I. INTRODUCTION

Weakly bound van der Waals (vdW) complexes between an aromatic molecule \( M \) and one or several rare-gas atoms \( R \) are prototype systems for the investigation of solvation at a microscopic level. Substitution of the atom \( R \) by a small molecule \( S \) represents a step towards more complex systems: The free molecules \( S \) exhibit rotational as well as translational degrees of freedom, hence, five or six intermolecular vibrations arise in the 1:1 vdW complexes \( M \cdot S \). Furthermore, as a result of the anisotropy of \( S \), the intermolecular potential energy surface (PES) is more complicated than for complexes containing rare-gas atoms. Despite extensive research on aromatic vdW complexes with small molecules,\(^{1-8}\) the vdW binding energies of these species are still not known accurately.

We recently introduced stimulated emission pumping–resonant two-photon ionization (SEP-R2PI) spectroscopy for the mass-selective determination of electronic ground-state vdW dissociation energies \( D_0 \) and vibronic spectra of jet-cooled aromatic complexes.\(^9-11\) Using the SEP-R2PI technique, very accurate values for \( D_0 \) (to within \( \pm \)1%) were obtained for carbazole–\( R \) (\( R = \text{Ne, Ar, Kr, Xe} \)).\(^11\) Here we extend our study to carbazole (Car) complexes with three simple molecules: \( \text{N}_2 \), CO, and CH\(_4\). These were chosen for the following reasons: the polarizabilities\(^12\) of \( \text{N}_2 \) (1.740 Å\(^3\)) and CO (1.95 Å\(^3\)) are similar to each other and also to that of Ar (1.641 Å\(^3\)), but, in addition, \( \text{N}_2 \) has a quadrupole and CO has both a dipole and quadrupole moment. The polarizability of CH\(_4\) (2.59 Å\(^3\)) is very close to that of Kr (2.484 Å\(^3\)), and its first nonvanishing moment is the octopole moment. Hence, a comparison of experimentally determined vdW binding energies should give insight into the relative importance of dispersive and electrostatic binding contributions in these vdW complexes.

SEP-R2PI spectroscopy is a variant of stimulated emission pumping (SEP), in which hot complexes or clusters are detected via mass-selective R2PI. In contrast to conventional SEP techniques,\(^13-20\) where population losses are monitored, SEP-R2PI spectroscopy probes only the “hot” \( S_0 \) products resulting from the pump/dump process followed by ground-state IVR. The method is thus essentially background-free and very sensitive.

Other techniques have been applied for the determination of limits on vdW dissociation energies: After excitation of the vdW complex, dispersed fluorescence from the bare aromatic molecule was detected subsequent to the excited state dissociation, yielding upper limits to \( D_0(S_1) \).\(^21-26\) Alternatively, the nonobservance of \( S_1 \) state vibrionic bands in the R2PI spectrum indicates vibrational predissociation (VP) of the vdW complex prior to ionization.\(^27,28\) Observation of relaxed fluorescence of the vdW complex following excitation implies that the energy content of the complex is less than the dissociation energy in the \( S_1 \) state, and lower limits to \( D_0(S_1) \) have been so inferred.\(^23\) However, in electronically excited states, VP usually competes with processes [fluorescence, intersystem crossing (ISC), internal conversion (IC), etc.],\(^29\) which may introduce uncertainties in the determination of the dissociation energy.

Recently mass-selective threshold pulsed field ionization was applied by Krause et al.\(^30\) to obtain information on the photodissociation process of cluster ions. By monitoring both the cluster-ion and product-ion channel, lower and upper limits to the ion-state dissociation energy become accessible. Adding the ionization potential shift (\( \Delta \text{IP} \)) of the vdW complex results in lower and upper limits for \( D_0(S_0) \). Therefore, with respect to the measurement of dissociation energies, this technique is a complementary scheme to the SEP-R2PI method described in this work.

Several molecular beam studies were performed in the past on aromatic vdW complexes with \( \text{N}_2 \) and \( \text{CO} \).\(^1-4,6,7,31\) However, to our knowledge, no direct measurements on dissociation energies of such complexes exist up to date. vdW complexes with CH\(_4\) were investigated by various groups.\(^5,8,27,32,33\) Molecular beam studies on vibrational pre-dissociation processes\(^27,29,33\) also yielded limits for binding energies. The methane/graphite system has stimulated considerable experimental and theoretical work.\(^34-38\)

From low...
pressure adsorption measurements of CH$_4$ on graphite, the
isosteric enthalpy at zero coverage was derived. Extrapolation
to 0 K provided a value for the dissociation energy of
one methane molecule on a graphite surface, which is
$D_0 = 1000-1200$ cm$^{-1}$.34-36,39 The relatively large uncertainty
($\pm 10\%$) in the obtained values reflects the difficulty of
such experiments.

A description of experimental details of the SEP-R2PI
technique is given in Sec. II. In Sec. III we present and
discuss the ground- and excited-state intermolecular and
intramolecular vibrational level structure as well as the
dissociation energies determined for $S_0$ and $S_1$ carbazole-$S$
($S=N_2$, CO, CH$_4$), respectively. The dissociation energies of
these vdW complexes are correlated and compared to the
values obtained for carbazole-$R$ ($R=Ne$, Ar, Kr, Xe) at the
end of Sec. III. The conclusions are given in Sec. IV.

II. METHODOLOGY AND EXPERIMENTAL DETAILS

A. Principle of the SEP-R2PI method

Detailed descriptions of the SEP-R2PI technique have
been given elsewhere.9–11 Here we only summarize its sa-
lient features, schematically displayed in Fig. 1. Jet-cooled
Car-$S$ complexes are pumped at the $S_0 \rightarrow S_1$ electronic or-
igin, shown as step (1). In the dump step, induced by a second
tunable laser (2) or (2’), a substantial part of the excited-state
population is transferred back to a specific intramolecular or
intramolecular $S_0$-state vibrational level, at an excitation en-
ergy $E$ relative to the vibrationless level. Steps (1), (2), or
(2’) are synchronized to within $\pm 2$ ns. Subsequently, the
vdW complex is left to evolve on the ground-state hypersur-
face, and can be probed during delay times $\Delta$ ranging from
50 ns to 15 $\mu$s, see Sec. II B. Initially, rapid relaxation occurs
out of the prepared $S_0$ set of mixed eigenstates; in the limit of
high vdW mode densities, rapid dissipative IVR occurs. If
$E>D_0(S_0)$, this is followed by vibrational predissociation
(VP)—typically on a longer time scale than IVR.10,13,14,23,40

