$8.25^{-0.05}_{+0.20}$ eV is considerably lower than the Berkowitz number. *If we take the highest* of the acceptable ethylene bond energies, $\Delta H^\circ_{BDE,0}[C_2H_3-H] = 109.7 \pm 0.8$ kcal/mol, and $IP[C_2H_3] = 8.25^{-0.05}_{+0.20}$ eV, we find that $\Delta H^\circ_{f,0}[C_2H_3^+] = 261.8-267.5$ kcal/mol. This range can barely be made consistent with $\Delta H^\circ_{f,0}[C_2H_3^+] = 267.8 \pm 0.5$ kcal/mol (and only if one includes the error bars) and extends well below the range of values derived from appearance potentials. Using any of the lower values of $\Delta H^\circ_{BDE,0}[C_2H_3-H]$ *would reduce* $\Delta H^\circ_{f,0}[C_2H_3^+]$ even further. We propose that a downward adjustment of $\Delta H^\circ_{f,0}[C_2H_3^+]$ by several kcal/mol is more consistent with the data. The same adjustment has been suggested by Hawley and Smith[29] on the basis of a thorough investigation of the $C_2H_2^{\bullet+} + H_2 \rightarrow [C_2H_4^{\bullet+}]^* \rightarrow C_2H_3^+ + H^\bullet$ ion-molecule reaction at temperatures below 3 K. They report rate measurements and a large deuterium kinetic isotope effect for a slightly exothermic tunneling reaction through an activation barrier on the $C_2H_4^{\bullet+}$ potential surface, which gives $\Delta H^\circ_{f,0}[C_2H_3^+] = 265^{-2}_{+1}$ kcal/mol. The presence of a small activation barrier for the dissociation of energized $C_2H_4^{\bullet+}$ to $C_2H_3^+$ is precisely the condition that would cause appearance potential measurements to overestimate $\Delta H^\circ_{f,0}[C_2H_3^+]$. The adjustment, strictly speaking, is not inconsistent with the original measurement in that the appearance potential of $C_2H_3^+$ from C_2H_4 rigorously places only an upper bound[23] on $\Delta H^\circ_{f,0}[C_2H_3^+]$. That upper bound can be safely interpreted as the actual value *only if* the $C_2H_4^{\bullet+} \rightarrow C_2H_3^+ + H^\bullet$ reaction is a simple bond rupture, and

competing reactions are absent at threshold. Given the extensive bonding changes in going from ethylene radical cation to the bridged vinyl cation, and the reported[25,26] $C_2H_4^{\bullet+} \rightarrow C_2H_2^{\bullet+} + H_2$ dissociation at very nearly the same appearance potential, neither condition is fulfilled, and one may question the derived value for $\Delta H^\circ_{f,0}[C_2H_3^+]$.

We suggest that the different reported ionization potentials for C_2H_3 arise from improvements in instrumental sensitivity and/or the different sensitivity to an ionization threshold in photoelectron spectra (PES), photoionization efficiency (PIE) curves, and electron impact ionization efficiency (EIE) curves, for an ionization with a poor Franck–Condon factor at threshold. In the simplest model,[30] the PES would be the derivative spectrum of the PIE curve, which would be the derivative spectrum of the EIE curve. For an ionization accompanied by gross changes in equilibrium geometry, as is the case for C_2H_3, both the PIE and EIE curves would miss the threshold and overestimate an adiabatic ionization potential seen by PES.

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Infrared Absorption Spectroscopy of the Weakly Bonded CO–Cl2 Complex

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High-resolution rovibrational absorption spectra of the weakly bonded CO–Cl2 complex have been recorded in the 2143-cm^{-1} region by exciting the CO chromophore with a tunable diode laser. The spectra indicate that CO–Cl2 is linear and semirigid. By fitting the data to a linear-molecule Hamiltonian, the following constants (in cm^{-1}) were obtained: $\nu_0 = 2149.5424$ (4), $B'' = 0.031\,582\,3$ (39), $B' = 0.031\,486\,7$ (52), $D_J'' = 4.37$ (25) $\times 10^{-8}$, and $D_J' = 4.58$ (35) $\times 10^{-8}$. The distance between the CO and Cl2 centers of mass is approximately 4.78 Å. The orientation of CO is not determined experimentally. However, Cl2 appears to act as a classical σ-electron acceptor, while CO behaves like a weak Lewis base, donating charge from the carbon side via the weakly antibonding 5σ orbital, thereby raising the CO vibrational frequency.

