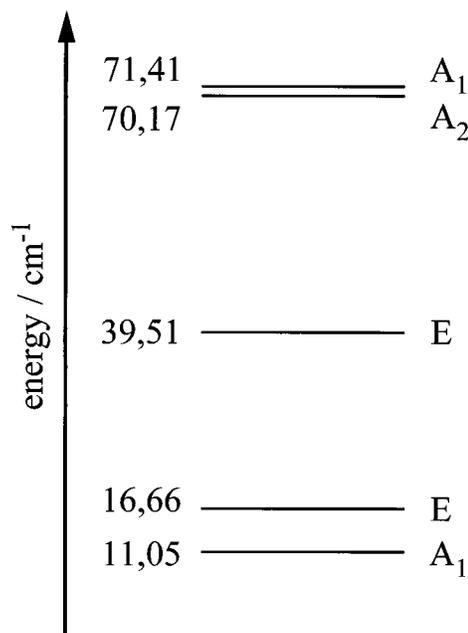[b]Gerhards *et al.* (Ref. 48).

FIG. 2. Calculated torsional energy levels of the electronic ground state of phenol-ammonia.

lated to 24.3 cm^{-1}. Further optimization of the transition state structure with the TS option of the GAUSSIAN program did not result in significant changes. This is in contrast to phenol-water where the transition state of the torsional motion cannot be described by a pure rotation about the OO axis since the water moiety lies 0.5 Å above the aromatic plane.[46] For the 2-naphthol-ammonia torsion in the electronic ground state, V_3 barriers of 34.2 cm^{-1} (*trans*-naphthol) and 41.1 cm^{-1} (*cis*-naphthol) were obtained from high resolution LIF measurements[75] which are of similar magnitude. Obviously ammonia is a nearly free rotor in this cluster, in distinct contrast to phenol-water where the second p orbital of the oxygen atom provokes a rotational barrier of 130 cm^{-1} as obtained from high-resolution LIF measurements.[83]

The potential can be fitted by a cosine function of the form $V = \frac{1}{2} V_0 [1 - \cos 3\alpha]$ without any higher order terms. The torsional levels for this potential are calculated according to Ref. 28 and shown in Fig. 2. The energy levels are classified in the point group C_{3v}, the local symmetry of the ammonia moiety. The splitting of the lowest A and E levels is 5.6 cm^{-1}.

The binding energie D_e of phenol(NH$_3$) is calculated at the HF and MP2 level of theory [$\Delta_{corr} = D_e(\text{MP2}) - D_e(\text{HF})$]. BSSE corrections of the binding energy are taken into account using the full counterpoise procedure of Boys and Bernardi.[46,84] Zero point energy (ZPE) contribution is included in the D_0 values. The calculated ZPE results from unscaled harmonic frequencies. Due to the stronger base character of ammonia the phenol-ammonia cluster turns out to be more stable than the phenol-water and phenol-methanol clusters. Similar to phenol-water and phenol-methanol, the uncorrected HF-binding energy (2981 cm^{-1}) is a good approximation of the true stabilization energy of the cluster, since BSSE (HF+MP2) correction and correlation energy contribution cancel rather closely.

TABLE III. Calculated binding energies (cm^{-1}) of phenol-ammonia, phenol-water and phenol-methanol computed with the 6-31G(d,p) basis set.

	Phenol-ammonia	Phenol-water	Phenol-methanol
D_e(HF)	−2981	−2537	−2547
D_0(HF)	−2316	−1946	−2094
ΔD_{corr}(MP2)	−860	−664	−855
BSSE(HF)	369	395	453
BSSE(MP2)	365	362	453
D_e(MP2, CP)	−3107	−2444	−2495
D_0(MP2, CP)	−2442	−1853	−2042

B. Intramolecular vibrations

The calculated intramolecular harmonic frequencies are collected in Table IV. As expected from group theory there are 27 intramolecular vibrations of a' and 12 of a'' symmetry. The frequencies are scaled with a factor 0.9 which was derived by Schütz *et al.* in comparing experimental and *ab*

initio frequencies of phenol.[42] Calculated frequency shifts (relative to bare phenol and ammonia, respectively) were also added. The two degenerate ammonia vibrations ν_3 and ν_4 (the asymmetric stretching and the bending vibration, respectively) correlate with one a' and one a'' vibration.