Finally, the relaxation products are detected in the probe
step using single-color R2PI, laser (3) or (3’) in Fig. 1. Two probe
schemes are distinguished: (i) If the complex has not dis-
sociated during $\Delta$, i.e., $E< D_0(S_0)$, the product Car-$S$ can be
probed via hot bands or sequence bands; this situation is
represented by laser (3) in Fig. 1. By scanning the dump
laser (2) and monitoring the ion signal from the probe laser
(3), ground-state vibrations with energies below the dissoci-
ation energy are mapped out and appear as positive signals in
the dump spectrum. (ii) Alternatively, if the Car-$S$ species has
dissociated $[E>D_0(S_0)]$ within the time $\Delta$, the hot
ground-state population originating from the SEP process has
vanished, hence, $S_0$ vibrations are no longer recorded as
positive signals. However, if the probe laser frequency is set
to the electronic origin of the complex [cf. laser (3’) in Fig.
1], each time the dump laser stimulates a $S_1 \rightarrow S_0$ down-
wards vibronic transition, the cold complex population in the
molecular beam is decreased, and a negative band appears in
the dump spectrum. If the dump laser stimulates transitions to $S_0$
levels that lie above the dissociation limit $D_0(S_0)$, the
ground-state level is depopulated by the vibrational predis-
sociation process and, hence, intense negative signals arise in

the dump spectrum. In contrast, $S_0$ transitions to ground-state
levels below $D_0(S_0)$ turn out to be weaker [cf. Car-CO (Sec.
III B), Car-CH$_4$ (Sec. III C)] or, for Car-N$_2$ (Sec. III A), not
detectable.

Thus, in a dump spectrum probed via hot bands or se-
quence bands, the $D_0(S_0)$ is bracketed by the last positive
band observed and the first nonobserved $S_0$ vibrational level.
The latter is identified in a separate dump spectrum, probing at
the $S_0$. For examples, see Secs. III A–III C.

B. Experimental details

1. Cluster synthesis

Car-$S$ ($S=N_2$, CO, and CH$_4$) complexes were synthe-
sized and cooled in pulsed, seeded supersonic expansions.
Carbazole (Fluka AG Switzerland, >99% purity) was heated
to 120–130 $^\circ$C, giving a vapor pressure of 0.1–0.3 mbar, and
seeded into mixtures of 1% N$_2$, CO, or CH$_4$ in 99% neon
carrier gas at a backing pressure $p_b = 1.2$ bar. The skimmed

FIG. 1. Schematic level diagram of the SEP-R2PI experiment, as applied to
the carbazole-$S$ (Car-$S$) vdW complexes. The vertical axis indicates vibra-
tional and/or electronic energy in the Car-$S$ complex, the horizontal axis
indicates time. In the pump step (1), the Car-$S$ complex is excited from $S_0$
to $S_1$, typically via the electronic origin. In the dump step (2), vibronic
transitions from the $S_1$ zero-point level are stimulated down to intramolecu-
lar or intermolecular vibrational levels in the $S_0$ state, which lie below the
Car-$S$ vdW binding energy ($D_0$). The system evolves in $S_0$ during a variable
time $\Delta = 50$ ns–15 $\mu$s. During this time, IVR leads to population of hot vdW
levels. Alternatively, in step (2’), the dump photon populates levels above
$D_0$, leading to vibrational predissociation (VP) during $\Delta$. The population
increase in hot vibrational levels is then probed by 1+1 resonant two-photon
ionization (R2PI) via sequence bands, using photons (3)+(3’); optionally the
decrease of cold cluster population can be monitored at the $0_0$ band with the
photons (3’)+(3’).
molecular beam was probed at a distance \( x/D = 400 \). Other details of the experiment are identical to that of our previous work.\(^{3-11}\)

### 2. Laser system

Three independently tunable nanosecond UV lasers are employed in the experiment. The pump and dump laser pulse beams [step (1) and (2) or (2') in Fig. 1] were provided by two frequency doubled dye lasers, pumped by the same 532 nm output of a Nd:YAG laser. Typical pulse widths were 4–5 ns, and pulse energies were 200 \( \mu \)J and 1 mJ for pump and dump laser pulses, respectively. Both beams were mutually overlapped in space and time, and crossed the molecular beam perpendicularly within the ion source. The frequency doubled UV output of a third pulsed dye laser, pumped by a second Nd:YAG laser was used in the probe step. The \( Q \)-switches of the two Nd:YAG lasers were digitally synchronized. The crossing point of the probe laser with the molecular beam could be varied from 0 to 13 mm downstream of the pump/dump beams. This is possible due to the relatively large acceptance diameter of the time-of-flight (TOF) mass spectrometer. With Ne carrier gas, this corresponds to a time delay \( \Delta \) up to 15 \( \mu \)s. The minimum delay time that could be usefully employed was 50 ns. The data presented in this work were recorded at \( \Delta = 2 \) \( \mu \)s. The typical probe laser pulse energy used was 300 \( \mu \)J. All three laser beams were unfo-cussed, and the beam profiles at the molecular beam were approximately 2 \( \times \) 2 mm.

### III. RESULTS AND DISCUSSION

#### A. Carbazole-N\(_2\)

1. Vibrations in the excited state

The two-color resonant two-photon ionization (2C-R2PI) spectrum of jet-cooled Car-N\(_2\) in the spectral region around the \( \Omega_0^0 \) band is shown in Fig. 2 (upper trace). The frequency of the \( S_0 \rightarrow S_1 \) electronic origin is \( \nu(\Omega_0^0) = 30759 \) cm\(^{-1}\); the electronic spectral shift of the complex relative to the origin of bare carboxaldehyde is to the red, \( \Delta \nu = -51.3 \pm 0.5 \) cm\(^{-1}\). This shift is about 10% larger than that previously found for Car-Ar, \( \Delta \nu = -45.9 \pm 0.4 \) cm\(^{-1}\).\(^{41}\) The width of the rotational contour of the \( \Omega_0^0 \) band under our expansion conditions is 1.9 cm\(^{-1}\) full width at half maximum (FWHM).

To the blue of the spectral origin we observe six transitions at \(+15.7, +18.9, +35.5, +39.6, \) and \(+64.8 \) cm\(^{-1}\) (see Fig. 2). Since the corresponding spectral range of bare carboxaldehyde is devoid of intramolecular transitions, all bands are attributed to excited-state intermolecular vibrations between carboxaldehyde and N\(_2\). The intensities of these intermolecular bands are large; this is typical for complexes with carboxaldehyde, cf. Car-Kr (Refs. 11 and 28) or Car-Xe (Ref. 11), and reflects a sizable change in geometry upon electronic excitation. However, the spectra in Fig. 2 are quite strongly saturated and the apparent Franck–Condon factors are too high.

