INFRARED SPECTROSCOPY OF JET-COOLED CATIONIC POLYAROMATIC HYDROCARBONS: NAPHTHALENE$^+$

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ABSTRACT

We present the infrared (IR) absorption spectrum of the jet-cooled naphthalene-Ar van der Waals cluster cation in the 400–1600 cm^{-1} range, which is expected to resemble closely the IR spectrum of the bare naphthalene cation. Cluster cations are produced in their ground states via resonance-enhanced two-color ionization. Subsequent irradiation of the ions with IR light of a free-electron laser causes cluster dissociation, if this light is resonant with IR-active transitions of the cationic cluster. Mass-selective measurement of the dissociated fraction as a function of IR wavelength yields the IR spectrum of the cationic cluster. Comparison with previously reported Ar matrix isolation spectra of naphthalene$^+$ shows good agreement, with more bands observed in the present study. The IR spectrum observed is compared to a calculated spectrum of the naphthalene cation, allowing for unambiguous assignments of all the observed modes. The experimental method presented is generally applicable to obtain laboratory IR spectra of ionized polyaromatic hydrocarbons under astrophysically relevant conditions.

Subject headings: ISM: lines and bands — ISM: molecules — methods: laboratory — molecular data

1. INTRODUCTION

The IR emission spectra of many celestial objects are dominated by relatively broad features at 3.3, 6.2, 7.7, 8.6, and 11.3 μm, with minor features observed at 3.4, 5.2, 5.8, 6.8, 7.0, and 12.3 μm. These features, collectively known as the unidentified infrared (UIR) bands, are nonthermal in nature and most probably originate from very small grains or free gas-phase molecules, which can be heated to peak temperatures of ~1000 K by absorption of a single UV/visual photon (Sellgren 1984; Leger & Puget 1984). Although the exact carriers of these bands are still unknown, it is widely accepted that polycyclic aromatic structures, which normally tend to have IR features around the UIR wavelengths, are likely candidates. In the last decades a number of materials, all composed primarily of polycyclic aromatics, have been proposed as possible carriers of the UIRs. Among species such as coal (Papoular et al. 1989) and quenched carbonaceous composite (Sakata et al. 1984, 1987, 1990), free polyaromatic hydrocarbons (PAHs), either in their neutral or cationic form, are proposed as important candidate carriers (Leger & Puget 1984; Allamandola et al. 1985, 1989; Hudgins, Allamandloa, & Sandford 1997). From UV-laser–induced infrared emission studies of neutral PAHs in the gas phase, it is concluded that neutral PAHs of small and moderate size can at best make a minor contribution to the UIRs (Cook et al. 1996, 1998). Their cations, as well as larger neutral PAHs and their cations, remain viable candidates for the origin of the UIRs, however.

For a conclusive identification of the UIR carriers, the IR spectroscopic properties of gas-phase candidate carriers under conditions similar to the interstellar environments, particularly under cold and collision-free conditions, need to be recorded in laboratory experiments. To date, the best laboratory IR spectra available of cooled ionized PAHs are those obtained in matrix isolation experiments (Szczepanski et al. 1992; Szczepanski & Vala 1993; Hudgins, Sandford, & Allamandola 1994; Hudgins et al. 1997). In these studies, neutral PAHs are deposited in noble gas matrices at temperatures of ~10–20 K, and, after recording the IR spectrum of the neutral sample, PAH cations are formed by in situ photolysis. Comparison of the IR spectrum of the photolyzed sample, containing a fraction

of up to 10% ionized PAHs, to the spectrum of the sample with neutral PAHs yields information about the IR spectrum of the cationic PAH. As a consequence of the weak matrix interaction, the neutral or cationic PAH IR matrix isolation spectra are assumed to resemble closely those of the gas-phase species. Since the method used is not species selective, the IR spectra can be difficult to interpret. For instance, correlations with known UV/visual band intensities of the ionic PAH of interest upon photolysis have to be determined in order to distinguish between contaminating species and/or fragmentation products. Integrated band strengths are calculated from the difference in column density between the spectra of the neutral PAH before and after photolysis (Hudgins et al. 1994).