As already mentioned, some intramolecular frequencies were measured by Hartland *et al.*[29] and Mikami *et al.*[69] The IDSRS spectra[29] show frequency shifts of ν_1 (in Ref. 29 indicated as ν_{12}), ν_{18a} and ν_{7a} which are in good agreement with our calculations (experimental: 1.1, −1.1, and 17.8 cm^{-1}; calculated: −1.5, −0.3, and 16.8 cm^{-1}). The dispersed fluorescence spectrum in Ref. 69 show $\nu_{6a}=525$ cm^{-1}, $\nu_{12}=822$ cm^{-1}, and $\nu_1=996$ cm^{-1}, also in good agreement with the corresponding values in Table IV.

The most striking frequency shifts due to complexation are associated with the OH-bending vibration, the torsion about the C–O axis and the ammonia, umbrella vibration. Here, the shifts can be explained by the additional mass of

TABLE IV. Intramolecular vibrations of phenol-ammonia computed with the 6-31G(d,p) basis set (frequency and Δ in cm^{-1}, force constant in Nm^{-1}, reduced mass in amu).

Symmetry/ label		Frequency (scaled)	Δ^a	Red. mass	Force const.	IR intensity	Raman activity	Depola rization
a''	11	237.0	5.7	3.6308	14.74	0.7512	4.1639	0.7500
a''	16a	417.4	1.0	3.0272	38.13	0.0629	0.0310	0.7500
a'	18b	433.8	35.1	3.9983	54.39	8.5318	0.7943	0.6226
a''	16b	515.9	2.9	2.7722	53.34	5.0030	0.2550	0.7500
a'	6a	520.6	2.1	7.2206	141.47	0.7223	3.7659	0.5298
a'	6b	613.2	0.6	6.4232	174.57	0.4742	4.9513	0.7498
a''	4	695.3	2.1	2.0639	72.13	0.3673	0.1442	0.7500
a''	Torsion	716.1	432.3	1.0710	39.70	179.9186	0.1742	0.7500
a''	10b	764.9	0.4	1.5934	67.38	77.6623	0.2139	0.7500
a'	12	810.0	4.7	5.6752	269.15	16.4424	16.5892	0.1206
a''	10a	839.2	4.8	1.2453	63.40	2.2635	3.4583	0.7500
a''	17b	897.2	−2.1	1.4866	86.50	16.2827	1.9386	0.7500
a'	1	978.2	−1.5	6.1338	424.29	4.7742	22.5516	0.1046
a''	17a	982.8	−1.4	1.3408	93.62	0.0075	0.2839	0.7500
a''	5	998.6	−4.9	1.2907	93.04	0.8355	0.3055	0.7500
a'	18a	1013.4	−0.3	2.0528	152.41	3.6305	9.5874	0.1062
a'	15	1062.6	0.1	1.5220	124.23	7.5916	1.2223	0.7330
a'	9b	1088.2	7.3	2.3923	204.78	17.4859	4.0179	0.5096
a'	NH$_3$ inv.	1097.0	64.1	1.1847	103.07	251.0229	4.2541	0.1301
a'	9a	1156.0	−1.5	1.1426	110.38	7.3834	6.0331	0.7045
a'	OH bend	1188.3	22.8	1.4648	149.54	26.9932	1.9505	0.7130
a'	14	1281.6	44.2	2.6789	318.08	194.0568	7.6267	0.1169
a'	7a	1284.5	16.8	1.6482	196.60	1.7184	1.6951	0.2312
a'	3	1373.2	29.2	1.2474	170.05	106.3478	0.1560	0.6578
a'	19b	1482.7	6.3	2.1128	335.75	80.7205	0.8133	0.7490
a'	19a	1512.2	3.5	2.3814	393.67	62.7218	1.0701	0.4283
a'	8b	1619.3	−3.9	4.6893	888.90	73.1580	14.3955	0.7349
a'	NH$_3$ 4a	1630.1	−4.8	1.2229	234.90	10.4733	3.5637	0.7365
a''	NH$_3$ 4b	1631.7	−3.4	1.0651	204.99	27.4230	11.3824	0.7500
a'	8a	1635.9	1.2	3.4790	673.00	79.4165	20.4696	0.6383
a'	13	3008.7	5.9	1.0859	710.61	5.8964	36.9295	0.6956
a'	7b	3016.8	−1.8	1.0902	717.23	10.8489	121.8244	0.7168
a'	2	3029.6	1.6	1.0938	725.75	40.3440	45.8325	0.4506
a'	20b	3039.3	−3.7	1.0966	732.26	32.4664	94.3866	0.1961
a'	20a	3047.0	−4.0	1.0973	736.42	8.4083	225.3391	0.1253
a'	NH$_3$ s.st.	3344.3	0.3	1.0266	830.00	8.5158	104.7511	0.0241
a'	NH$_3$ 3a	3465.2	−2.3	1.0911	947.10	10.2910	66.0669	0.7451
a''	NH$_3$ 3b	3467.4	−0.8	1.0913	948.52	9.0348	51.1267	0.7500
a'	OH st.	3568.0	−221.2	1.0688	983.62	752.9166	187.6252	0.3200

$^a\Delta$ is the calculated frequency shift due to clustering, available experimental shifts are given in the text.