Introduction

Spectroscopic studies of weakly bonded binary complexes containing molecular chlorine have provided much information on their properties, structure, and dynamics. For example, He–Cl2, Ne–Cl2, Ar–Cl2, Xe–Cl2, and Kr–Cl2 have been shown to be T-shaped in both the ground state and the electronically excited state that correlates to Cl2(B$^3\Pi_{0+}$), with bonding dominated by van der Waals forces in both electronic states.[1,2] Going one step further with these systems, Boivineau et al. carried out experiments in which Xe–Cl2 was excited to a chemically reactive surface by a two-photon process.[3] The first photon excites the Cl2 moiety to dissociative $^1\Pi_u$, but before the complex can dissociate a second photon is absorbed and excites either the Xe–Cl or the Cl–Cl pair.

The excited complex then dissociates and forms a Xe–Cl* excimer. In addition, such weakly bonded complexes can provide a basis for detailed studies of photoinitiated reactive and/or inelastic processes.[4]

Baiocchi et al. determined the structure of the HF–Cl2 complex from molecular beam electric resonance spectroscopy by fitting to the HF hyperfine structure.[5] Their results indicate that the three heavy atoms are linear and that the hydrogen atom is off-axis with an average H–F–Cl angle of 125°. They argue against a

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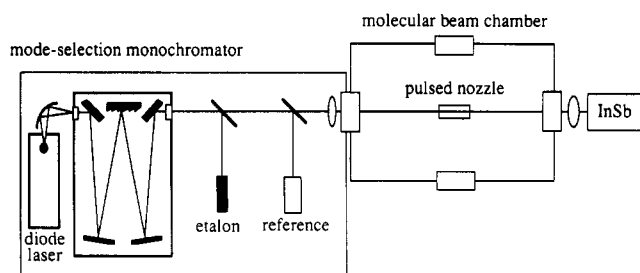
Figure 1. Schematic drawing of the experimental arrangement.

linear equilibrium geometry on the basis that zero-point oscillations are insufficient to account for such a large departure from 180°. However, the reduced mass for hydrogen motion in this system is ~1 amu and even heavier systems have been shown to exhibit very large amplitude zero-point oscillations due to shallow potentials.[6] Thus, HF–Cl_2 can be described by the general linear structure of the form D–AB, where D is a Lewis base and AB is a diatomic halogen.[5] The linear geometry is ascribed to the overlap of a filled valence orbital of the HF weak Lewis base with an empty σ^* orbital of the halogen.[5]

Carbon monoxide can act as a weak Lewis base. It is known to coordinate to metals with linear bonds in which the carbon acts simultaneously as a base, donating σ electron density, and as a weak π acid accepting back donation from the metal.[7] Sometimes the CO frequency is lowered and sometimes it is raised, depending on the respective contributions from σ donation and back bonding. On surfaces, it is also known that the frequency can be either raised or lowered, depending on the type of interaction.[8] How CO will behave in a weak van der Waals bond is hard to predict a priori, but it is possible that σ donation will play an important role in complexes with diatomic halogens. Thus, our motivation was to see if CO–Cl_2 is linear, since there should be relatively little ambiguity arising from large-amplitude zero-point oscillations. Consequently, we carried out an infrared spectroscopic study of CO–Cl_2. The results indicate that it is indeed linear, in agreement with the donor–acceptor model described by Baiocchi et al.[5] However, the orientation of the CO cannot be determined *experimentally* without isotopic substitution on the CO.

Experimental Results

CO–Cl_2 complexes were produced by pulsed expansions of CO/Cl_2/Ar mixtures through a slit nozzle similar to one described earlier,[9] the only modification being an increase in the slot size to 127 mm × 0.5 mm to achieve higher throughputs (see Figure 1). The chamber is pumped by a vapor jet booster (Edwards Model 18B4A, 4000 L s⁻¹) backed by a roots blower and a mechanical pump. Chamber pressures are typically 1–10 mTorr. The chamber is connected to the pump by a 30 cm diameter inverted U-shaped pipe which serves as a buffer volume and an oil trap, i.e., minimizing pump oil contamination.