Our interpretation and assignment of the \( S_1 \) state intermolecular bands of Car-N\(_2\) is based on the analysis of the vdW vibrational level structure of Car-Kr (Refs. 11 and 28) or Car-Xe (Ref. 11), combined with the interpretation given for \( S_1 \) benzene-N\(_2\) by Nowak et al.\(^1\). The band observed at 64.8 cm\(^{-1}\) for Car-N\(_2\) matches the transition found at 65 cm\(^{-1}\) in benzene-N\(_2\),\(^1\) which was assigned as the out-of-plane fundamental \( \nu'_z \). This assignment is supported by a comparison between Car-N\(_2\) and Car-Ar in an admittedly crude harmonic oscillator model: the ratio of the out-of-plane frequencies \( \nu'_z(Car-N_2)/\nu'_z(Car-Ar) \) is given by the ratio of the reduced masses (\( \mu \)) and force constants (\( k_z \)) as

\[
\nu'_z(Car-N_2)/\nu'_z(Car-Ar) = \frac{1}{\frac{m_{Car-N_2}}{m_{Car-Ar}}\left(\frac{\mu_{Car-Ar}}{\mu_{Car-N_2}}\right)}
\]

Assuming a Lennard-Jones potential form, \( k_z \) is proportional to \( 1/\sigma^2 \) (\( \sigma \) is the well depth, \( \sigma \) the equilibrium distance); \( \epsilon(Car-Ar) \approx 530.4 \) cm\(^{-1}\); \( \epsilon(Car-N_2) \approx 627.2 \) cm\(^{-1}\) (see the following and Table II). Note that \( \epsilon \) is approximated by the vdW binding energy, e.g., the zero-point vibrational energy is neglected. Since \( \sigma \) is not known for Car-N\(_2\), we use the values which have been determined experimentally in the electronic excited state \( S_1 \) for benzene-N\(_2\)

\[
[S_{Car-N_2}] = 3.455 \text{ Å}^2 \quad \text{and benzene-Ar}[S_{Car-N_2}] = 3.52 \text{ Å}^2
\]

respectively. With these numbers the ratio of force constants is \( k_z(Car-N_2)/k_z(Car-Ar) = 1.227 \). Using \( \mu(Car-N_2) = 23.98 \text{ amu} \), \( \mu(Car-Ar) = 32.28 \text{ amu} \) and \( \nu'_z(Car-Ar) = 50.8 \) cm\(^{-1}\),\(^{11}\) one derives \( \nu'_z(Car-N_2) = 65.3 \) cm\(^{-1}\).
The other four peaks in the 2C-R2PI spectrum of Fig. 2 (upper trace) are interpreted as a progression in the in-plane y mode, along the short axis of carbazole; the fundamental of this progression is \( \nu'_y = 17.3 \text{ cm}^{-1} \) (\( \approx 18 \text{ cm}^{-1} \) for benzene-N\(_2\)).\(^1\) Its first overtone, \( 2 \cdot \nu'_y \), is at 37.5 cm\(^{-1}\) (37 cm\(^{-1}\) for benzene-N\(_2\)).\(^1\) Splittings are observed for both the \( \nu'_y \) and \( 2 \cdot \nu'_y \) band, being \( \Delta \nu = 3.2 \text{ cm}^{-1} \) and \( \Delta \nu = 4.1 \text{ cm}^{-1} \), respectively. Since no such splittings are observed for any of the rare-gas vDW complexes of carbazole, we conclude that they arise from one of the two torsional (hindered rotation) modes of N\(_2\). We propose that the excitation observed involves torsion of N\(_2\) twisting around an axis parallel to the long axis of carbazole, since the geometry along this coordinate may be affected by the change of dipole moment of carbazole upon electronic excitation. The splitting may be due to a change of the effective barrier to internal rotation with increasing excitation in \( \nu'_y \); alternatively, the second band may be due to a Fermi resonance of \( \nu'_y \) with either of the torsional vibrations. We note that no splitting is observed for the \( 0_0^0 \) origin transition.

2. Vibrations in the ground state

In Fig. 3 (lower trace) we present a dump spectrum recorded for Car-N\(_2\) with the probe laser frequency \( v_{\text{probe}} = 30787 \text{ cm}^{-1} \), e.g., 28 cm\(^{-1}\) to the blue of the \( S_0 \rightarrow S_1 \) origin. The assignment of the SEP-R2PI dump spectrum given here is based on earlier spectroscopical work in molecular beams\(^3\) and low-temperature crystals\(^4\) as well as on \( ab\ initio \) calculations.\(^10,45\) Although the carbazole \( S_0(A_1) \rightarrow S_1(A_1) \) transition is in-plane and short- or y-axis polarized, \( b_2 \) vibrations also occur with moderate intensities due to Herzberg–Teller coupling to the \( S_2(B_2) \) electronic state.\(^11,44\) Note that \( a_2 + b_1 \) combination bands are also of \( b_2 \) symmetry. The intramolecular modes are classified in terms of the \( C_{2v} \) point group of bare carbazole.

Between 200 and 700 cm\(^{-1}\) the dump spectrum (Fig. 3, lower trace) consists of three groups of bands centered at 250, 450, and 600 cm\(^{-1}\), respectively. Table I compiles the observed \( S_0 \) vibrational frequencies and intensities. Within the first group, the strongest intramolecular vibration observed is \( \nu_3(a_1) \). The most prominent band in the second

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency</th>
<th>Intermolecular frequency</th>
<th>Rel. intensity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2\nu_1 )</td>
<td>211.6</td>
<td>39.6</td>
<td></td>
</tr>
<tr>
<td>( \nu_1 )</td>
<td>214.8</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>( 2\nu_1 + \nu_2 )</td>
<td>234.6</td>
<td>23.0</td>
<td>15.1</td>
</tr>
<tr>
<td>( \nu_2 + 2\nu_1 )</td>
<td>237.6</td>
<td>22.8</td>
<td>76.7</td>
</tr>
<tr>
<td>( 2\nu_1 + \nu_z )</td>
<td>258.6</td>
<td>43.8</td>
<td>35.9</td>
</tr>
<tr>
<td>( \nu_z + \nu_z )</td>
<td>274.6</td>
<td>63.0</td>
<td>20.5</td>
</tr>
<tr>
<td>( \nu_z + 3\nu_z )</td>
<td>277.1</td>
<td>62.3</td>
<td>29.1</td>
</tr>
<tr>
<td>( \nu_z + \nu_3 + \nu_z )</td>
<td>279.4</td>
<td>64.6</td>
<td>9.3</td>
</tr>
<tr>
<td>( \nu_1 + \nu_3 + \nu_z )</td>
<td>287.9</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>( \nu_3 + \nu_3 + \nu_z )</td>
<td>298.8</td>
<td>84.0</td>
<td>16.1</td>
</tr>
<tr>
<td>( \nu_3 + 2\nu_3 + \nu_z )</td>
<td>319.5</td>
<td>104.7</td>
<td>11.4</td>
</tr>
<tr>
<td>( \nu_3 + a )</td>
<td>378.9</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>( \nu_3 + 2a )</td>
<td>399.6</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>( 2\nu_3 )</td>
<td>414.0</td>
<td>7.0</td>
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<tr>
<td>( 2\nu_3 + a )</td>
<td>429.7</td>
<td>44.6</td>
<td></td>
</tr>
<tr>
<td>( 2\nu_3 + 2a )</td>
<td>451.8</td>
<td>14.7</td>
<td></td>
</tr>
<tr>
<td>( 2\nu_3 + 3a/2\nu_1 + \nu_z )</td>
<td>452.9</td>
<td>23.2</td>
<td>24.5</td>
</tr>
<tr>
<td>( 2\nu_3 + 4a/3\nu_1 + \nu_z )</td>
<td>473.7</td>
<td>44.0</td>
<td>9.0</td>
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<tr>
<td>( 2\nu_3 + 5a/4\nu_1 + \nu_z )</td>
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<td>( \nu_1 )</td>
<td>530.9</td>
<td>6.8</td>
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<td>534.8</td>
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<td>( \nu_1 + a )</td>
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<td>( \nu_1 + 2a )</td>
<td>565.0</td>
<td>6.2</td>
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<td>( \nu_1 + 3a )</td>
<td>575.5</td>
<td>38.1</td>
<td></td>
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<tr>
<td>( \nu_1 + 4a )</td>
<td>596.5</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>( \nu_1 + 5a )</td>
<td>607.1</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>( \nu_1 + 6a )</td>
<td>619.3</td>
<td>42.5</td>
<td></td>
</tr>
<tr>
<td>( \nu_1 + 7a )</td>
<td>635.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 3\nu_1 )</td>
<td>642.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>653.1</td>
<td>22.5</td>
<td></td>
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<tr>
<td>( \nu_2 + a )</td>
<td>657.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu_2 + 2a )</td>
<td>665.1</td>
<td></td>
<td></td>
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<td>668.5</td>
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<tr>
<td>( \nu_2 + 4a )</td>
<td>676.4</td>
<td>43.2</td>
<td></td>
</tr>
<tr>
<td>( \nu_2 + 5a )</td>
<td>678.2</td>
<td>43.8</td>
<td></td>
</tr>
<tr>
<td>( \nu_2 + 6a )</td>
<td>686.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu_2 + \nu_3 + \nu_6 )</td>
<td>697.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Percentage intensity, relative to strongest band.
TABLE II. Experimental van der Waals dissociation energies \( D_0 \) in the ground \( S_0 \) and first excited state \( S_1 \) (in \( \text{cm}^{-1} \)) and electronic spectral shifts \( \delta \nu \) for carbazole-S (S=N\(_2\), CO, and CH\(_4\)).