TABLE V. Harmonic intermolecular vibrations of phenol-ammonia (frequency in cm^{-1}, force constant in Nm^{-1}, reduced mass in amu.) computed with the 6-31G(d,p) basis set.

	Symmetry	Frequency (unscaled)	Force constant	Reduced mass	Isotopic ratio[a]	Parentage (ammonia)
ρ_1	a''	31.0	0.18	3.2113	0.97	T_z
τ	a''	37.3	0.09	1.0670	0.70	R_x
β_1	a'	63.6	0.80	3.3402	0.92	T_y
σ	a'	165.0	7.26	4.5298	0.94	T_x
ρ_2	a''	242.4	4.29	1.2390	0.75	R_y
β_2	a'	304.5	6.56	1.2012	0.76	R_z

[a]$\nu(C_6H_5OD-ND_3):\nu(C_6H_5OH-NH_3)$.

the ammonia moiety and the unfeasible NH$_3$ inversion in the cluster.

C. Intermolecular vibrations

Six intermolecular vibrations arise from complexation due to loss of three translational and three rotational motions. According to Schütz *et al.*[46] they are labeled as $\beta_{1,2}$ (wagging modes), $\rho_{1,2}$ (rocking modes), σ (stretching mode), and τ (torsional mode). The β and σ modes are of a' symmetry whereas the ρ and τ modes are of a'' symmetry. The stretching vibration σ and the β_1 and ρ_1 modes correspond to the translations in x, y, and z direction of the free ammonia (x direction: direction of the O$\cdots$N bond, z direction: perpendicular to the phenol ring, y direction: perpendicular to x and z direction). The τ, ρ_2, and β_2 vibrations correspond to rotations about the inertial axes of free ammonia, with rather small elongations at the phenol moiety compared to the corresponding translations of ammonia. The calculated data are displayed in Table V, views of the vibrations are shown in Fig. 3.

The calculated isotopic ratios for d-phenol-ND$_3$ are also included in Table V. Inspection of this table shows that vibrations which descend from ammonia translations have isotopic ratios close to one whereas vibrations which inherit rotational character on the ammonia unit show a considerable isotopic effect. Together with the fact that the nuclear spin statistics for the deuterated isotopomer C$_6$H$_5$OD-ND$_3$ is not 1:1 but 11:16 for the A/E levels shown in Fig. 2, its spectra will give valuable advice in assigning the correct vibrations to the observed bands.

IV. EXPERIMENTAL RESULTS

Figure 4 shows three mass traces of the two color REMPI spectrum of phenol-ammonia at the higher frequency side of the origin at 35 714.0±1.0 cm^{-1}. In the range from 0 to 300 cm^{-1} we observed more bands than expected for the 1:1 complex for which only the three totally symmetric intermolecular vibrational modes and possibly some weaker combination bands and overtones should be allowed (cf. Sec. III). The spectrum shows much more structure than the total ion spectrum of Mikami *et al.*[69] and the overview spectrum of Solgadi *et al.*[70] The bands at 43 and 182 cm^{-1} coincide with the results of Mikami *et al.* They assigned the 182 cm^{-1} band to the H-bond stretching vibration by analogy with
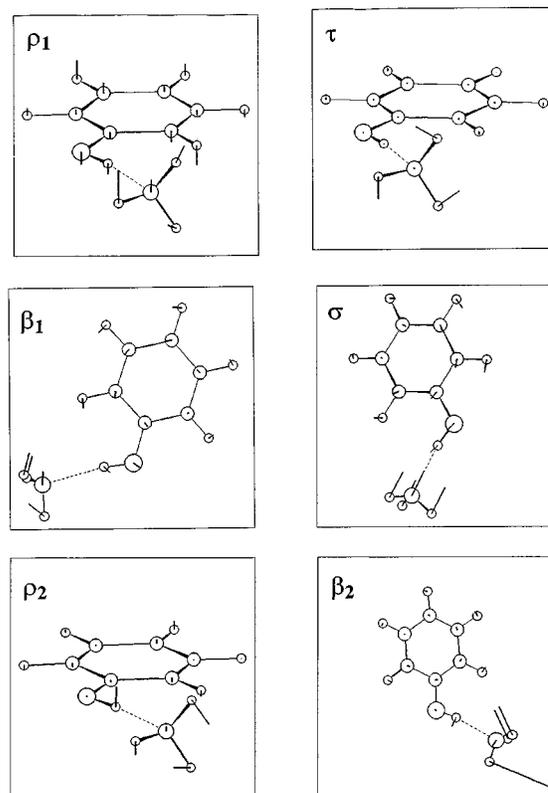