Tunable IR radiation was provided by a diode laser (Laser Analytics). A single mode was selected by passing the laser beam through a 0.5-m monochromator whose output was split and directed along three paths. One beam passed through an air-spaced etalon (Laser Analytics SP5945, free spectral range of 0.009 827 cm⁻¹) which served as a relative frequency marker. Another beam was directed through a reference cell containing N_2O, which provided an absolute frequency reference. The third beam, containing >90% of the single-mode laser power, was sent to the chamber where it made a single pass through the expansion at a height of 0.5 cm above the slit. All three beams were monitored simultaneously using InSb detectors. Each detector was connected to a preamplifier and transient digitizer (4000
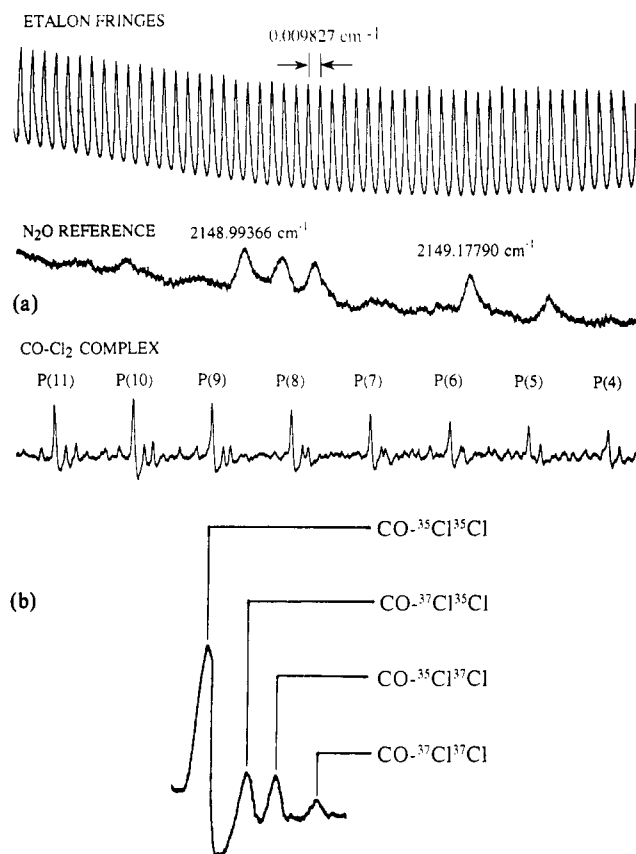

Figure 2. (a, top) Portion of the CO–Cl_2 P-branch; the etalon, reference, and jet traces were acquired simultaneously; (b, bottom) absorption spectrum showing the four CO–Cl_2 isotopomers.

samples). Spectra were taken by accumulating 200 scans alternately with the pulsed nozzle on and then off, and then storing the difference between the on and off signals. Data acquisition was controlled by a personal computer.

A typical experiment proceeds as follows. Acoustic noise from the laser cold-head compressor triggers a master clock at ~3 Hz. Following a delay, the nozzle is triggered, and after a stable expansion has formed another trigger initiates the laser frequency ramp, the three digitizers, and an oscilloscope. One scan usually covers a 0.5-cm⁻¹ range. Broad spectral coverage is obtained by overlapping a number of individual scans. Coarse frequency tuning is obtained by adjusting the current applied to the diode and the diode temperature. Instrumental resolution was ~20 MHz.

All gases were used without purification, and ultrahigh purity Ar (99.995%) was used as the carrier. CO and Cl_2 had stated purities of ≥99.5%. The stagnation pressure behind the nozzle was typically 3–5 atm and rotational temperatures in the expansion were typically 10 K. Cl_2/CO/Ar mixtures in the ratio 1/30/300 were prepared in a stainless steel and monel gas manifold. Signals were optimized by adjusting the expansion conditions and the nozzle position.

Absorption spectra of CO–Cl_2 were recorded in the 2147–2151-cm⁻¹ region by exciting the CO stretch. Detailed spectra were taken in panels, each containing at least one overlapping feature. One such panel showing a portion of the P branch is shown in Figure 2a. The regularity seen in both the P- and R-branches and the absence of a Q-branch is indicative of a linear or nearly linear structure.