Obviously, it is desirable to obtain IR absorption spectra of cooled and ionized species in the gas phase, for instance, in the collision-free environment of a molecular beam. However, this is experimentally challenging because normally in such a molecular beam experiment only a small number of ions can be generated, asking for bright and tunable IR light sources and sensitive, species-selective detection schemes.

In this Letter, we report the results of a molecular beam experiment in which the IR spectrum of the jet-cooled naphthalene-Ar cluster cation is obtained using a free-electron laser as a tunable IR light source. The dissociation of the cluster cation at IR resonances is detected in order to obtain the IR spectrum of the ionic cluster (Piest, von Helden, & Meijer 1999; Brechignac & Pino 1999). This IR spectrum of the naphthalene-Ar cationic cluster is expected to resemble that of the bare naphthalene cation; experiments have shown that the vibrational modes of the naphthalene chromophore are affected only on the order of a few wavenumbers (mostly ≤1 cm^{-1}) by the presence of the weakly bonded Ar atom (Troxler & Leutwyler 1991; Vondrák, Sato, & Kimura 1996). The IR spectrum observed is compared to a calculated spectrum of the naphthalene cation, allowing for unambiguous assignments of all the observed modes.

2. EXPERIMENTAL PROCEDURE

Experiments are carried out at the Free-Electron Laser for Infrared Experiments (FELIX) user facility in Nieuwegein, The
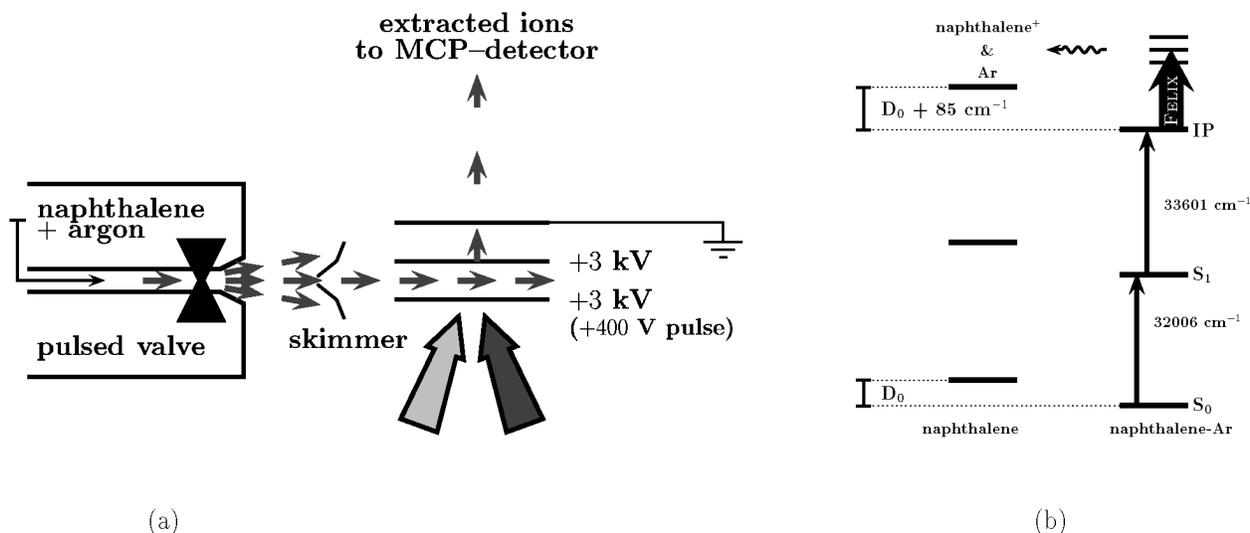
Fig. 1.—(a) Scheme of the experimental setup. (b) Excitation-ionization-dissociation scheme for monitoring the IR absorption spectrum of cationic naphthalene-Ar. Cluster cations are produced via (1+1′)-REMPI under field free conditions. IR-laser–induced dissociation of the ionic cluster is detected via the appearance of bare cationic naphthalene that is pulse-extracted several microseconds after ionization of the cluster.