<table>
<thead>
<tr>
<th>S</th>
<th>( D_0(S_0) )</th>
<th>( \delta \nu )</th>
<th>( D_0(S_1) )</th>
<th>Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>627.2(\pm) 7.9</td>
<td>-51.3(\pm) 0.5</td>
<td>678.5(\pm) 8.0</td>
<td>8.2%</td>
</tr>
<tr>
<td>CO</td>
<td>716.5(\pm) 29.8</td>
<td>-162.7(\pm) 0.5</td>
<td>879.2(\pm) 29.9</td>
<td>22.7%</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>668.6(\pm) 15.1</td>
<td>-85.2(\pm) 0.5</td>
<td>753.8(\pm) 15.2</td>
<td>12.7%</td>
</tr>
</tbody>
</table>

*Relative to the carbazole 0\(_0\) band at 30 809 cm\(^{-1}\).*

The upper trace of Fig. 3 also displays a dump spectrum recorded with the probe laser set to the electronic origin 0\(_0\) of carbazole-CO: we expect that the CO molecule is localized above the central pyrrolic ring plane of carbazole.

Figure 2 (bottom trace) shows the 2C-R2PI spectrum of carbazole-CO in the vicinity of its \( S_0\rightarrow S_1 \) electronic origin at 30 647 cm\(^{-1}\). The electronic spectral shift of the complex relative to bare carbazole is to the red, \( \delta \nu = -162.7\pm 0.5 \) cm\(^{-1}\). Compared to both the Car\(-Ar\) and Car\(-N_2\) complexes this shift is exceptionally large. This very different spectral shift induced by the two isoelectronic molecules CO and N\(_2\) in vdw bound to carbazole can be understood in terms of differences in their electrostatic interaction (see Sec. III D).

Under the expansion conditions used the rotational contour of the 0\(_0\) band is 2.0 cm\(^{-1}\). To the blue of the 0\(_0\) band intermolecular vibrational excitations are detected at 23.4, 35.4, 56.7, and 68.9 cm\(^{-1}\). At larger excitation energies (but still below 200 cm\(^{-1}\)) the 2C-R2PI spectrum exhibits a surprisingly high density of transitions and becomes extremely complicated. Moreover, the intensity of several features strongly depends on the cooling conditions in the beam.

The lower trace of Fig. 4 shows the dump spectrum of \( S_0 \) with probe laser frequency \( \nu_{\text{probe}} = 30 660 \) cm\(^{-1}\), for the transition of the complex. Frequency, intensity and assignment of the transitions observed are listed in Table III. The intense
TABLE III. Intramolecular and intermolecular vibrational frequencies (in cm$^{-1}$) and relative band intensities for $S_0$ carbazole-CO in the 200–900 cm$^{-1}$ range. The upper part refers to levels detected at 0$^0_{00} + 13$ cm$^{-1}$ (Fig. 4, lower trace), the levels listed in the lower part are probed at the electronic origin (Fig. 4, upper trace). Intermolecular frequencies are derived from combination bands with intramolecular modes.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency</th>
<th>Rel. intensity$^a$</th>
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<tbody>
<tr>
<td>$\nu_3$</td>
<td>214.3</td>
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</tr>
<tr>
<td>2$\nu_1$</td>
<td>218.2</td>
<td>34.1</td>
</tr>
<tr>
<td>$\nu_1 + \nu_4$</td>
<td>231.5</td>
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<tr>
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<tr>
<td>$\nu_4$</td>
<td>251.6</td>
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<td>17.2</td>
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</table>

$^a$Percentage intensity, relative to strongest band.

transitions detected at 214.3 and 218.2 cm$^{-1}$ are assigned to the intramolecular vibrations $\nu_1$ and 2$\nu_1$, respectively. Other purely intramolecular modes are observed at 428.5 (2$\nu_3$), 553.3 ($\nu_3$), 636.9 ($\nu_1$), and 653.3 cm$^{-1}$ ($\nu_3$).

As for Car-N$_2$, several intramolecular plus intermolecular vibrational combination bands are observed in the dump spectrum (Fig. 4, lower trace). The corresponding intramolecular frequencies are also listed in Table III. In contrast to the complex with N$_2$, for which two different intermolecular modes were identified, namely $\nu_4^c$ (the short-axis in-plane mode) and $\nu_4^e$ (the out-of-plane mode), just one vdW vibration is observed for Car-CO. The fundamental frequency of this mode is 17.3 cm$^{-1}$ (averaged value). In analogy to the assignment given for Car-N$_2$ ($\nu_4^e = 22.9$ cm$^{-1}$), this mode is tentatively identified as in-plane $\nu_4^c$ vibration. Combination bands including single excitations in $\nu_4^c$ are found at 231.5 ($\nu_3 + \nu_4^c$), 235.7 (2$\nu_1 + \nu_4^c$), 653.3 ($\nu_1 + \nu_4^c$), and 671.0 cm$^{-1}$ ($\nu_1 + \nu_4^c + 2\nu_4^c$). The transitions detected at 248.1 (2$\nu_3 + \nu_4^c$), 251.6 (2$\nu_1 + 2\nu_4^c$), 671.0 ($\nu_1 + 2\nu_4^c$), and 686.7 cm$^{-1}$ ($\nu_1 + 2\nu_4^c$) are assigned as combination bands involving an excitation of the first overtone of $\nu_4^c$, i.e., 2$\nu_4^c = 33.7$ cm$^{-1}$ (averaged value).