In Figure 2b, a magnified portion of the spectrum shows the absorption features of the four isotopomers of CO–Cl_2: CO–$^{35}Cl^{35}Cl$, CO–$^{37}Cl^{35}Cl$, CO–$^{35}Cl^{37}Cl$, and CO–$^{37}Cl^{37}Cl$. The natural abundance of the chlorine isotopes ($^{35}Cl/^{37}Cl$) is 3/1. Therefore, the intensities of the absorption features should be very close to the statistical ratio of 9/3/3/1, with $^{35}Cl^{35}Cl$ the strongest and $^{37}Cl^{37}Cl$ the weakest. These features are clearly resolved only at high rotational quantum numbers. Unfortunately, the signal-to-noise ratio in the R-branch region was smaller than in the

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TABLE I: Observed and Calculated CO–Cl$_2$ Transitions (cm^{-1}) (σ_{rms} = 0.0004 cm^{-1})

P(J)^a	obsd	obsd – calcd	R(J)	obsd	obsd – calcd
			0	2149.6051	−0.0003
1	2149.4818		1	2149.6686	0.0004
2	2149.4180		2	2149.7306	−0.0001
3	2149.3543		3	2149.7928	−0.0003
4	2149.2898		4	2149.8558	0.0005
5	2149.2245	−0.0002	5	2149.9174	−0.0000
6	2149.1606	0.0000	6	2149.9792	0.0000
7	2149.0958	−0.0005	7	2150.0409	0.0001
8	2149.0316	−0.0003	8	2150.1023	0.0001
9	2148.9677	0.0005	9	2150.1633	−0.0000
10	2148.9029	0.0006	10	2150.2245	0.0001
11	2148.8370	−0.0003	11	2150.2854	0.0002
12	2148.7716	−0.0005	12	2150.3452	−0.0006
13	2148.7075	0.0007	13	2150.4054	−0.0007
14	2148.6405	−0.0007	14	2150.4660	−0.0002
15	2148.5753	−0.0000	15	2150.5269	0.0006
16	2148.5094	−0.0001	16	2150.5868	0.0009
17	2148.4434	0.0001	24	2151.0558	−0.0003
18	2148.3771	0.0000	25	2151.1135	−0.0008
19	2148.3107	0.0001	26	2151.1710	−0.0003
20	2148.2432	−0.0007	27	2151.2282	−0.0000
21	2148.1765	−0.0005	28	2151.2852	0.0004
22	2148.1101	0.0000	29	2151.3419	0.0008
23	2148.0437	0.0008	30	2151.3984	−0.0000
24	2147.9754	−0.0001	31	2151.4547	0.0001
25	2147.9081	0.0002			
26	2147.8406	0.0004			
27	2147.7724	0.0001			
28	2147.7043	0.0001			
29	2147.6360	0.0000			
30	2147.5676	0.0001			
31	2147.4986	−0.0002			
32	2147.4300	0.0000			
33	2147.3611	0.0001			
34	2147.2920	0.0002			
35	2147.2221	−0.0003			

^{a} P-branch J = 1–4 transitions are not included in the fit.

P-branch region because of lower laser power. Thus, we were only able to determine accurately the molecular constants for CO–^{35}Cl^{35}Cl, and further references to CO–Cl$_2$ in this paper are specific to this isotopomer. Also, we are unable to determine experimentally whether the complex is bonded CO–Cl$_2$ or OC–Cl$_2$. For this to be ascertained, ^{13}C substitution is required.

Because the absorption signals have been passed through low-pass and high-pass filters in the data acquisition system, the line widths observed in Figure 2 are distorted. Line widths measured without signal filtering are about 60 MHz. The instrument line width, due to both Doppler and laser effects, is limited to 20–30 MHz, although this number depends severely on the characteristics of the actual diode used. The typical narrowest line widths that we have obtained for other species such as CO$_2$–HF have been ~40 MHz,[10] corresponding to excited-state lifetimes of 6 ns. Thus the lifetime for this excited state of CO–Cl$_2$ are somewhat shorter, about 3 ns.