FIG. 3. Intermolecular harmonic vibrations of phenol–ammonia. The displacements shown in the figure were calculated with a 6-31G(d,p) basis set.

other hydrogen bonded clusters while the 43 cm^{-1} band was only classified as intermolecular. However, a two-color spectrum with an ionization wavelength of 355 nm (28 169 cm^{-1}, i.e., only 200 cm^{-1} above the ionization threshold of the 1:1 complex[69]) shows clearly that the 43 cm^{-1} band belongs to the $n=2$ cluster (Fig. 5).

It should be noted that a series of bands in Figs. 4 and 5 shows a splitting of about 2.5 cm^{-1}, but as our analysis will show, these bands belong to higher clusters which will be discussed in a later publication.
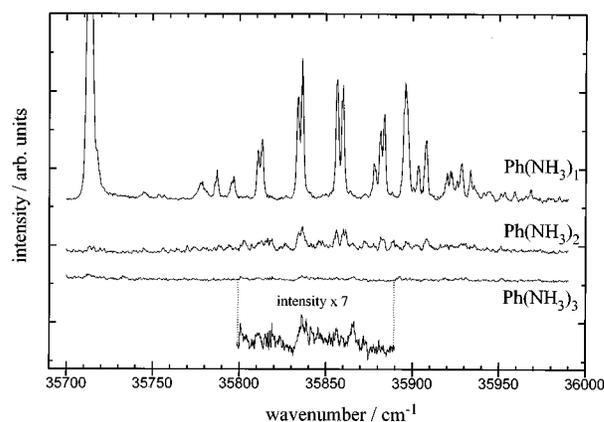

FIG. 4. Two color REMPI spectra of phenol-(ammonia)$_n$ clusters ($n=1-3$) in the region of intermolecular vibrations of the 1:1 complex; ionization laser at 30 300 cm^{-1}.
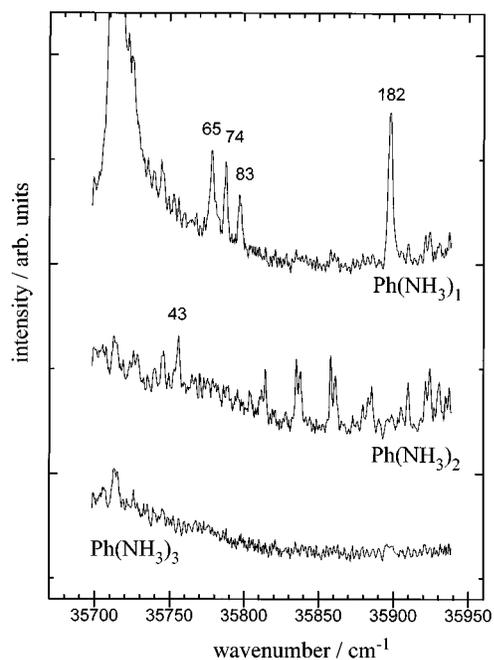
FIG. 5. Two color REMPI spectra of phenol-(ammonia)$_n$ clusters ($n = 1-3$) in the region of intermolecular vibrations of the 1:1 complex; ionization laser at 28 169 cm^{-1}.
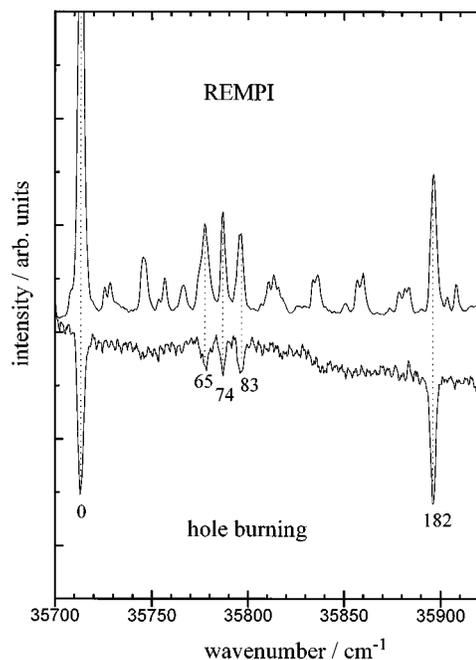

FIG. 6. Hole burning spectrum of phenol-ammonia probed by the electronic origin. The upper trace is the synchronously measured one color REMPI spectrum. Spectral positions are given relative to the electronic origin.