1. vdW binding energy

A very accurate ground-state vdW binding energy $D_0(S_0)$ was also obtained for Car-CO. As for Car-N$_2$, the lower limit to $D_0(S_0)$ is appointed by the last positive signal in the dump spectrum [probed at 0$^0_{00} + 13$ cm$^{-1}$ (Fig. 4, lower trace)], which is detected at 686.7 cm$^{-1}$ ($\nu_1 + 2\nu_4^c$) for Car-CO.

In Fig. 4 (upper trace) we present the dump spectrum recorded with the probe laser set to the electronic origin 0$^0_{00}$ of the complex (for frequencies and intensities, see Table III). The first four transitions between 636.9 and 686.7 cm$^{-1}$ are detected at identical energies as the bands in the lower trace. At 746.2 and 763.3 cm$^{-1}$ (and also at excitation energies >830 cm$^{-1}$, cf. Table III for frequencies and assignments) additional features appear as negative signals in the upper trace, which are not observed in the lower dump spectrum detected to the blue of the cluster origin. Hence, the first negative band at 746.2 cm$^{-1}$ in the upper trace which is absent in the lower trace defines an upper limit to the vdW binding energy $D_0(S_0)$ in combination with the lower limit the binding energy in the ground electronic state is derived as $D_0(S_0) = 716.5 \pm 29.8$ cm$^{-1}$. Taking into account the spectral shift $\delta \nu = -162.7 \pm 0.5$ cm$^{-1}$ upon electronic excitation, results in the dissociation energy of the first excited state, $D_0(S_1) = 879.2 \pm 29.9$ cm$^{-1}$ (see Table II).

C. Carbazole-CH$_4$

The analysis of molecular vdW complexes containing CH$_4$ or analogous tetrahedral molecules is delicate. The high symmetry and small anisotropy of the CH$_4$ electron density might give rise to nearly free internal rotation of the CH$_4$ molecule in the vdW complexes in either one, two, or three dimensions. The extent of the hindrance to CH$_4$ rotation is not clear and probably varies considerably for different substrate molecules. In their investigation of the $S_1$ intermolecular vibrational spectra of benzene-CH$_4$ and CD$_4$ complexes, Menapace and Bernstein$^{32}$ included a normal-coordinate analysis and a three-dimensional hindered-rotor analysis. They assigned the main features in the spectrum and concluded that the benzene-CH$_4$ complex is (semi)rigid, that is, the CH$_4$ rotation relative to the benzene ring is strongly hindered, with a barrier of $\approx 300$ cm$^{-1}$. On the other hand, Champagne and co-workers$^8$ recently concluded from rotationally resolved $S_0 - S_1$ electronic spectra of the 1- and 2-fluorophenanthrene-CH$_4$ complexes that the adsorbed CH$_4$ molecule rotates almost freely in the complex. For a CH$_4$ monolayer on graphite,$^{37}$ which was investigated by inelastic neutron scattering, the barrier height for hindered single-molecule rotation of one CH$_4$ molecule around its $C_3$ axis perpendicular to the graphite surface was derived from the torsional energy level structure as $\nu_3 = 150 - 200$ cm$^{-1}$. However, several theoretical investigations show, that about 90% of the barrier can be attributed to CH$_4$-\cdot-CH$_4$ interaction in the monolayer.$^{37}$

1. Vibrations in the excited state

Figure 2 (central trace) shows the R2PI spectrum of carbazole-CH$_4$. We assign the bands at 20.2 and 73.2 cm$^{-1}$ to the $\nu_4^c$ and $\nu_4^e$ vibrations, respectively. This assignment is
compatible with the normal-coordinate analysis in Ref. 32 for benzene-CH₄ and the neutron scattering data of Ref. 37 for the CH₄/graphite system, where an out-of-plane vibration was found at 100 cm⁻¹, given the fact that the binding energy is considerably larger for CH₄ on graphite than for the carbazole–CH₄ complex (see the following). The prominent band at 30.5 cm⁻¹ is possibly due to the librational mode tₓ around the axis parallel to the long axis of carbazole, with a possible overtone band 2·tₓ at 57.8 cm⁻¹. This would imply that, as suggested by Menapace et al. for the benzene–CH₄ system, the rotation around this axis is appreciably hindered. We note that the assignment of the bands at 20.2 and 30.5 cm⁻¹ to νₙ and tₓ is tentative, and a reverse assignment, i.e., tₓ at 20.2 cm⁻¹ and νₙ at 30.5 cm⁻¹ is possible. The band at 4.8 cm⁻¹ might be due to rotation of the methane molecule around the axis perpendicular to the carbazole plane. Moreover, weak bands can be seen in the spectrum approximately 5 cm⁻¹ to the blue of the 20.2, 30.5, and 73.4 cm⁻¹ transitions. Finally, the band at 107.4 could be assigned to the first intramolecular vibration ν₁ (“butterfly” mode), which becomes slightly allowed due to complexation.

2. Vibrations in the ground state

Figure 5 shows two SEP-R2PI spectra for the carbazole–CH₄ complex. In the lower spectrum, the probe laser was set 26 cm⁻¹ to the blue of the S₀→S₁ origin transition, while for the upper spectrum, the probe laser was set at the origin. Thus, when the dump laser is resonant, a decrease in the cold cluster population results in a negative band in the upper spectrum, while in the lower spectrum an increase in warm complex population is monitored as positive band. As discussed earlier, several bands in the SEP-R2PI spectrum can be assigned to intramolecular vibrations (see Table IV): at 214.4 (ν₂), 429.3 (2·ν₁), 553.3 (ν₁₁), 619.7 (ν₅ + ν₆), 632.3 (ν₁₄), 653.5 (ν₁₅), and 683.6 cm⁻¹ (ν₂ + ν₅ + ν₆).

Intermolecular vibrations are observed at 18.9 and 70.3 cm⁻¹ in combination with the ν₃ band, and the former in combination with 2·ν₃ at 429.3+18.5 cm⁻¹. Intermolecular frequencies as well as a tentative assignment are given in Table IV. In analogy to the S₁ excited state we assign the band at 18.9 cm⁻¹ to the translational mode ν₃ along the short axis and the band at 70.3 cm⁻¹ as the out-of-plane vibration ν₄. The bands corresponding to ν₁, ν₅ + ν₆ and 2·ν₁ + ν₄ exhibit shoulders on the high frequency side approximately 6 cm⁻¹ from the band center. These shoulders, as well as the splitting of the ν₅ + ν₆ band could be attributed to the torsion of the methylene molecule around its axis perpendicular to the carbazole plane. Interestingly, no excitation at ≈30 cm⁻¹ is observed in the ground-state spectrum. A possible explanation for these findings is a Duschinskii rotation of the ν₄ and tₓ modes between the S₀ and S₁ states.