A nonrigid linear rotor Hamiltonian with the following equation for transition frequencies was used[11]

$$\nu = \nu_0 + B'J'(J' + 1) - D_J'J'^2(J' + 1)^2 - B''J''(J'' + 1) + D_J''J''^2(J'' + 1)^2 \quad (1)$$

where B'', D'', B', and D' are the rotational and centrifugal distortion constants for the ground and excited vibrational states, respectively, J' and J'' are the upper and lower state rotational quantum numbers, and ν_0 is the band center of the complex. A least-squares combination-difference technique was used to determine B and D for the upper and lower vibrational states. This

TABLE II: CO–Cl$_2$ Molecular Constants and Structural Parameters (cm^{-1})

B'', cm^{-1}	0.0315823 (39)	R_{cm}, Å	4.776
D'', cm^{-1}	4.37 (25) × 10^{-8}	R_{CO}, Å	1.128^b
B', cm^{-1}	0.0314867 (52)	R_{Cl_2}, Å	1.987^b
D', cm^{-1}	4.58 (35) × 10^{-8}	k_s, mdyn/Å	0.029
ν_0, cm^{-1}	2149.5424 (4)	ν_s, cm^{-1}	49.5
$\Delta\nu_0$,^{a} cm^{-1}	6.2884 (4)		

^{a} Shift relative to uncomplexed CO. ^{b} Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*, Van Nostrand Reinhold: New York, 1979; Vol. 4.

method is useful in decoupling the highly correlated ground and upper state constants. The upper state was fit with $\Delta F(J) = R(J) - P(J)$, and the lower state was fit with $\Delta F(J) = R(J - 1) - P(J + 1)$, where $\Delta F(J)$ is given by

$$\Delta F(J) = B(4J + 2) - D(8J^3 + 12J^2 + 12J + 4) \quad (2)$$

The band origin of the complex was determined from a least-squares analysis using the observed transition frequencies and the rotational constants obtained from eq 2. The band origin was determined to be at 2149.5424 (4) cm^{-1}, a *blue* shift of 6.2884 (4) cm^{-1} from uncomplexed CO. Frequencies, assignments, and residuals are listed in Table I. Due to experimental difficulties in accurately measuring the frequencies of P(1)–P(4), they were not included in the fit. The molecular constants are listed in Table II.

By using the measured CO–Cl$_2$ ground-state rotational constant and by assuming that the internuclear distances between each subunit remains constant upon complexation, the distance between the centers-of-mass of the constituents was calculated by using

$$\mu R_{cm}^2 = I_{complex} - I_1 - I_2 \quad (3)$$

where μ is the reduced mass of the two constituent molecules, I_1 and I_2 are their moments of inertia, and $I_{complex}$ is the moment of inertia of the complex (I_B for CO–Cl$_2$, since it is linear). In addition, the force constant for the internuclear stretch can be estimated by using[12]

$$k_s = (4\pi)^4\mu^2(R_{cm})^2(B'')^4/(2hD_J'') \quad (4)$$

Finally, the intermolecular stretch frequency can be estimated with a harmonic oscillator approximation:

$$\nu_s = (k_s/\mu)^{1/2}/2\pi c \quad (5)$$

These structural parameters are listed in Table II.

Conclusions

Attractive interactions in weakly bonded complexes can vary from multipolar interactions to electron sharing.[13] In the case of CO–Cl$_2$, it appears that bonding can be characterized in terms of the latter. The CO HOMO is a weakly antibonding σ orbital, and the Cl$_2$ LUMO is a σ^* orbital. Thus, as with HF–Cl$_2$, bonding is due to overlap of the filled CO σ orbital with the empty Cl$_2$ σ^* orbital.

It is interesting to compare this bonding scheme with that observed in molecular compounds containing CO. Hurlburt et al. recently reported synthesizing Ag(CO)B(OTeF$_5$)$_4$, the first silver carbonyl to be isolated.[14] Its IR spectrum exhibited ν(CO) at 2204 cm^{-1}, a 61-cm^{-1} blue shift from free CO. This suggests that CO is acting as a Lewis base in this compound rather than a π-acid, as is frequently observed in metal–carbonyl compounds. The same trend is seen in the increase in the CO stretching frequency in CO–Cl$_2$, although to a much lesser degree due to the weakness of the van der Waals bond. The frequency increase is due to the fact that the CO orbital donating charge is slightly antibonding,[15] so donation to the halogen increases the bonding

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character, thereby strengthening the C–O bond and raising the frequency. Because the antibonding orbital is predominately on the carbon, we suspect that the structure of the complex is OC–Cl$_2$ rather than CO–Cl$_2$. However, isotopic substitution (^{13}C^{16}O) can establish the CO orientation unambiguously. If we assume that the carbon is attached to the Cl$_2$, then the C–Cl bond length would be 3.12 Å which is approximately the sum of the van der Waals radii for these two atoms.