What possibility do we have to assign the bands which belong to the 1:1 complex? The two-color spectra which are taken at a ionization laser frequency of 30 300 cm^{-1} (5300 cm^{-1} below the one color energy) show massive fragmentation of the higher clusters. Closer examination of these spectra reveals that the splitted progression in Fig. 4 is repeated on the phenol-(NH$_3$)$_2$ trace which was not scanned by Solgadi et al.[70] This is even more evident in Fig. 5. Hence the progression cannot belong to the 1:1 complex, but to $n = 2$ or higher clusters. But what about the other bands?

We choose a mass resolved hole burning experiment to solve this problem. Spectral hole burning was introduced by Lipert et al.[16] for the analysis of gas phase cluster spectra. As a double resonance experiment, it is not only mass but species selective and we successfully applied this method in the LIF and REMPI variants to the analysis of phenol-(water)$_3$, phenol-methanol, phenol dimer, and o-, m-dihydroxy-benzenes.[34,85–87] The principal problem of the spectral hole burning technique is that signal/noise ratio is not determined by the (small) background noise of the REMPI experiment but by the stability of the REMPI signal itself. Probe laser and molecular beam should be as stable as possible here.

The hole burning spectrum of the 1:1 complex probing the electronic origin is shown in Fig. 6. The upper trace is the simultaneously recorded one-color REMPI spectrum, the lower one is the hole burning spectrum. Molecular beam conditions were optimized to produce only small clusters which has been checked by the nonresonant mass spectrum. As already observed for the naphthol–ammonia system[68] cluster distribution depends strongly on the time delay between valve opening and laser firing. We achieved best conditions for small clusters by probing the early expansion. Later in the expansion, e.g., after 200 μs, phenol-(ammonia)$_n$

clusters of $n = 30$ and higher could be observed.

Besides the origin, four bands can easily be identified in the hole burning spectrum with a shift of 65, 74, 83, and 182 cm^{-1} relative to the electronic origin. The band at 43 cm^{-1} could not be attributed to the 1:1 complex. This is in accordance with the two-color REMPI spectrum shown in Fig. 5. Spectral positions, intensities and hole depths are summarized in Table VI.

While REMPI spectroscopy is the key to the vibrations in the excited cluster state, dispersed fluorescence reveals the vibrational pattern of the electronic ground state. Before attempting an interpretation of the REMPI spectrum we should have a look on the corresponding dispersed fluorescence spectrum. Our dispersed fluorescence (DF) spectra are similar to those reported by Mikami et al.[69] The DF spectrum obtained by pumping the electronic origin shows three bands in the intermolecular region at 62, 162, and 322 cm^{-1}.

The phenol-ammonia cluster of C_s symmetry has three allowed intermolecular vibrations of a' symmetry called β_1, β_2, and σ. The σ intermolecular stretch mode often has the highest frequency as observed in the phenol-water (156/155 cm^{-1}[46]), phenol-methanol (176/162 cm^{-1}[85]) and the

TABLE VI. Excited state (S_1) vibrational frequencies (cm^{-1}) and relative intensities of phenol-ammonia.

Frequency	Intensities	Hole depth (%)	Possible assignment
0(35 714)	1.00	57	0,0
65	0.21	11	see the text
74	0.24	13	see the text
83	0.18	11	see the text
182	0.32	53	σ

(phenol)$_2$ (120/109 cm^{-186} donor part) cluster (S_1/S_0 frequencies, respectively). Due to the strong anharmonicity of some intermolecular modes a simple harmonic normal mode analysis is not necessarily adequate as outlined in the theoretical section, but the harmonic frequency of the intermolecular stretching vibration σ generally reproduces the experimental value fairly well. Based on this argumentation we assign the 182/162 cm^{-1} bands (S_1 and S_0, respectively) to the intermolecular stretch vibration.

Assignment of the other three observed bands is not straightforward. Normal coordinate analysis has shown that from the allowed a' modes only σ has both a high force constant and a large reduced mass while β_1 has a small force constant and β_2 a small reduced mass. This leads to large amplitude motions and hence to possibly large anharmonic corrections. However the β_2 frequency will very probably not decrease from 304.5 to 62 cm^{-1} on including anharmonic corrections. Hence the 62 cm^{-1} vibration in the S_0 state can be assigned to the β_1 mode (assumed as harmonic).