3. vdW binding energy

The bracketing measurement is also represented in Fig. 5. The last observed positive band in the lower spectrum is the ν₁₅ band at 653.5 cm⁻¹, yielding the lower limit for the ground-state binding energy D₀(S₀) of the Car–CH₄ complex. In the upper spectrum, a band appears at 683.6 cm⁻¹ (ν₂ + ν₅ + ν₆), which is not observed in the lower spectrum.
and is an upper bound (see the dotted lines in Fig. 5) giving a value for the ground-state binding energy of $D_0(S_0) = 668.6 \pm 15.1 \text{ cm}^{-1}$. The relative error of the determination is $\pm 2.2\%$. With the measured spectral shift for the Car-CH$_4$ complex relative to bare carbazole ($-85.2 \pm 0.5 \text{ cm}^{-1}$) the binding energy in the $S_1$ excited state is $D_0(S_1) = 753.8 \pm 15.2 \text{ cm}^{-1}$ (cf. Table II).

The problem of relaxation of nuclear spin species in molecular beams has been addressed by several groups.\textsuperscript{5,8,46} Free CH$_4$ exists in three spin states ($I=0,1,2$). From symmetry considerations it follows that the $J=0$ rotational level is only accessible for a nuclear spin species and the $J=1$ level only for $F$ species, while the $J=2$ level is accessible for both $E$ and $F$ species.\textsuperscript{37} Since the nuclear spin relaxation in gases is very slow (seconds), compared to the relaxation time scales in the supersonic jet (tens of microseconds), the high temperature ratio of spin species $A:E:F = 5:9:2$ prevails and a large fraction of the methane molecule (the spin species $E$ and $F$) cannot rotationally cool completely.\textsuperscript{46} The free methane rotational levels correlate with different torsional levels in the vdW complex, which in turn have slightly different geometric and energetic properties.

Topp and co-workers concluded from their spectra that resolvable spin species exist in the perylene-CH$_4$ complex.\textsuperscript{3} However, the spectra did not allow to determine the extent of free rotation of the methane molecule in the complex. Pratt and co-workers have recently investigated such effects in detail by rotationally resolved electronic spectra of the 1- and 2-fluoronaphthalene-CH$_4$ complexes.\textsuperscript{8} We note that the SEP-R2PI method is potentially isomer-specific and hence nuclear-spin species specific. However, we were not able to resolve any splittings due to individual spin species at our laser resolution of $\approx 0.7 \text{ cm}^{-1}$ in the UV. We conclude that the subbands of the electronic origins and all vdW excitations of the three spin species probably lie within $1 \text{ cm}^{-1}$. Moreover, the difference in binding energy for the three spin species is probably less than the error of our determination ($\pm 15 \text{ cm}^{-1}$).

### D. Correlation of results

The vdW binding energies $D_0$ of the carbazole-S ($S=N_2$, CO, and CH$_4$) complexes in the $S_0$ and $S_1$ electronic states as obtained by the SEP-R2PI technique are listed in Table II together with the measured spectral shifts $\delta \nu$ and the relative increases of the binding energy upon $S_0 \rightarrow S_1$ electronic excitation. The relative errors for the determination of $D_0(S_0)$ are 1.3\%, 4.2\%, and 2.2\% for the complex of carbazole with N$_2$, CO, and CH$_4$, respectively. It is instructive to compare these results with data for other systems.

For the benzene-N$_2$ vdW complex, where the N$_2$ molecule is known to be bound to the aromatic system on the $C_6$ axis of benzene,\textsuperscript{23,31} a ground-state binding energy of $D_0(S_0) = 501 \text{ cm}^{-1}$ was derived by Nowak and co-workers\textsuperscript{3} based on a model potential which was fitted to the $S_1$ intermolecular vibrational structure. Using microwave spectroscopy, Bauder and co-workers fitted a different model potential to the measured centrifugal distortion constants and obtained $D_0(S_0) = 227 \text{ cm}^{-1}$. Comparison of the two independently determined values for benzene-N$_2$ shows that the approach of fitting a model potential to data obtained near the minimum of the intermolecular potential energy surface and subsequent extrapolation to the dissociation limit is by no means trivial. Both determined $D_0$ values for benzene-N$_2$ are smaller than the corresponding value for carbazole-N$_2$, as would be expected. By analogy with calculated binding energies of carbazole-Ar and benzene-Ar, using the same Lennard-Jones potential model, we crudely estimate the $D_0$ of benzene-N$_2$ to be about half that of carbazole-N$_2$, or $\approx 310 \text{ cm}^{-1}$.

Bauder and co-workers carried out analogous microwave studies on benzene-CO,\textsuperscript{4} pyrrole-CO\textsuperscript{6} and pyridine-CO,\textsuperscript{7} and derived binding energies of $D_0(S_0) = 211, 293,$ and 486 cm$^{-1}$, respectively. In the complex with pyrrole, which is structurally related to carbazole, the CO molecule was found to be bound to the $\pi$ electron system at a center-of-mass distance of $\approx 3.50 \text{ Å}$ above the aromatic plane. Again, all the determined $D_0$ values are smaller or much smaller than the $D_0(S_0) = 716.5 \text{ cm}^{-1}$ measured for carbazole-CO.

Nimlos and co-workers\textsuperscript{27} investigated the aniline-CH$_4$ complex. They measured dispersed fluorescence spectra after exciting different complex bands. The appearance of bare aniline fluorescence after exciting a complex band 494 cm$^{-1}$ to the blue of the origin transition gives an upper limit for the excited-state binding energy of $D_0(S_1) < 494 \text{ cm}^{-1}$. Given the spectral shift of about $85 \text{ cm}^{-1}$ for aniline-CH$_4$ the ground-state binding energy $D_0(S_0)$ must be smaller than 409 cm$^{-1}$. The $D_0(S_0) = 668.6 \pm 15.1 \text{ cm}^{-1}$ for carbazole-CH$_4$ is significantly higher than for the aniline-CH$_4$ complex, in agreement with the fact that carbazole is larger than aniline. By fluorescence measurements Outhouse and co-workers\textsuperscript{33} determined an upper limit for the binding energy of indole-CH$_4$ as $D_0(S_0) < 682 \text{ cm}^{-1}$, which falls into the range determined for carbazole-CH$_4$, $D_0(S_0) = 668.6 \pm 15.1 \text{ cm}^{-1}$.