In summary, the CO–Cl$_2$ complex has been studied using infrared spectroscopy and is found to be linear (R_{cm} = 4.78 Å), with a 6.28-cm^{-1} blue shift relative to uncomplexed CO. Like HF–Cl$_2$, the structure can be rationalized as a donor–acceptor complex between a weak Lewis base and a halogen molecule.

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Vibrational Spectroscopy of Ammoniated Sodium Ions: Na$^+$(NH$_3$)$_M$, M = 6–12

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Vibrational spectra of Na$^+$(NH$_3$)$_M$, M = 6–12, in the region from 1020 to 1090 cm^{-1} (9.6-μm band of the CO$_2$ laser) are reported. The spectra, associated with the ν_2 mode of NH$_3$, reflect the influence of the Na$^+$–NH$_3$ and NH$_3$–NH$_3$ interactions. From the spectral dependence on cluster size, it appears that six ammonia molecules form the first solvent shell about the Na$^+$ ion. Ammonia molecules in a bulklike environment appear for ammoniated sodium ions with 10 or more solvent molecules.

Introduction

There have been a number of recent gas-phase studies on ammoniated ammonium ions. The vibrational spectrum of the ammoniated ammonium ion was reported in the 2500–4000-cm^{-1} region.[1] Spectral features were assigned to the NH$_4^+$ core and ammonia molecules in the first solvent shell. Four ammonia molecules were found to complete the first solvent shell. Protonated ammonia clusters were investigated mass spectrometrically using both electron impact ionization[2] and multiphoton ionization.[3] The translational kinetic energy release, following unimolecular decomposition of NH$_4^+$(NH$_3$)$_N$, has been measured for N = 2–17.[2,3] Measurements of decay fractions have been used to determine relative binding energies.[4] All of the dynamical studies[2–4] have found unusual stability associated with NH$_4^+$-(NH$_3$)$_4$, where the first solvent shell is filled.

The solvation of other ions by ammonia has been mainly characterized by high-pressure mass spectrometry (HPMS).[5–9] A significant decrease in the binding energy was observed for the attachment of a fifth ammonia for both Li$^+$ and Na$^+$, suggesting the existence of a solvation shell of four ammonia molecules for these two ions.[6] This decrease was not observed for the larger K$^+$ and Rb$^+$ ions.[5]

We have recently investigated the vibrational spectra of Cs$^+$(CH$_3$OH)$_N$, N = 4–25,[10] and Na$^+$(CH$_3$OH)$_P$, P = 6–25,[11] in the 1020–1060-cm^{-1} region. From the spectral dependence of the methanol C–O stretch on cluster size and from supporting Monte Carlo simulations, we observed that 10 and 6 methanols filled the first solvation shells of Cs$^+$ and Na$^+$, respectively. A similar sensitivity to bonding environment is also exhibited by the ν_2 vibrational mode of NH$_3$, varying from 950 cm^{-1} for the monomer[12] to 980 and 1004 cm^{-1} for (NH$_3$)$_2$,[13–17] 1016 cm^{-1} for (NH$_3$)$_3$,[14–17] 1044–1050 cm^{-1} for larger aggregates,[16,17] and 1115 cm^{-1} when complexed to Na$^+$.[18] Since the ν_2 or "umbrella" mode of ammonia is affected by coordination with either the nitrogen lone pair or the hydrogens, sensitivity to the position of the ammonia in the cluster is expected. A large portion of this region in the infrared is covered by the 9.6-μm R- and P-branch transitions of the CO$_2$ laser, making Na$^+$(NH$_3$)$_M$ ideal candidates for an experimental study.

Experimental Section

A detailed description of the experimental apparatus may be found in our previous publications.[10,11] Briefly, Na$^+$ ions are generated from a thermionic emitter downstream from the nozzle of a continuous molecular beam source. The ions merge into the cluster beam and collide with and are solvated by the ammonia clusters. The solvated ions are stabilized by evaporative cooling and possess a significant amount of internal energy.[10,11] The cluster ions are guided by a series of aperture lenses into a quadrupole mass filter, where a single cluster ion size is selected. A CW CO$_2$ laser with from 4 to 20 W of power (depending on the particular laser transition) propagates along the axis of the quadrupole.

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