The 322 cm^{-1} vibration is probably the first overtone of the 162 cm^{-1} vibration, cf. Ref. 69. As shown in Table IV, there are low frequency intramolecular vibrations in that region (ν_{11} and ν_{16a}) but the vibronic transitions are forbidden by symmetry. A correlation with the a' mode ν_{18b} seems not very reasonable because of the large shift between experiment and calculation. An assignment of the 322 cm^{-1} vibration to the β_2 vibrational mode seems also unlikely.

The REMPI and hole burning spectra in Figs. 4, 5, and 6 show at least three bands in the low frequency region below 100 cm^{-1}. The shape of the 65 cm^{-1} feature suggests that it consists of two or more bands. One of the three bands (e.g., the band at 65 cm^{-1}) should correlate with the 62 cm^{-1} band in the S_0 state and corresponds to an in plane wag vibration. The other bands could be (allowed) overtones and/or combination bands of the low frequency a'' vibrations, cf. Table V and Fig. 2.

When pumping the 0^0-state resonance fluorescence is by far the strongest feature in the dispersed fluorescence spectrum. Similarly the electronic origin is the dominant feature in the REMPI spectra of phenol-ammonia. These facts suggest that the potential of the ground and excited states of the complex are not shifted significantly so that the Franck–Condon principle favors the vibrationless transition.

Because of the absence of a discernible torsional splitting originating from the ammonia moiety it can be assumed that the $A-E$ splittings in both electronic states of phenol-ammonia and probably also its barriers are of the same order of magnitude.

V. CONCLUSIONS

In the present work REMPI spectroscopy is applied to the phenol-ammonia complex in the range of its intermolecular vibrations. By means of mass resolved spectral hole burning the bands of the 1:1 complex are selected from higher clusters. High level *ab initio* calculations were carried out to determine the structure of this cluster. The experimental S_1 frequencies have been compared to the results of dispersed fluorescence measurements and *ab initio* normal mode calculations. The intermolecular stretching vibration and the

ground state β_1 wag vibration are assigned safely in this way while merely proposals could be made for the other intermolecular vibrations. The ammonia torsional mode was calculated in some detail. In contrast to higher clusters, no splitting of vibrational bands from torsional tunneling has been observed with our present laser resolution. We hope that the investigation of the deuterated isotopomer which is currently on the way in our laboratory will clear off some of the remaining uncertainties in the vibrational spectra of this interesting cluster system.

[1] T. R. Dyke, K. M. Mack, and J. S. Muenter, J. Chem. Phys. **66**, 498 (1977).
[2] H. Abe, N. Mikami, and M. Ito, J. Phys. Chem. **86**, 1768 (1982).
[3] J. A. Odutola and T. R. Dyke, J. Chem. Phys. **72**, 5062 (1980).
[4] H. Abe, N. Mikami, M. Ito, and Y. Udagawa, J. Phys. Chem. **86**, 2567 (1982).
[5] M. F. Vernon, D. J. Krajnovich, H. S. Kwok, J. M. Lisy, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. **77**, 47 (1982).
[6] K. Fuke and K. Kaya, Chem. Phys. Lett. **94**, 97 (1983).
[7] A. Oikawa, H. Abe, N. Mikami, and M. Ito, J. Phys. Chem. **87**, 5083 (1983).
[8] K. Fuke, H. Yoshiuchi, K. Kaya, Y. Achiba, K. Sato, and K. Kimura, Chem. Phys. Lett. **108**, 179 (1984).
[9] H. Page, J. G. Frey, Y.-R. Shen, and Y. T. Lee, Chem. Phys. Lett. **106**, 373 (1984).
[10] D. F. Coker, R. E. Miller, and R. O. Watts, J. Chem. Phys. **82**, 3554 (1985).
[11] L. H. Coudert, F. J. Lovas, R. D. Suenram, and J. T. Hougen, J. Chem. Phys. **87**, 6290 (1987).
[12] A. Engdahl and B. Nelander, J. Chem. Phys. **86**, 4831 (1987).
[13] S. Wuelfert, D. Herren, and S. Leutwyler, J. Chem. Phys. **86**, 3751 (1987).
[14] B. Nelander, J. Chem. Phys. **88**, 5254 (1988).
[15] K. L. Busarow, R. C. Cohen, G. A. Blake, K. B. Laughlin, Y. T. Lee, and R. J. Saykally, J. Chem. Phys. **90**, 3937 (1989).
[16] R. J. Lipert and S. D. Colson, J. Chem. Phys. **89**, 4579 (1988).
[17] R. J. Lipert and S. D. Colson, J. Phys. Chem. **93**, 135 (1989).
[18] R. J. Lipert and S. D. Colson, J. Phys. Chem. **93**, 3894 (1989).
[19] R. J. Lipert and S. D. Colson, Chem. Phys. Lett. **161**, 303 (1989).
[20] A. Engdahl and B. Nelander, J. Mol. Struct. **193**, 101 (1989).
[21] Z. S. Huang and R. E. Miller, J. Chem. Phys. **91**, 6613 (1989).
[22] L. L. Connel, S. M. Ohnline, P. W. Joireman, T. C. Corcoran, and P. M. Felker, J. Chem. Phys. **94**, 4668 (1991).
[23] M. Pohl, M. Schmitt, and K. Kleinermanns, J. Chem. Phys. **94**, 1717 (1991).
[24] M. Pohl, M. Schmitt, and K. Kleinermanns, Chem. Phys. Lett. **177**, 252 (1991).
[25] G. Reiser, O. Dopfer, G. Henri, K. Müller-Dethlefs, E. Schlag, and S. Colson, Chem. Phys. Lett. **181**, 1 (1991).
[26] R. J. Stanley and A. W. Castleman, J. Chem. Phys. **94**, 7744 (1991).
[27] L. L. Connel, S. M. Ohnline, P. W. Joireman, T. C. Corcoran, and P. M. Felker, J. Chem. Phys. **96**, 2585 (1992).
[28] M. Gerhards, B. Kimpfel, M. Pohl, M. Schmitt, and K. Kleinermanns, J. Mol. Struct. **270**, 301 (1992).
[29] G. V. Hartland, B. F. Henson, V. A. Venturo, and P. M. Felker, J. Phys. Chem. **96**, 1164 (1992).
[30] S. Tanabe, T. Ebata, M. Fujii, and N. Mikami, Chem. Phys. Lett. **215**, 347 (1993).
[31] E. Cordes, O. Dopfer, T. G. Wright, and K. Müller-Dethlefs, J. Phys. Chem. **97**, 7471 (1993).
[32] O. Dopfer, G. Lehmbach, T. G. Wright, and K. Müller-Dethlefs, J. Chem. Phys. **98**, 1933 (1993).