Although indole and carbazole are structurally similar, carbazole is larger by one benzene ring and the binding energy must be larger than for indole-CH$_4$. For the even larger system perylene-CH$_4$ the ground-state binding energy was determined as $623 < D_0(S_0) < 818 \text{ cm}^{-1}$ by Wittmeyer and co-workers,\textsuperscript{29} using dispersed emission measurements. The exact binding energy for this complex is probably higher than for carbazole-CH$_4$. Compared to the (extrapolated) binding energy of a single CH$_4$ molecule adsorbed on a graphite surface ($D_0 = 1000–1200 \text{ cm}^{-1}$),\textsuperscript{29} the carbazole-CH$_4$ binding energy is much less, reflecting the difference between methane adsorption on a two-dimensional finite (carbazole) and a three-dimensional “infinite” system (graphite).

Figure 6 shows a plot of the determined $S_0$ ground-state binding energies $D_0(S_0)$ for the carbazole-S ($S=N_2$, CO, and CH$_4$) and carbazole-R ($R=\text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$) (Ref. 11) complexes vs the polarizability (Ref. 12) of the adatom or molecule. As a general trend, the experimental vdW binding energies are seen to increase with increasing polarizability. From this one concludes that the largest part of the binding energy results from dispersive interactions. For the rare-gas atom complexes the dispersive interaction accounts for most of the binding energy, since dipole-induced–dipole interaction is small,\textsuperscript{29} while for the complexes with $S=N_2$, CO, and...
CH$_4$, electrostatic contributions might be considerable (see the following). An estimate of point-dipole-induced–dipole interactions (as given in Ref. 28) in carbazole–$S$ complexes indicates that their contribution to the vdW binding energy should be of the order of $\approx 10$ cm$^{-1}$ for the electronic ground state $S_0$ and $\approx 20$ cm$^{-1}$ for the excited state $S_1$. Both values are very close to the experimental error bars determined by the SEP-R2PI bracketing measurements (cf. Table II).

1. Electrostatic contributions to the binding energy

The investigated molecules CO, N$_2$, and CH$_4$ have different electrostatic properties: CO has a small dipole moment of $0.37\times10^{-30}$ cm (0.11 D; negative end at C) and a quadrupole moment of $-6.47\times10^{-40}$ cm$^2$. The isoelectronic N$_2$ molecule has no dipole moment and a quadrupole moment of $-3.67\times10^{-40}$ cm$^2$, about half that of CO. For CH$_4$ the first nonvanishing moment is the octopole moment.

To estimate the electrostatic contribution to the binding energy of the complexes we used an atom-centered point-charge model for both the carbazole substrate and the admolecules N$_2$, CO, and CH$_4$ and calculated the electrostatic interaction energy as a sum over all pairwise Coulomb interactions between the charge sites. For carbazole, the atomic charge distribution were modeled by an extended Hückel molecular orbital calculation; Table V lists the atom charges, derived from a Mulliken population analysis, as well as the atom coordinates of carbazole. The calculated dipole moment for this carbazole model is 2.22 D and compares quite well with the experimental value of $\mu_{S_0} = 2.0\pm0.3$ D. In contrast, $ab$ initio self-consistent field (SCF) calculations with standard basis sets gave dipole moments which did not agree with experiment and were, hence, not used.

The N$_2$ molecule was represented by three charge sites, one site ($-0.41|\epsilon|$) at each atom and one site ($0.82|\epsilon|$) at the center of mass, resulting in a quadrupole moment of $-3.96\times10^{-40}$ cm$^2$. The N–N distance was set to 1.098 Å. A similar model was used for CO with a C–O distance of 1.099 Å and charge sites on C ($-0.5875|\epsilon|$), O ($-0.7325|\epsilon|$) and the center of mass (1.32|\epsilon|), yielding a dipole moment of $0.38\times10^{-30}$ cm (0.11 D) and a quadrupole moment of $-6.31\times10^{-40}$ cm$^2$.

For CH$_4$ a point-charge model with sites on the atoms was derived from a method introduced by Chirlian and Franel. Atomic charges are fitted to the electrostatic potential evaluated at a grid of points around the molecule, constraining the total molecular charge to zero. For this purpose an $ab$ initio calculation for CH$_4$ was performed in the SCF approximation using a 6-31 $G(d,p)$ basis set. The resulting charges were $0.0376|\epsilon|$ and $-0.0094|\epsilon|$ for C and H, respectively, and the C–H distance was $R_{C-H} = 1.084$ Å. The calculated electrostatic interaction of the carbazole–CH$_4$ complex with the CH$_4$ molecule on top of carbazole at a distance of $3.5$ Å (distance from C to the carbazole plane) was less than $1$ cm$^{-1}$ and is thus negligible compared with the dispersion interaction. For the complexes with N$_2$ and CO the electrostatic contribution to the binding energy was calculated for several geometries; N$_2$ and CO were placed on top of the carbazole molecule, in the $yz$ plane, parallel to the $y$ axis (for axes definition, cf. Table V). For CO the C atom pointed towards the carbazole N atom, (a corresponding structure was determined for the pyrrole–CO complex previously).
complex by microwave spectroscopy\(^6\)). The center of mass of the diatomic molecules were offset by 0.6 Å in the \(y\) direction relative to the carbazole center of mass. Both the distance \(r_z\) of the center of mass of the diatomic molecule from the carbazole plane and the tilt angle \(\phi\) of the diatomic molecule relative to the carbazole \(y\) axis were varied. Table VI lists the electrostatic contributions to the binding energy calculated with the model described earlier, and in Fig. 7 the electrostatic interaction energy for carbazole\(-S\) (\(S=N_2, CO\)) is plotted against \(\phi\). From Table VI and Fig. 7 one sees the following: (i) CO is electrostatically more strongly bound to carbazole than \(N_2\). This is expected, given that CO has both a (small) dipole moment and a larger quadrupole moment than \(N_2\). (ii) The distance dependence of the electrostatic interaction is not large (=8\%) in the range \(r_z=3.4 - 3.5\) Å. For the pyrrole-CO complex a distance of \(r_z=3.49\) Å was determined and the equilibrium distance for carbazole-CO is expected to be about 0.05 Å smaller. For carbazole-\(N_2\) the equilibrium distance is expected to be slightly larger than for carbazole-CO. (iii) The electrostatic interaction increases quite strongly with increasing tilt angle \(\phi\). This finding can be rationalized by the angular dependence of the dipole–quadrupole interaction, which is the first nonvanishing electrostatic interaction term for carbazole-\(N_2\) and the dominating term for carbazole-CO. Dipole–dipole interaction plays a minor role because of the smallness of the CO dipole moment. This is illustrated by a calculation, where the C and O atoms were exchanged (\(r_z=3.4\) Å and \(\phi=180^\circ\)), reversing the dipole–dipole interaction but keeping the same dipole–quadrupole interaction. Instead of an electrostatic interaction energy of \(-70.8\) cm\(^{-1}\) a value of \(-52.6\) cm\(^{-1}\) was found.

Figure 6 shows that the \(D_0(S_0)/\alpha_{R,S}\) points for the carbazole-\(R\) (\(R=\text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}\)) describe a steadily increasing but flattening curve. We note that, within the errors for \(D_0(S_0)\) and the polarizability \(\alpha\), CH\(_4\) lies on the same curve. Its polarizability and vdW binding energy with carbazole are very similar to Kr.