Netherlands (Oepts, van der Meer, & van Amersfoort 1995; Knippels et al. 1995). The pulsed IR laser radiation produced by FELIX is continuously tunable over the 40–2000 cm^{-1} range. The light output consists of macropulses (∼4 μs duration), each with a substructure of micropulses (∼1 ps duration) with a 1 ns separation. In the present experiment, the macropulse repetition rate is 5 Hz and the laser bandwidth is typically 0.5%–1.0% of the central frequency. The molecular beam spectrometer, including the two tunable pulsed UV laser systems, is operated at a 10 Hz repetition rate and has been described previously (Boogaarts, von Helden, & Meijer 1996). A scheme of the experimental setup is shown in Figure 1a. Naphthalene is put in the sample compartment of the pulsed valve body (R. M. Jordan Co.), kept at a temperature of 45°C, and is seeded in the carrier gas (Ar, 3 bar backing pressure). Through the 0.5 mm orifice, ∼30 μs gas pulses are released into vacuum of 10^{-5} torr. Upon entering a differentially pumped Wiley-McLaren–type linear time-of-flight (TOF) mass spectrometer, the molecular beam is skimmed. At the crossing point of the mutually perpendicular molecular beam axis, laser beam axis, and TOF-tube axis, the molecules in the beam interact with the incoming UV laser beams and with the collimated FELIX beam (approximately 2–3 mm diameter). The ions are produced in this region via two-color ionization under field-free conditions, irradiated by FELIX, and subsequently pulse-extracted and accelerated to a microchannel plate (MCP) detector, yielding mass spectra with a resolution of $M/\Delta M \approx 200$. The maximum energy density of FELIX used in these experiments is about 0.15 J cm^{-2} per macropulse. The MCP detector signal is amplified and fed into a 10 bit, 100 Ms s^{-1} digital oscilloscope (LeCroy 9430), which is read out by a PC. The PC also controls the wavelength scanning of both UV lasers and of FELIX. The molecular beam spectrometer is synchronized to the FELIX output to nanosecond precision using a four-channel digital delay/pulse generator (SRS DG535).

The IR spectrum of jet-cooled cationic naphthalene-Ar is measured using the IR-UV double-resonance scheme shown in Figure 1b. Naphthalene-Ar$^+$ clusters are generated by two-color (1+1′)-REMPI via the $S_1 \leftarrow S_0$ origin band at 32006 cm^{-1} (Troxler & Leutwyler 1991; Vondrák et al. 1996) of the neutral

cluster. The high density of lines in the one color REMPI spectrum of neutral naphthalene(-Ar) (Cockett et al. 1993) around the ionization frequency (∼33594 cm^{-1}: Troxler & Leutwyler 1991; ∼33601 cm^{-1}: Vondrák et al. 1996) asks for a careful setting of this frequency. To avoid one color REMPI signal of the ionization laser alone, UV scans around the ionization potential are carried out to select an appropriate ionization frequency just barely (within 10 cm^{-1}) above the cluster ionization threshold, thus leaving the cluster in its ionic ground state.

Following subsequent irradiation with FELIX, the cluster cation dissociates if the FELIX photon energy is tuned to an IR-active resonance of the ionic cluster and if its energy is sufficiently high to induce dissociation either by single or by multiple photon absorption. Dissociation of the ionic cluster leads to the appearance of naphthalene cations against zero background. All ions are pulse-extracted and mass-selectively detected several microseconds after ionization. Monitoring the fraction of dissociated clusters as a function of IR wavelength yields an IR absorption spectrum of the cluster cation.