[33] T. G. Wright, E. Cordes, O. Dopfer, and K. Müller-Dethlefs, J. Chem. Soc. Faraday Trans. **89**, 1601 (1993).

[34] M. Schmitt, H. Mueller, and K. Kleinermanns, Chem. Phys. Lett. **218**, 246 (1994).

[35] L. A. Curtiss and J. A. Pople, J. Mol. Spectrosc. **55**, 1 (1975).

[36] D. J. Swanton, G. D. Bacskay, and N. S. Hush, Chem. Phys. **82**, 303 (1983).

[37] D. J. Swanton, G. D. Bacskay, and N. S. Hush, Chem. Phys. **83**, 69 (1984).

[38] K. S. Kim, M. Dupuis, G. C. Lie, and E. Clementi, Chem. Phys. Lett. **131**, 451 (1986).

[39] E. Honneger and S. Leutwyler, J. Chem. Phys. **88**, 2582 (1988).

[40] R. Knochenmuss and S. Leutwyler, J. Chem. Phys. **96**, 5233 (1992).

[41] O. Mo, M. Yanez, and J. Elguero, J. Chem. Phys. **97**, 6628 (1992).

[42] M. Schütz, T. Bürgi, and S. Leutwyler, Theochem. **276**, 117 (1992).

[43] S. S. Xantheas and T. H. Dunning, Jr., J. Chem. Phys. **99**, 8774 (1993).

[44] S. S. Xantheas and T. H. Dunning, Jr., J. Chem. Phys. **98**, 8037 (1993).

[45] D. Feller and M. W. Feyereisen, J. Comput. Chem. **14**, 1027 (1993).

[46] M. Schütz, T. Bürgi, S. Leutwyler, and T. Fischer, J. Chem. Phys. **98**, 3763 (1993).

[47] M. Schütz, T. Bürgi, S. Leutwyler, and T. Fischer, J. Chem. Phys. **99**, 1469 (1993).

[48] M. Gerhards, K. Beckmann, and K. Kleinermanns, Z. Phys. D **29**, 223 (1994).

[49] P. Hobza, R. Burcl. V. Spirko, O. Dopfer, K. Müller-Dethlefs, and E. W. Schlag, J. Chem. Phys. **101**, 990 (1994).

[50] G. T. Fraser, D. D. Nelson, Jr., A. Charo, and W. Klemperer, J. Chem. Phys. **82**, 2535 (1985).

[51] M. J. Frisch, J. E. Del Bene, J. S. Binkley, and H. F. Schaefer III, J. Chem. Phys. **84**, 2282 (1986).