\(N_2\) and CO, for which electrostatic contributions to the binding energy are not negligible, lie above this curve by about 70±10 and 125±30 cm\(^{-1}\), respectively. Since we have shown that the dipole-induced–dipole interaction is small (<2\% in the \(S_0\) and <3\% in the \(S_1\) state, respectively), this additional vdW binding energy must be attributed almost exclusively to the electrostatic interactions. As shown in Table VI, this “extra” binding energy is of the same order of magnitude as the calculated electrostatic interaction for \(\phi=30^\circ\).

Note that the increase in binding energy upon \(S_0\rightarrow S_1\) excitation is nearly a factor of 2 larger for CO than for \(N_2\), in good agreement with the electrostatic model calculation.

Summing up, we conclude that the major contribution to the vdW binding energy of the Car-\(S\) (\(S=N_2, CO, CH_4\)) complexes is due to dispersive interactions, followed by important electrostatic interactions for \(N_2\) and CO. Inductive interactions are of the order of 10–15 cm\(^{-1}\), i.e., of the experimental uncertainties. Assuming electrostatic contributions to the binding energy of \(\approx 55\% (S=N_2), \approx 100\% (S=CO),\) and \(\approx 0\) cm\(^{-1}\) (\(S=CH_4\)) (see Table VI and Fig. 7), a relative contribution to the dissociation energy \(D_0(S_0)\) due to dispersive interaction can be calculated as \(\approx 90\% (N_2), \approx 85\% (CO),\) and \(\approx 98\% (CH_4)\).

The relative increase in binding energy on going from \(S_0\) to \(S_1\) for the carbazole-\(R\) (\(R=\text{Ar}, \text{Kr}, \text{Xe}\)) complexes was found to increase with the polarizability and \(S_0\) state binding energy, by 9–12\%.\(^{11}\) In comparison, the carbazole-CO complex has an unusually large spectral red shift \(\delta \nu = -162.7 \pm 0.5\) cm\(^{-1}\), and a relative increase of 22.7\%. A large part of this shift must be ascribed to the change of electrostatic interactions. The dipole moment of carbazole increases from about 1.9 to 3.0 D upon electronic \(S_0\rightarrow S_1\) excitation. Since the dipole moment of CO is small, the major term in the electrostatic interaction is the carbazole dipole–CO quadrupole interaction. This electrostatic interaction term is proportional to the dipole moment of carbazole. Hence, if the electrostatic contribution to the binding energy in the \(S_0\) state is

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**TABLE VI. Calculated electrostatic interaction energies (in cm\(^{-1}\)) for different intermolecular arrangements of the carbazole-\(S\) (\(S=N_2, CO\)) complexes.**

<table>
<thead>
<tr>
<th>(\phi) / degree</th>
<th>(r_z=3.4) Å</th>
<th>(r_z=3.5) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>-38.8</td>
<td>-49.6</td>
</tr>
<tr>
<td>10°</td>
<td>-56.7</td>
<td>-59.1</td>
</tr>
<tr>
<td>20°</td>
<td>-53.9</td>
<td>-45.8</td>
</tr>
<tr>
<td>30°</td>
<td>-52.2</td>
<td>-54.3</td>
</tr>
<tr>
<td>(N_2)</td>
<td>-70.8</td>
<td>-88.5</td>
</tr>
<tr>
<td>CO</td>
<td>-100.3</td>
<td>-104.6</td>
</tr>
<tr>
<td></td>
<td>-66.0</td>
<td>-82.1</td>
</tr>
</tbody>
</table>

**FIG. 7.** Plot of the electrostatic interaction energy for carbazole-\(S\) (\(S=N_2, CO\)) as a function of \(\phi\), which is the angle between the carbazole \(y\)-axis and the diatomic molecular axis. Electrostatic interaction energies are given for distances \(r_z=3.4\) Å and \(r_z=3.5\) Å between the carbazole plane and the diatomic center of mass (see text).
IV. CONCLUSIONS

The binding energies (D0) of three aromatic-small molecule van der Waals complexes were experimentally determined in the electronic ground (S0) and first excited (S1) state, using the recently developed SEP-R2PI laser spectroscopic technique. The D0(S0) values for the systems carbazole-S are 627.2±7.9 (S=N2), 716.5±29.8 (S=CO), and 668.6±15.1 cm⁻¹ (S=CH4), respectively, with relative uncertainties of less than ±4.2%. The absolute accuracy of the dissociation energy determination depends on the density of optically active vibronic bands in the spectrum at the dissociation threshold.

By taking into account the S0/S1 electronic spectral shifts δν of the complexes relative to bare carbazole, excited-state dissociation energies D0(S1) were derived with similar precision: D0(S1) = 678.5 ± 8.0 cm⁻¹ for S=N2, D0(S1) = 879.2 ± 29.9 cm⁻¹ for CO, and D0(S1) = 753.8 ± 15.2 cm⁻¹ for CH4.

Comparison between the binding energies D0(S0) obtained for the species Car·S (S=N2, CO, CH4) in this work, and the corresponding values previously gained for rare-gas atoms R bound to carbazole, i.e., Car·R (R=Ne, Ar, Kr, Xe), revealed that the attractive vdW interaction between N2, CO, or CH4 and the carbazole molecule is dominated by the dispersion term: The contribution of this term to the binding energy in the electronic ground-state S0 is ~90% for Car·N2, ~85% for Car·CO and ~98% for Car·CH4. The dipole-induced–dipole interaction is small, being <2% in the S0 and <3% in the S1 state, respectively.

The remaining 8% (for Car·N2) or 13% (for Car·CO) are due to electrostatic interactions: N2 and CO are isoelectronic both having a quadrupole moment, but only CO possesses a dipole moment. For both Car·N2 and Car·CO the electrostatic contribution to the binding energy is governed by dipole-quadrupole interaction. Since the dipole moment of CO is very small, being 0.11 D only, the dipole–dipole interaction between the carbazole and CO molecules plays only a minor role.

The increase in binding energy upon S0→S1 electronic excitation is extremely large for Car·CO (δν = −162.7 cm⁻¹) when compared to Car·N2 (δν = −51.3 cm⁻¹) or to Car·Ar (δν = −45.9 cm⁻¹). Since the polarizabilities of Ar, N2, and CO are similar, and the dipole moment of CO is small, we trace the large increase of spectral shift to the increase in the carbazole dipole–CO quadrupole interaction. Upon S0→S1 excitation the dipole moment of carbazole increases from 1.9 to 3.0 D. Additionally, the dump spectra acquired with the SEP-R2PI technique yielded mass specific ground-state vibronic spectra of the carbazole-S complexes below (dump spectra detected via sequence or hot bands) and above (dump spectra detected at the electronic origin) the dissociation limit. Further applications of the SEP-R2PI method to the measurement of dissociation energies D0 of hydrogen-bonded complexes 1-naphthol·S (with S=H2O, CH3OH, and NH3) are in progress.

ACKNOWLEDGMENT

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