3. RESULTS

The observed IR spectrum of the naphthalene-Ar cation is shown in the top panel of Figure 2. The spectrum shows major bands at positions listed in Table 1. The observed bandwidths are almost solely due to the FELIX bandwidth. A calculated spectrum of the bare naphthalene cation is shown in the lower panel of the same figure and is also tabulated. The band frequencies and intensities are calculated using the BECKE3LYP method (Becke 1993) with Dunning's D95(d,p) basis set (Dunning & Hay 1976) as implemented in GAUSSIAN 94 (Frisch et al. 1995). Convolution with a Gaussian line shape (FWHM = 5 cm^{-1}) yields the spectrum shown in the figure. The calculated spectrum compares very well to the calculated spectrum reported by Bauschlicher & Langhoff (1997).

A comparison of the observed spectrum to the spectrum calculated yields unambiguous assignments of all strong modes. Band positions as well as the relative band intensities agree well with the calculated ones. A three-dimensional computer
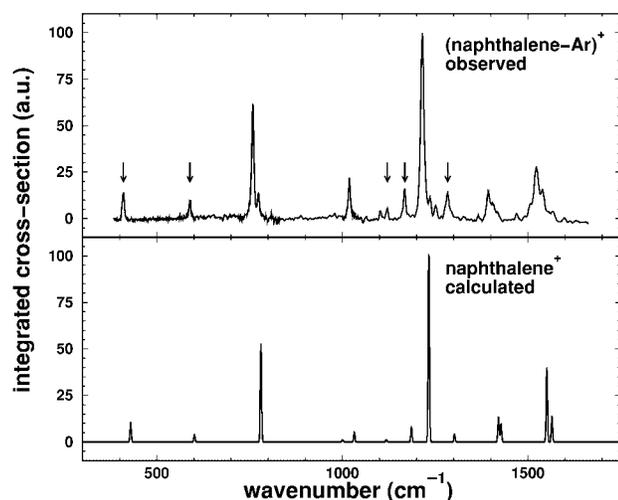
FIG. 2.—*Top:* Observed IR absorption spectrum of jet-cooled cationic naphthalene-Ar. Peaks not reported in matrix isolation experiments are marked with arrows. *Bottom:* Calculated IR absorption spectrum of cationic naphthalene.

animation of the calculated vibrational displacements gives a good impression of the specific vibrational modes involved in the spectrum observed. At the blue side of the strong transitions at 759 cm^{-1} (C–H out-of-plane bend) and 1215 cm^{-1} (C–C stretch), van der Waals bands with a frequency spacing of ~15 cm^{-1} reveal the cluster nature of the species observed. These bands can be assigned to one of the van der Waals bending modes (Vondrák et al. 1996). Data obtained in Ar matrix isolation experiments (Szczepanski et al. 1992; Hudgins

et al. 1994), also listed in Table 1, show good agreement to data recorded in this experiment. The modes indicated with arrows in Figure 1b (two low-frequency modes at 410 and 589 cm^{-1} together with modes at 1121, 1168, and 1284 cm^{-1}), however, have not been observed in the matrix experiments. From matrix isolation spectra of neutral naphthalene obtained by Hudgins et al. (1994), it is likely that the ionic modes observed at 1121 and 1284 cm^{-1} are overlapped by strong modes of the neutral species. The other three modes not observed in matrix isolation experiments do not coincide with strong bands of neutral matrix-isolated naphthalene. Although the low-frequency spectral region was searched (Hudgins et al. 1994) no bands were observed, whereas in the gas-phase spectrum presented here the two bands at 410 and 589 cm^{-1} are readily detected.