[52] L. Latajka and S. Scheiner, J. Chem. Phys. **84**, 341 (1986).

[53] Shi-Yi Liu, C. E. Dykstra, K. Kohlenbrander, and J. M. Lisy, J. Chem. Phys. **85**, 2077 (1986).

[54] D. D. Nelson Jr., W. Klemperer, G. T. Fraser, F. J. Lovas, and R. D. Suenram, J. Chem. Phys. **87**, 6364 (1987).

[55] J. Sadlej and L. Lapinski, J. Mol. Struct. (Theochem) **150**, 223 (1987).

[56] F. Huisken and T. Pertsch, Chem. Phys. **126**, 213 (1988).

[57] L. Jaroszewski, B. Lesyng, J. T. Tanner, and J. A. McCammon, Chem. Phys. Lett. **175**, 282 (1990).

[58] D. M. Hassett, C. J. Marsden, and B. J. Smith, Chem. Phys. Lett. **183**, 449 (1991).

[59] J. W. I. van Bladel, A. van der Avoird, P. E. S. Wormer, and R. J. Saykally, J. Chem. Phys. **97**, 4750 (1992).

[60] M. Havenith, H. Linnartz, E. Zwart, A. Kips, J. J. ter Meulen, and W. L. Meerts, Chem. Phys. Lett. **193**, 261 (1992).

[61] J. G. Loeser, C. A. Schmuttenmaer, R. C. Cohen, M. J. Elrod, D. W. Steyert, R. J. Saykally, R. E. Bungarner, and G. A. Blake, J. Chem. Phys. **97**, 4727 (1992).

[62] L. Jaroszewski, B. Lesyng, and J. A. McCammon, J. Mol. Struct. (Theochem) **283**, 57 (1993).

[63] H. Linnartz, A. Kips, W. L. Meerts, and M. Havenith, J. Chem. Phys. **99**, 2449 (1993).

[64] Fu-Ming Tao and W. Klemperer, J. Chem. Phys. **99**, 5976 (1993).

[65] B. Nelander and L. Nord, J. Phys. Chem. **86**, 4375 (1982).

[66] K. Y. Choo, H. Shinohara, and N. Nishi, Chem. Phys. Lett. **95**, 102 (1983).

[67] P. Herbine and T. R. Dyke, J. Chem. Phys. **83**, 3768 (1985).

[68] O. Cheshnovsky and S. Leutwyler, J. Chem. Phys. **88**, 4127 (1988).

[69] N. Mikami, A. Okabe, and I. Suzuki, J. Phys. Chem. **92**, 1858 (1988).

[70] D. Solgadi, C. Jouvet, and A. Tramer, J. Phys. Chem. **92**, 3313 (1988).

[71] A. Engdahl and B. Nelander, J. Chem. Phys. **91**, 6604 (1989).

[72] R. Knochenmuss and S. Leutwyler, J. Chem. Phys. **91**, 1268 (1989).

[73] C. Jouvet, C. Lardeux-Dedonder, M. Richard-Viard, D. Solgadi, and A. Tramer, J. Phys. Chem. **94**, 5041 (1990).

[74] C. Crepin and A. Tramer, Chem. Phys. **156**, 281 (1991).

[75] D. F. Plusquellic, X.-Q. Tan, and D. W. Pratt, J. Chem. Phys. **96**, 8026 (1992).

[76] J. E. Del Bene, J. Phys. Chem. **92**, 2874 (1988).

[77] L. Latajka and S. Scheiner, J. Phys. Chem. **94**, 217 (1990).

[78] G. A. Yeo and T. A. Ford, Can. J. Chem. **69**, 632 (1991).

[79] A. L. Lehninger, *Biochemistry*, 2nd ed. (Worth, New York, 1978).

[80] L. Stryer, *Biochemistry*, 2nd ed. (Freeman, San Francisco, 1981).

[81] GAUSSIAN 92, Revision C, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople (Gaussian, Inc., Pittsburgh, 1992).

[82] W. C. Wiley and I. H. McLaren, Rev. Sci. Instrum. **26**, 1150 (1955).

[83] G. Berden, W. L. Meerts, M. Schmitt, and K. Kleinermanns (to be published).

[84] S. F. Boys, F. Bernardi, Mol. Phys. **19**, 553 (1970)

[85] M. Schmitt, H. Müller, U. Henrichs, M. Gerhards, W. Perl, and K. Kleinermanns, J. Chem. Phys. (submitted).

[86] M. Schmitt, U. Henrichs, H. Müller, and K. Kleinermanns (to be published).

[87] M. Gerhards, W. Perl, and K. Kleinermanns (to be published).