The feature at 1393 cm^{-1} cannot be resolved by FELIX, but is likely originating from the two modes calculated at 1421 [1393(I)] and 1428 cm^{-1} [1393(II)], which is indicated by the asymmetric line shape showing a shoulder to the blue. The mode at 1539 cm^{-1} is assigned to the mode calculated at 1565 cm^{-1}. Additional, but very weak, features are observed in the 1000–1600 cm^{-1} region of the spectrum. The origin of these features is unknown, but they might be attributed to IR-active combination bands. Furthermore, the calculations show that no IR-active modes are expected higher than 1600 cm^{-1} besides the C–H stretching modes above 3000 cm^{-1}, which are calculated as weak features.

From the dependence of the fraction of ionic clusters dissociated upon the FELIX-fluence (~I) at the 410 cm^{-1} resonance, a $[1 - \exp(-\sigma I)]$ behavior, with σ the spectrally integrated cross section, is observed, indicating a single-photon absorption process. Using an ionization potential shift of −85 cm^{-1} (Vondrák et al. 1996) due to the presence of the Ar

TABLE 1
CALCULATED NAPHTHALENE+ IR-ALLOWED VIBRATIONAL MODES AND INTEGRATED IR
ABSORPTION INTENSITIES

| D_{2h} | CALCULATED | | OBSERVED ν_{vib} | | |
	ν_{vib}	Intensity	This Work	Hudgins et al. 1994	Szczepanski et al. 1992
B_{3u}	161	3	...	...	...
B_{1u}	354	0	...	...	...
B_{3u}	429	23	410	...	...
B_{2u}	601	8	589	...	...
B_{3u}	781	113	759	758.7	...
B_{1u}	801	0	...	...	...
B_{3u}	1000	2	...	...	...
B_{2u}	1032	11	1019	1023.2	1016
B_{1u}	1118	3	1121	...	...
B_{2u}	1186	17	1168	...	...
	1233	215	1215	1214.9/1218.0	1215/1218
B_{1u}	1302	9	1284	...	...
	1421	30	1393(I)	1400.9	1401
B_{2u}	1428	20	1393(II)	...	...
B_{1u}	1551	85	1523	1518.8/1525.7	1519/1525
B_{2u}	1565	30	1539	...	...
B_{1u}	3208	0	...	...	...
B_{2u}	3209	1	...	...	...
B_{1u}	3223	1	...	...	...
B_{2u}	3234	1	...	...	...

NOTE.—Frequencies are given in cm^{-1}, and intensities are in km mol^{-1}. The frequencies observed are deduced from the measurements of the IR spectrum of the (naphthalene-Ar)+ van der Waals cluster. For comparison, IR data observed in (Ar)–matrix isolation experiments (Hudgins et al. 1994; Szczepanski et al. 1992) are listed.

atom, an upper limit of the bond energy $D_0 \leq 325$ cm^{-1} of the neutral van der Waals cluster is obtained, which is lower than the bond energies calculated by Troxler & Leutwyler (1991; 435 cm^{-1}) and by Vondrák et al. (1996; 430 cm^{-1}). This upper value is similar to that of the aniline-Ar cluster, for which the bond energy was bracketed in between 273 and 329 cm^{-1} (Piest et al. 1999).

4. CONCLUSIONS

In this experiment, we have obtained the linear IR absorption spectrum of gas-phase, cationic naphthalene, clustered with an argon atom in the 400–1600 cm^{-1} region under collision-free conditions. The results are compared to calculations from which it is concluded that all the strong modes and most of the weak modes expected in the 400–1600 cm^{-1} range are observed. Comparison with matrix isolation spectra demonstrates the advantages of the detection method presented in this Letter. In the absence of matrix interaction and using a species-selective and sensitive detection scheme, five more modes are observed in the present experiment. The modes observed in both types of experiments agree well, both in position and relative intensity. An upper value of the dissociation energy D_0 of the neutral naphthalene-Ar cluster is found at 325 cm^{-1}. The experimental method presented is generally applicable to obtain laboratory IR spectra of ionized polyaromatic hydrocarbons under astrophysically relevant conditions.

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